

Cooper Pair Insulator State Near Superconductor-Insulator Transition Probed by Magnetic Impurity

by

Xue Zhang

M.Sc in Physics, Brown University, USA, 2014

B.Sc in Physics, Nanjing University, China, 2012

A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR

THE DEGREE OF DOCTOR OF PHILOSOPHY

IN THE DEPARTMENT OF PHYSICS AT BROWN UNIVERSITY

Providence, Rhode Island

May, 2019

© Copyright 2018 by Xue Zhang

This dissertation by Xue Zhang is accepted in its present form by
Department of Physics as satisfying the
dissertation requirement for the degree of
Doctor of Philosophy

Date
James M. Valles, Jr., Advisor

Recommended to the Graduate Council

Date
Brad Marston, Reader

Date
Derek Stein, Reader

Approved by the Graduate Council

Date
Andrew G. Campbell
Dean of the Graduate School

Curriculum Vitae

Xue Zhang
182 Hope Street, Providence, RI
Email: zhangxuecq@gmail.com

Education

- **Brown University**, USA, PhD, Physics, 2012 - 2018
- **Brown University**, USA, M.Sc, Physics, 2012 - 2014
- **Nanjing University**, China, B.Sc, Physics, 2008 - 2012

Experience

Research Assistant, Brown University, 01/2013 - 05/2018

- Study two dimensional superconductor-insulator transition.
- Fabricate highly ordered anodic aluminum oxide substrate.
- Design the experiment and collect data to study the magnetic impurity effect on localized Cooper pair state

Teaching Assistant, Brown University, 09/2012 - 05/2018

- PHYS 0040 : Basic Physics
- PHYS 0160 : Introduction to Relativity and Quantum Physics
- PHYS 0470 : Electricity and Magnetism
- PHYS 2010 : Techniques in Experimental Physics

List of Publications

- Xue Zhang, James C Joy, Chenwei Zhao, Jin Ho Kim, Gustavo Fernandes, J M Xu and James M Valles Jr, 2017. Evaporating metal nanocrystal arrays. *Nanotechnology*, 28(10), p.105302.
- Xue Zhang, James C. Joy, Chunshu Wu, Jin-Ho Kim, J.M. Xu, and James M. Valles Jr, Quasiparticle Screening near a Bosonic Superconductor-Insulator Transition Revealed by Magnetic Impurity Doping. Submitted.
- Chunshu Wu, Xue Zhang, James C. Joy, Jin-Ho Kim, J.M. Xu, James M. Valles Jr, Effects of Nanoscale Inhomogeneities on the Cooper Pair Insulator Phase. Submitted.

List of Presentations

- Magnetic Impurity Effects on Cooper Pair Localization, APS march meeting, 2018.
- Effects of magnetic impurities on the Cooper Pair Insulator state, APS march meeting, 2017.
- Film Growth on Nanoporous Substrate, APS march meeting, 2016.

Acknowledgments

It has been a long way from the graduate student orientation to the graduation commencement. This journey is filled with joy, surprise, sadness, frustration, and the most important of all, growing. I owe many people a debt of gratitude who have been teaching, accompanying and encouraging me. I have been trying hard deserve your help.

First, many many many thanks to James Valles, my PhD advisor at Brown. You have been one of the best person I ever met. You are energetic, knowledgeable, patient and caring. I had a lot of silly comments and ideas when we meet but thanks for being such a good listener and encourage me to overcome many difficult situations. Those things I learned from you not only help me get the degree, but also will benefit my entire life, I believe.

Also, I am very grateful for Brown University as a whole. We received English training and campus tour even before we started our study here. The Office of International Student and Scholar Services(OISSS) did a great job helping us reduce the culture shock at the beginning. The physics department is not large but it makes me feel comfortable. All the people I met working here are very nice. Also, I would like to thank the graduate school and the graduate student council(GCS) for providing the conference travel fund.

To my other committee members, Prof. Marston and Prof. Stein and Prof. Xiao. All of you are brilliant and inspiring physicists. Thanks a lot for sharing your ideas and being the committee members for my preliminary presentation and PhD thesis

defense.

Next, I acknowledge the instructors for my courses at Brown. Those include Gang Xiao, Dmitri Feldman, J. Michael Kosterlitz, Humphrey Maris, See-Chen Ying, Brad Marston and Anastasia Volovich. Thanks for all your effort in the teaching. I learned a lot from those courses.

Then, to my mentor in the lab, James Joy. We spent many days working together, searching and solving many kinds of problems. As you said, we do not learn things until something goes wrong. Thanks for being an instructor in my research and a good friend in the daily life. Also, many thanks to other lab members, including Ilyong, Lidong, Chunshu. Your presence makes the lab more joyful.

Lastly, to my family. I may never be able to pay the debt of love I owed to my parents. Thanks for supporting me all the way up, and trusting me all the time. I am so lucky to be your child. Also to my love, Hongyi. Your accompanying during those year is a great treasury to me. I love you so much and I cannot wait to explore the world with you for the rest of my life.

Contents

Curriculum Vitae	iv
Acknowledgments	vii
Contents	viii
List of Figures	xiii
List of Tables	xviii
1 Introduction	2
1.1 Superconductivity	5
1.1.1 Ginzburg-Landau Theory	6
1.1.2 BCS Theory	8
1.1.3 Little-Parks Effect	10
1.1.4 Josephson Effect	11
1.1.5 Finite Size Effect	13
1.1.6 Impurity Effect	14
1.2 Metal Insulator Transition	17
1.2.1 Mott Transition	17
1.2.2 Anderson Transition	18
1.2.3 Weak Localization and Weak Antilocalization	19
1.3 Superconductor Insulator Transition	21

1.3.1	Experimental Platform	23
1.3.2	Theoretical Studies	25
1.4	Study of SIT on AAO Substrate	30
1.4.1	Little-Parks Oscillation	31
1.4.2	Giant Magnetoresistance	35
1.4.3	Activated Transport	35
1.5	Outline of the Remaining Chapters	38
	Bibliography	40
2	AAO substrate fabrication and characterization	51
2.1	Introduction	54
2.2	Fabrication Process	56
2.3	AAO Characterization	58
2.3.1	Inter-pore Spacing	58
2.3.2	Pore Diameter	61
2.3.3	Ordering	63
2.3.4	Roughness	66
2.4	Conclusion	70
	Bibliography	72
3	Evaporating Metal Nanocrystal Arrays	77
3.1	Introduction	80
3.2	Materials and Methods	82
3.3	Results and Analysis	84
3.3.1	Model Description	84
3.3.2	Evaporation on Tilted Substrate	87
3.3.3	Effect of Substrate Temperature	91
3.3.4	Small Dots Form on the Peak	98

3.3.4.1	Liquid Droplet Model	98
3.3.4.2	Model Calculation Results	100
3.4	Conclusions	104
	Bibliography	105
4	Experimental Apparatus and Techniques	112
4.1	Introduction	115
4.2	Experimental Apparatus	115
4.2.1	Anodization setup	115
4.2.2	Evaporator	116
4.2.3	Dilution Refrigerator	119
4.2.3.1	Source and Sample Stage	119
4.2.3.2	Superconducting Magnet	122
4.2.3.3	Cooling Components	124
4.2.4	Helium Recovery System	128
4.2.5	Transport Measurement Equipments	129
4.3	Experimental Techniques	130
4.3.1	Source Calibration	130
4.3.2	Gd Evaporation In the Fridge	132
4.3.3	Resistance Measurement	133
4.3.4	Isodissipative Measurement	135
4.4	Experiment Procedure	137
4.4.1	Prepare to Cool Down	139
4.4.2	Cool Down to LN2	139
4.4.3	Cool Down to Base Temperature	140
4.4.4	Warming Up	142
	Bibliography	143

5	Evidence of Dissipative Process with Cooper Pair Tunneling	145
5.1	Introduction	148
5.2	Activated Transport	149
5.3	Increasing Bi Thickness	151
5.3.1	R(T) on AAO	151
5.3.2	R(T) on Reference	154
5.3.3	Fermion Insulator to Boson Insulator Crossover	155
5.3.4	Phase Diagram	159
5.4	Magnetic Impurity Doping	160
5.4.1	T_C Shifts on Reference Films	160
5.4.2	R(T) on AAO with Doping	164
5.4.2.1	Effects on Reentrance Behavior	164
5.4.2.2	Resistance at Low Temperature Limit	169
5.4.3	T_0 Changes with Doping	171
5.5	Other Experiments	175
5.6	Renormalization of Charging Energy	177
5.7	Conclusion	181
	Bibliography	182
6	Shrinking Magnetoresistance Peak with Magnetic Impurity	188
6.1	Introduction	191
6.2	Magnetoresistance with Gd Doping	194
6.2.1	Peak and Oscillation	194
6.2.2	Adding Magnetic Impurity	196
6.3	Activation Energies in Fields	198
6.3.1	T_0^{peak} and B^{peak}	200
6.3.2	High Field Region	203
6.4	Results from Experiment I	207

6.5	Discussion	209
6.6	Conclusion	214
	Bibliography	216
7	Summary and Outlook	222
7.1	Summary	225
7.2	Future Experiments	227
	Bibliography	229

List of Figures

1.1.1 Little-Parks effect.	10
1.1.2 Josephson junction.	12
1.1.3 Depression of T_c with increasing pair breaking strength.	16
1.2.1 Two symmetrical loops starting from node 0.	20
1.3.1 $R(T)$ for a-Bi films with varying thicknesses	22
1.3.2 $R(T)$ curves for a series of Pb films quenched condensed on flat glass substrates	24
1.3.3 Suppression of T_c in a-MoGe film.	26
1.3.4 Tunneling measurements on Sb and Pb samples.	27
1.3.5 Experimental evidences that show the onset of superconductivity on the insulating side of the transition.	28
1.3.6 Critical resistance for various InO samples.	29
1.4.1 Morphology of film deposited onto AAO.	30
1.4.2 Vortices configuration for $f = 1, 1/3, 1/4$ and $1/7$ in nanohoneycomb.	32
1.4.3 Resistance oscillation in Jan2017 experiment.	33
1.4.4 a-Bi film deposited on flat nano-patterned Si substrate.	34
1.4.5 Surface plot of $R(T,H)$ for the lasting insulating film.	36
1.4.6 The peak moves to higher fields with increasing superconducting pairing temperature.	37
1.4.7 Activated transport.	38

2.1.1 Inter-pore spacing increases linearly with voltage in different anodizing conditions for sulfuric, oxalic, and phosphoric acid.	55
2.2.1 General procedures for two-step anodization.	56
2.3.1 AAO substrates with various inter-pore spacings.	59
2.3.2 Inter-pore spacing increases linearly with anodic voltage.	61
2.3.3 Fast Fourier Transform(FFT) of the SEM images	62
2.3.4 Pore size distribution.	63
2.3.5 Pore size distribution after 50 min pore opening process.	64
2.3.6 Unit cell size distribution	65
2.3.7 Viewing the substrate with an angle.	66
2.3.8 Linescan around the pore.	67
2.3.9 Linescans of AFM images for different substrates.	69
2.3.10 Thickness maps for films deposited on the substrate using quench condensation.	70
3.1.1 Pb films deposited on AAO and flat glass substrates.	81
3.2.1 Homemade sample holder with a NiCr heater and a Pt thermometer installed	83
3.2.2 SEM of Pb films with various thicknesses.	84
3.3.1 Nano-array formation onto tilted substrates.	88
3.3.2 Fourier transforms analysis	89
3.3.3 Resistance measurement for Ag films on untilted substrate and tilted substrate.	90
3.3.4 Effect of substrate temperature on Ag grain structure.	93
3.3.5 Effects of substrate temperature on Sn grain structure.	95
3.3.6 Pb grain structure on a heated substrate.	96
3.3.7 SEM images of 15nm of Pb thermally evaporated onto AAO substrates held at (a) 100 °C and (b) 200 °C	97

3.3.8	SEM images of 15nm of Sb thermally evaporated onto AAO sub-	
	strates held at (a) 100 °C and (b) 200 °C	97
3.3.9	Droplets on a convex surface and a concave surface.	98
3.3.10	Cross section of droplets with 45 degree wetting angle.	101
3.3.11	Cross section of droplets with 135 degree wetting angle.	101
3.3.12	Surface energy of a liquid droplet as a function of the radius of the	
	spherical substrate surface.	102
3.3.13	The binding energy of a liquid droplet as a function of the radius of	
	the spherical substrate surface.	103
3.3.14	Surface energy of a liquid droplet in the flat substrate limit as a func-	
	tion of wetting angle.	103
4.2.1	Anodizing cell for AAO fabrication.	116
4.2.2	Evaporator setup.	117
4.2.3	Dilution refrigerator.	120
4.2.4	Sample stage and evaporating sources.	121
4.2.5	Persistent current switch.	123
4.2.6	Vapor pressure of liquid He3 and He4 at various temperatures. . . .	124
4.2.7	Gas handling system.	125
4.2.8	Phase diagram of He3 and He4 mixture at saturated vapor pressure.	127
4.2.9	Helium recovery lines.	129
4.3.1	Source calibration for (a) Sb and (b) Bi.	130
4.3.2	Source calibration for Gd.	131
4.3.3	A series of Gd evaporations in the fridge.	132
4.3.4	4-point DC current measurement.	134
4.3.5	4-point AC current measurement.	135
4.3.6	Flattening of AC measurement due to phase shift at high resistance	
	region.	136

4.3.7 Isodissipative measurement of temperature versus magnetic field with fixed resistance.	137
4.4.1 A typical workflow in our lab.	138
5.3.1 Normal state conductance increases with Bi thickness.	152
5.3.2 Sheet resistance at zero field versus temperature with increasing Bi thickness	153
5.3.3 Resistance versus $1/T$ in two experiments.	154
5.3.4 The development of δT_0 on the last three films in two experiments. .	155
5.3.5 Resistance versus temperature for reference films in two experiments.	156
5.3.6 The crossover from Fermion insulator to Boson insulator.	158
5.3.7 Phase diagram.	159
5.4.1 The effect of successive magnetic impurity doping on reference films.	161
5.4.2 The kink appears in another experiment (Dec2016) where the dop- ing concentration is so high that the film becomes normal.	162
5.4.3 T_C drops with increasing Gd concentration in Experiment II.	163
5.4.4 Weak localization correction for Experiment I.	164
5.4.5 Normalized resistance at high temperature.	166
5.4.6 Weak localization correction for Experiment II following the same procedure.	167
5.4.7 T_C calculated from AAO and Reference for Experiment II.	168
5.4.8 Resistance versus $1/T$ for two experiments.	170
5.4.9 $R(T = 150mK)$ changes with Gd Doping.	171
5.4.10 Disappearing of $h/2e$ oscillation at 300 mK.	172
5.4.11 T_0 changes with Gd Doping.	173
5.5.1 Data from Jan2017 experiment.	176
5.6.1 E_C and E_J change with the pair breaking effect.	178

5.6.2 Comparison of the data with the Mott insulator with virtual quasiparticle screening model.	180
6.1.1 Isotherms $R(B)$ for perpendicular and parallel magnetic field.	192
6.2.1 Field sweep at 300 mK for the last Bi film before deposition of Gd.	195
6.2.2 Resistance oscillations at low fields.	196
6.2.3 Possible vortex configuration.	197
6.2.4 Surface plot $R(T = 150 \text{ mK}, \alpha_{Gd}, B)$	198
6.3.1 $R(T)$ in fields for the zero doping film.	199
6.3.2 Response of activation energies to magnetic field and magnetic impurity.	200
6.3.3 T_0^{peak} decreases linearly with increasing doping concentration.	201
6.3.4 B^{peak} moves to zero with increasing doping concentration.	202
6.3.5 $R(T)$ curves at 3 T, 5 T and 7 T with increasing doping.	204
6.3.6 T_0 changes with doping under specific fields.	205
6.3.7 Scaling of T_0 versus α_{Gd} in fields.	206
6.4.1 High field data from Experiment I.	208
6.5.1 T_0 peak induced by magnetic field and magnetic impurity.	210
6.5.2 Model plot using Eq. 6.5.1.	213
6.5.3 T_0 versus B with increasing doping.	214

List of Tables

2.1	Conventional Two-step Anodization	54
3.1	Vapor pressure (Pa) at specified temperatures.	97
4.1	Crystal calibration	118
5.1	List of major parameters with increasing Bi thickness in two experiments.	157

Chapter 1

Introduction

Superconductivity is arguably one of the most fundamental physics discoveries in the last century. This field still remains extremely active due to its great potential in both academia and industry. Among various theoretical and experimental work, two dimensional systems turn out to be particularly intriguing as they provide a playground for the interplay between superconductivity, which causes the resistance to drop, and disorder, which by contrast enhances the resistance.

The study of the superconductor-insulator transition (SIT) arose from the study of metal-insulator transition (MIT) in two dimensional limit. It is a typical example of a quantum phase transition (QPT) which involves the change of quantum ground state. This transition is realized in several different systems with lots of rich physics involved. In our lab, thin films are prepared on anodic aluminum oxide (AAO) substrates. The special film morphology imposed by the substrate enables us to conduct unique investigation into the nature of the SIT.

In this chapter, I will give a historical view of this field. I will show some important concepts related to the SIT. Main results discovered by previous members in our lab are also presented as the foundation for my projects.

1.1 Superconductivity

Superconductivity was discovered along with advances in refrigeration techniques. With continuous improvement of liquefaction systems, oxygen ($T = 90$ K) was liquefied by Raoul Pictet and Louis Paul Cailletet using different methods in 1877. In 1883, Zygmunt Wroblewski successfully liquefied nitrogen ($T = 77$ K). In 1898, James Dewar liquefied hydrogen ($T = 20$ K), and made his far-reaching invention of the vacuum flask 'Dewar'. Heike Kamerlingh Onnes won the last competition to liquefy the 'permanent gas' helium ($T = 4.2$ K) in 1908. This is crucial for his discovery of superconductivity three years later in 1911 when he observed the sudden drop of mercury electrical resistance when the temperature was below 4.2 K[1, 2]. As was established later, superconductors show dissipationless transport below a critical temperature T_c . The transition temperature for most Type I superconductors is below 10 K.

For many years after the discovery of superconductivity, it had been thought of as simply a resistance vanishing phenomenon. A major breakthrough came in 1933 when Messiner and Ochsenfeld found that superconductors were perfect diamagnets [3]. The magnetic field was excluded from entering the superconductors beyond a very thin penetration region. This so-called 'Messiner effect' cannot be explained by perfect conductance and it is actually a more fundamental feature of superconductivity. Later people found that superconductors were classified into two distinct groups, namely Type I and Type II superconductors[4], by their magnetic properties.

Theoretical studies were carried out along with the discoveries of these intriguing behaviors. Initially, without sufficient understanding of the microscopic mechanism, most of the theories were phenomenological. Based on superconductors' electrodynamic properties, F. London and H. London proposed two equations [5].

Combining them with Maxwell equations, they were able to show the phenomena of diamagnetism and penetration depth. Pippard[6] generalized their theory to the nonlocal case and proposed a parameter called the superconducting coherence length ξ_0 . The coherence length represents the size of a superconducting wave packet. It is of the order of μm for pure metals. More comprehensive studies were carried out by Ginzburg and Landau [7] based on their studies of second order phase transitions and later by Bardeen, Cooper, and Schrieffer [8] who focused more on the microscopic mechanism of superconductivity.

1.1.1 Ginzburg-Landau Theory

Because of the discontinuity in the heat capacity, a superconducting phase transition is classified as second order phase transition. Landau's theory for continuous phase transition is based on a minimization of free energy. In terms of superconductivity, the free energy density can be written as [9],

$$f = f_{n0} + \alpha|\psi|^2 + \frac{\beta}{2}|\psi|^4 + \frac{1}{2m^*} \left| \left(\frac{\hbar}{i} \Delta - \frac{e^*}{c} A \right) \psi \right|^2 + \frac{h^2}{8\pi} \quad (1.1.1)$$

where ψ is a complex number representing the superconducting order parameter. Originally, it was written as a function of local charge carrier n_s density and phase ϕ .

$$\psi(r) = n_s^{1/2}(r) e^{i\phi(r)} \quad (1.1.2)$$

n_s and ϕ are conjugate variables obeying uncertainty principle in quantum field theory. Thus, large phase fluctuations indicate localized charge carriers while explicit superconducting phase indicates large uncertainty of the charge carrier numbers, corresponding to extended states in transport. Upon the discovery of BCS theory, people found n_s is proportional to the superconducting gap Δ . Thus, it can also be written as $\psi = \Delta^{1/2} e^{i\phi}$. In this context, the amplitude of the order parameter is

equal to the BCS gap.

The parameters α and β in Eq. 1.1.1 vary at the transition. β must always be positive since the free energy needs to have a minimum. In fact, it is approximately a constant. The value of α depends on the temperature. When $\alpha > 0$, f has a single minimum located at $\psi = 0$, corresponding to the normal state. If $\alpha < 0$, there are two minima occurring at $|\psi|^2 = -\alpha/\beta$, indicating superconducting state. Thus, with lowering the temperature near the transition, α changes sign from positive to negative.

The superconducting current can be calculated by taking the derivative of Eq. 1.1.1 and plugging in the expression for the order parameter.

$$J_s = \frac{n_s e^*}{m^*} \left(\hbar \nabla \psi - \frac{e^*}{c} A \right) = n_s e^* v_s \quad (1.1.3)$$

where $v_s = (\hbar \nabla \psi - \frac{e^*}{c} A) / m^*$ is the supercurrent velocity. As we will see later, this expression helps us understand the Little-Parks experiment which is used as a probe to detect Cooper pairs in our lab.

GL theory also introduces a new coherence length $\xi_{GL} = \frac{\hbar}{[2m^* \alpha(t)]^{1/2}}$. Since $\alpha(t)$ goes to zero at the transition, the GL coherence length diverges at T_c . In the low temperature limit, ξ_{GL} equals the Pippard coherence length ξ_0 . GL theory also introduces an important dimensionless parameter κ which is the ratio of the penetration length and coherence length. κ determines the magnetic properties of superconductors so that Type I superconductors show a single critical field B_c while Type II superconductors have two critical field B_{c1} and B_{c2} . Interestingly, GL theory was totally based on intuition without understanding the microscopic physics but it was able to capture many features of the superconducting phase. It did not attract much attention in the beginning but later it was found to be a limiting case of the microscopic theory. Since the theory is straightforward, it is still widely used to show the macroscopic picture of superconductivity.

1.1.2 BCS Theory

BCS theory proposed by John Bardeen, Leon Cooper, and John Robert Schrieffer in 1957 [10, 8] explains the microscopic physics behind superconductivity in simple metals. Before it was published, there were already some experiments implying the existence of a energy gap [11, 12, 13, 14]. To explain the energy gap, L.N. Cooper showed the Fermi sea is unstable against any arbitrary small attractive interactions between the electrons, creating energy lower than the Fermi energy [15]. The question is how can the Coulomb interaction between electrons be attractive. We can think of two electrons moving in the ion matrix. The motion of the first electron distorts the ion lattice, making it attractive for the second electron. This attractive potential is maximized when the two electrons have opposite momenta. Therefore, the binding energy comes from electron-phonon interaction. With the attractive interaction, one can write down the Hamiltonian for the system,

$$H = \sum_{k\sigma} \epsilon_k n_{k\sigma} + \sum_{kl} V_{kl} c_{k\uparrow}^* c_{-k\downarrow}^* c_{-l\downarrow} c_{l\uparrow} \quad (1.1.4)$$

where $c_{-l\downarrow} c_{l\uparrow}$ is the annihilation operators for the paired electrons $(-l \downarrow, l \uparrow)$ and V_{kl} is the interaction matrix element. For s-wave superconductors, it is not strongly momentum-dependent. Following Cooper's method [15], we can assume V_{kl} is a negative constant within cutoff frequency, i.e. $|\epsilon_k| < \hbar\omega_c$, and zero otherwise. The Schrodinger equation can be solved by a variational method to find the ground state energy. Following the standard procedure, one can find,

$$\Delta = \frac{\hbar\omega_c}{\sinh[1/N(0)V]} \approx 2\hbar\omega_c e^{-1/N(0)V} \quad (1.1.5)$$

Eq. 1.1.4 can also be solved to find the excited states using a Bogoliubov transformation [16, 17].

$$\begin{aligned} c_{k\uparrow} &= u_k^* \gamma_{k0} + v_k \gamma_{k1}^* \\ c_{-k\downarrow}^* &= -v_k^* \gamma_{k0} + u_k \gamma_{k1}^* \end{aligned} \quad (1.1.6)$$

where the coefficients satisfy $|u_k|^2 + |v_k|^2 = 1$. Substituting the operators in Eq. 1.1.4, one can calculate the gap with a specific choice of coefficients that diagonalize the Hamiltonian.

$$\Delta_k = \sum_l V_{kl} u_l^* v_l < 1 - \gamma_{l0}^* \gamma_{l0} - \gamma_{l1}^* \gamma_{l1} > \quad (1.1.7)$$

Continuing with Cooper's approximation that Δ_k is a constant, we get the self consistency equation that determines the temperature dependence of the gap.

$$\begin{aligned} E_k &= (\xi_k^2 + \Delta^2)^{1/2} \\ \frac{1}{V} &= \frac{1}{2} \sum_k \frac{\tanh(\beta E_k/2)}{E_k} \end{aligned} \quad (1.1.8)$$

where $\xi_k = \epsilon_k - \mu$ is the energy relative to the Fermi surface. One of the most important results from Eq. 1.1.8 is the relation between zero temperature gap and the superconducting critical temperature T_c . T_c can be calculated when $\Delta = 0$. The numerical result gives,

$$\frac{2\Delta_0}{kT_c} = 2\pi e^{-0.577} = 3.53 \quad (1.1.9)$$

In fact, $\Delta(T)$ is a flat function when $T \ll T_c$. Thus, the above relation is still valid even we cannot reach zero temperature. It should be noted that the value 3.53 is not universal. It is 3.5 for weak-coupling limit, while in strong coupling regime, the ratio can be increased to 4.0 or more[18].

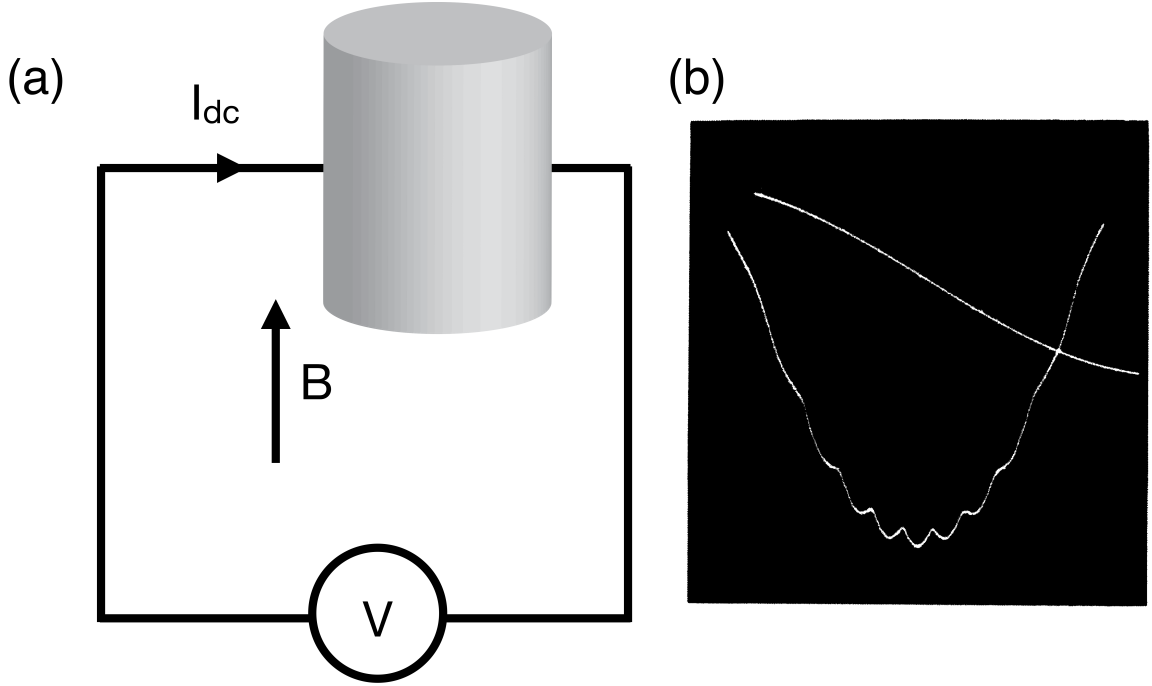


Figure 1.1.1: Little-Parks effect. (a) Experimental setup. A constant DC current ($\sim 10 \mu\text{A}$) is applied while measuring the voltage across the cylinder. (b) Experiment result. The upper trace is the field sweep line. The lower one trace is the variation of resistance.

1.1.3 Little-Parks Effect

The Little-Parks experiment [19] showed electron pairing and thus was one of the earliest experiments that support BCS theory. The effect was observed with a thin cylinder of tin (see Fig. 1.1.1). For a magnetic field oriented along the cylinder axis, the resistance oscillates with period of $hc/2e$. The parabolic background shows the weakening of the binding in magnetic field.

This effect can be well understood from GL theory and BCS pairing. Consider the superconducting order parameter, it should remain unchanged after traveling along a closed loop. Thus, the phase of the order parameter must change by $2\pi n$.

$$\oint \Delta\phi \cdot ds = 2\pi n \quad (1.1.10)$$

Combining with the supercurrent velocity in Eq. 1.1.3, we get,

$$\oint \left(\frac{m^* c}{e^*} v_s + A \right) \cdot ds = n \Phi_0 \quad (1.1.11)$$

where $\Phi_0 = \frac{hc}{e^*}$ is the flux quantum. We know $e^* = 2e$ from BCS theory. Thus, $\Phi_0 = 2.07 \times 10^{-15}$ Wb. Solving the equation above,

$$v_s = \frac{\hbar}{m^* R} (n - \Phi/\Phi_0) \quad (1.1.12)$$

where $\Phi = \oint A \cdot ds = \pi R^2 B$. The integer n is chosen to minimize v_s . Therefore, v_s reaches a minimum when Φ/Φ_0 is an integer, and a maximum if Φ/Φ_0 is a half integer. A maximum in v_s indicates the Cooper pairs are more likely to stay at the origin. The resistance is maximized in this case. More fundamentally, $v_s^2 \propto -\Delta T_c(\Phi)$. Specifically,

$$\frac{\Delta T_c(\Phi)}{T_c} = \begin{cases} 0.55 \frac{\xi_0^2}{R^2} \left(n - \frac{\Phi}{\Phi_0} \right)^2 & \text{Clean Limit} \\ 0.73 \frac{\xi_{0l}^2}{R^2} \left(n - \frac{\Phi}{\Phi_0} \right)^2 & \text{Dirty Limit} \end{cases} \quad (1.1.13)$$

The oscillation of T_c has been observed in various experiments. Since transport measurements are relatively easy to do, the Little-Park effect is widely used as a tool to detect Cooper pairs [20, 21].

1.1.4 Josephson Effect

In 1962, Brian David Josephson [22] made a remarkable predication that in a system where two superconductors coupled by a weak link, the current can flow through the link without applying a voltage. The weak link can be a normal metal, an insulator or a weak superconductor. Later, the theory was generalized as two

equations governing the current and voltage across the junction [23],

$$\begin{aligned} I(t) &= I_c \sin(\phi(t)) \\ U(t) &= \frac{\hbar}{2e} \frac{\partial \phi}{\partial t} \end{aligned} \quad (1.1.14)$$

where $\phi(t)$ is the phase difference across the junction. The first equation is called DC Josephson effect and the second one is the AC Josephson effect. Combining those two equations, we can see the current oscillates with frequency $2eU/\hbar$ when applying a DC voltage across the junction.

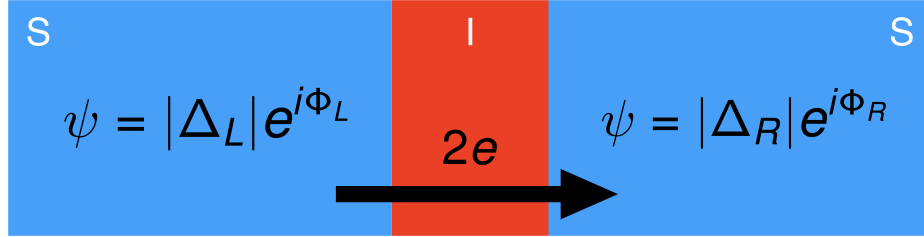


Figure 1.1.2: Josephson junction. Two superconducting electrodes connected by an insulator.

There are two characteristic energy scales associated with Josephson junction, [9, 24].

$$\begin{aligned} E_C &= \frac{(2e)^2}{2C} \\ E_J &= \frac{\hbar I_c}{2e} = \frac{\hbar \Delta}{8e^2 R_n} \tanh\left(\frac{\Delta}{2k_B T}\right) \end{aligned} \quad (1.1.15)$$

where R_n is the normal state resistance. E_C is the charging energy, representing the energy barrier for tunneling. E_J is the Josephson coupling energy that aids the transport. At sufficiently low temperature, $E_J \sim g\Delta$ because the hyperbolic tangent is approximately equal to 1.

The behavior of a Josephson junction at low temperature depends on the ratio of E_C and E_J (see Fig. 1.1.2). With $E_C \gg E_J$, the Cooper pair numbers on the two electrodes are well defined while the phase fluctuates. Thus the junction becomes a Mott-like insulator. In the other limit, the phase difference is a well

defined parameter while the charge number fluctuates. Then the Cooper pairs are delocalized. The Josephson junction shows wide applications, including the recent hotly studied quantum computing. Researchers are able to generate several coherent qubits using Josephson junctions in both two limits [25].

1.1.5 Finite Size Effect

The BCS theory applies for bulk materials where mean field theory applies. Many novel features appear with lowering dimension, which lead to either enhancement or suppression of superconductivity.

In two dimensional systems, the film thickness is typically several monolayers, which is lower than the superconductivity coherence length. It has been observed in many materials, like Pb [26], InOx [27], Nb [28], that T_c reduces with decreasing thickness or increasing normal state resistance. The change of T_c is either attributed to the reduction of the superconductivity gap or the increased phase fluctuation which leads to Cooper pair localization.

The studies of one dimensional system are usually carried out in nanowires with width below 50 nm [29]. The dependence of T_c on the size of the characteristic dimension is quite complicated. In granular films of indium [30], aluminum [31], T_c is reported to increase with decreasing size. On the contrary, MoGe [32, 33], Pb [34] show suppression of T_c with decreasing size. The origin of the size dependence remains an open question so far [35] and it may due to several factors, including different phonon spectrum or even the morphology of the film. A distinct feature in one dimensional superconducting systems is the quantum phase slip (QPS). In the course of a phase slip, the superconducting order parameter fluctuates to zero at some point along the wire. It can be either thermally activated near T_c (LAMH theory) [36, 37] or driven by quantum fluctuation at low temperature [38]. The superconducting phase across the point changes by $\pm 2\pi$, resulting in a resistive

voltage. Therefore, the system shows a finite resistance tail below T_c . It is unclear whether 1d-QPS is related to 2d-SIT. People have found that QPS are actually dual to Josephson junction tunneling, which is a widely used model to study 2d-SIT [39, 40].

Zero dimensional superconductivity studies are carried out in nano-grains. For bulk materials in a normal state, the energy level spectrum is almost continuous. Upon decreasing grain size, the energy level spacing δ is enlarged. According to Anderson's criterion [41], superconductivity ceases to appear when δ is greater than the superconducting gap Δ . Thus, the minimum critical size for superconductivity to exist is [42],

$$b_{SC} = (g_0 \Delta)^{-1/3} \quad (1.1.16)$$

where g_0 is the density of state near the Fermi surface in bulk material. For typical materials, $E_F \sim 10$ eV, $\Delta \sim 5$ K. Thus, b_{SC} is in order of several nanometers. The evolution of T_c before the size reaches b_{SC} is more complicated. For most elementary materials like Al, Ga, Sn, In, etc, T_c is enhanced with decreasing grain size whereas Pb does not show significant change [43, 44]. T_c for nanostructured Nb grains is suppressed with decreasing size [45]. Different factors may contribute to the change of T_c . Primarily, they can be related to either the surface effect which is due to the larger surface volume ratio in nano-grains, or the quantum size effect which enlarges the energy level spacing [46].

1.1.6 Impurity Effect

One of the most distinctive features of superconductivity is that it is insensitive to enormous amounts of non-magnetic impurities [47]. The scattering term from the

non-magnetic impurity can be written as [48]

$$H_{imp} = \sum_{\alpha} \int dr \Psi_{\alpha}^{\dagger}(r) U_{imp}(r) \Psi_{\alpha}(r) \quad (1.1.17)$$

Note that the spin is preserved during the scattering. It simply adds a constant term to the electron-electron interaction which does not change the basic assumption of BCS theory. Thus, as long as local time reversal symmetry is preserved during the scattering, the density of states is unchanged and T_c is barely affected. One thing that will be modified in presence of impurity scattering is the coherence length.

$$\frac{1}{\xi} = \frac{1}{\xi_0} + \frac{1}{l} \quad (1.1.18)$$

where l is the mean free path. It decreases with increasing amount of impurities. The superconductor becomes 'dirty' when $l < \xi_0$. However, l cannot be arbitrarily small. Based on uncertainty principle, Ioffe and Regel [49] pointed out that the usual electron conduction theory breaks when the mean free path l is comparable to the atomic spacing a . This idea is generalized as,

$$k_F l \approx 1 \quad (1.1.19)$$

Eq. 1.1.19 is known as Ioffe-Regel limit. When the system reaches this limit, the superconductivity is strongly affected by the disorder. In fact, in disorder tuned SIT (d-SIT), most experiments are carried out in this regime.

Another important kind of impurity is the magnetic impurity (MI). In contrast to non-magnetic impurity, the conduction electron spin is coupled to the impurity spin, known as Kondo effect [50]. The hamiltonian can be written as,

$$H_{imp} = \sum_{\alpha\beta} \int dr J(r) \Psi_{\alpha}^{\dagger}(r) S \cdot \delta_{\alpha\beta} \Psi_{\beta}(r) \quad (1.1.20)$$

Note the exchange of spins. For superconductivity, this coupling breaks time reversal symmetry. In 1960, Abrikosov and Gor'kov (AG) [51] showed a strong depression of T_c and modification of the density of states by tiny amounts of MI. They made the startling prediction of a gapless superconductor. Assuming the pair breaking strength is α , which is proportional to MI concentration. The change of T_c follows the self consistent equation,

$$\ln \frac{T_c(\alpha)}{T_{c0}} = \psi\left(\frac{1}{2}\right) - \psi\left(\frac{1}{2} + \frac{\alpha}{2\pi k_B T_c(\alpha)}\right) \quad (1.1.21)$$

where $\psi(x) = \frac{d}{dx} \ln(\Gamma(x)) = \frac{\Gamma'(x)}{\Gamma(x)}$ is a digamma function. The relation is plotted in Fig. 1.1.3.

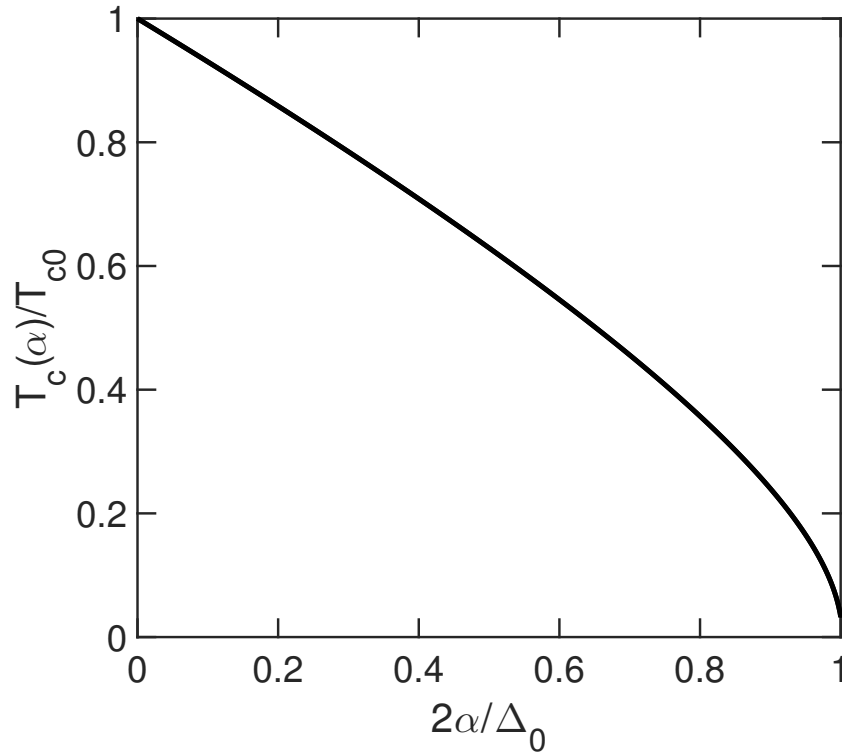


Figure 1.1.3: Depression of T_c with increasing pair breaking strength. $\Delta_0 = 1.76k_B T_{c0}$ is the BCS gap.

T_c goes to zero at $\alpha_c = \Delta_0/2$. However, the spectral gap closes at $\alpha' = \Delta_0 \exp(-\pi/4)$ [48]. Thus in a small regime where $\alpha' < \alpha < \alpha_c$, a gapless su-

perconductor appears.

In the other limit, when the pair breaking strength is weak, the digamma function can be expanded around 1/2.

$$k_B(T_{c0} - T_c(\alpha)) = \frac{\pi\alpha}{4} \quad (1.1.22)$$

As a result, we get the simple linear relationship between T_c and α when α is small.

1.2 Metal Insulator Transition

In classical theory, an insulator has a gap between the valence band and the conduction band, and the Fermi level is in the gap. For a metal, there is no gap between them and the electron states are partially filled. The metal insulator transition can happen through the change of the band structure. More interestingly, in addition to the band structure change, other major mechanisms that can drive a metal insulator transition include electron-electron interactions and disorder. The electron interaction induced MIT is called a Mott transition and the disorder induced MIT is called Anderson transition.

1.2.1 Mott Transition

While the band theory is successful explaining many properties in solids, it ignores the electron-electron interactions which made some materials insulating although their bands are only partially filled. Mott [52] first considered the effects of the interactions and pointed out that a gap opens at the Fermi level due to strong coulomb repulsion between electrons at the same site. As a result, the initially partially filled band becomes fully filled in the lower band of the gap and the system turns into an insulator. The theoretical understanding of the Mott transition is achieved by

Hubbard model[53],

$$H_H = -t \sum_{\langle ij \rangle} (c_{i\sigma}^\dagger c_{j\sigma} + h.c.) + U \sum_i (n_{i\uparrow} - \frac{1}{2})(n_{i\downarrow} - \frac{1}{2}) - \mu \sum_i n_i \quad (1.2.1)$$

The first term represents nearest neighbor hopping between site i and j . The second term is the repulsive coulomb interaction at the same site. The electronic property is given by the relative size of t and U . The last term is the chemical potential controlling the filling of the band.

For superconductors, the charge carriers are bosons. The spinless boson version of Hubbard model is given in a similar form,

$$H_{BH} = -t \sum_{\langle ij \rangle} b_i^\dagger b_j + \frac{U}{2} \sum_i n_i(n_i - 1) - \mu \sum_i n_i \quad (1.2.2)$$

This Bose-Hubbard model is found to be very useful understanding the superfluid-insulator transition [54].

1.2.2 Anderson Transition

Another driving force for MIT is the random disorder of the system. The pioneering work was done by Anderson [55] who pointed out that with sufficiently strong disorder, all electrons will be localized, resulting in an insulating state even though the band structure is unchanged. Consider the Hamiltonian,

$$H = - \sum_{\langle ij \rangle} (t_{ij} c_{i\sigma}^\dagger c_{j\sigma} + h.c.) + \sum_i \epsilon_i n_i \quad (1.2.3)$$

The first term is the hopping to the nearest neighbor and the the second term is the on-site potential. With disorder, ϵ_i is a random distribution function centered at Fermi level with width W . The transport behavior depends on the value of W . It is metallic if W small. With large W , the wavefunction of nearby sites no longer

overlaps and system becomes insulating. In this case, the transport is governed by the 'mobility edge' beyond which the electrons are delocalized. The resistance shows Arrhenius form of dependence on temperature,

$$R = R_0 \exp(E_m/T) \quad (1.2.4)$$

where E_m is the activation energy from Fermi level to the mobility edge.

In real system, disorder and coulomb interaction can coexist. The Hamiltonian is a combination from Eq. 1.2.1 and 1.2.3. This kind of transition is called Mott-Anderson transition. The transport behavior depends on the relative size of coulomb repulsion U and distribution width W . In fact, those two effects are not independent. Intuitively, in the presence of disorder, electron density is high in certain areas, which further increases the electron-electron interaction.

1.2.3 Weak Localization and Weak Antilocalization

Weak localization is a phenomenon that the electrons tend to stay in one spot rather than traveling away. Comparing to the strong localization, i.e. the Anderson localization, weak localization takes place at lower disorder and the electrons are able to hop from site to site without losing coherent phase.

Weak localization provides the quantum correction to the electron conductance. Consider the possibility that an electron returns to its origin after several coherent scattering events, we need to calculate all the paths that forms a closed loop. For every path returning to the origin, there is a symmetrical loop as shown in Fig. 1.2.1. Classically, the probability is the sum of the amplitude $P_{classical} = |A_p|^2 + |A_{p'}|^2 = 2|A|^2$. From the quantum viewpoint, there is constructive interference between those two coherent trajectories so that the possibility should be $P_{quantum} = |A_p^2 + A_{p'}|^2 = 4|A|^2$. Therefore, the possibility for the electrons staying at the origin is

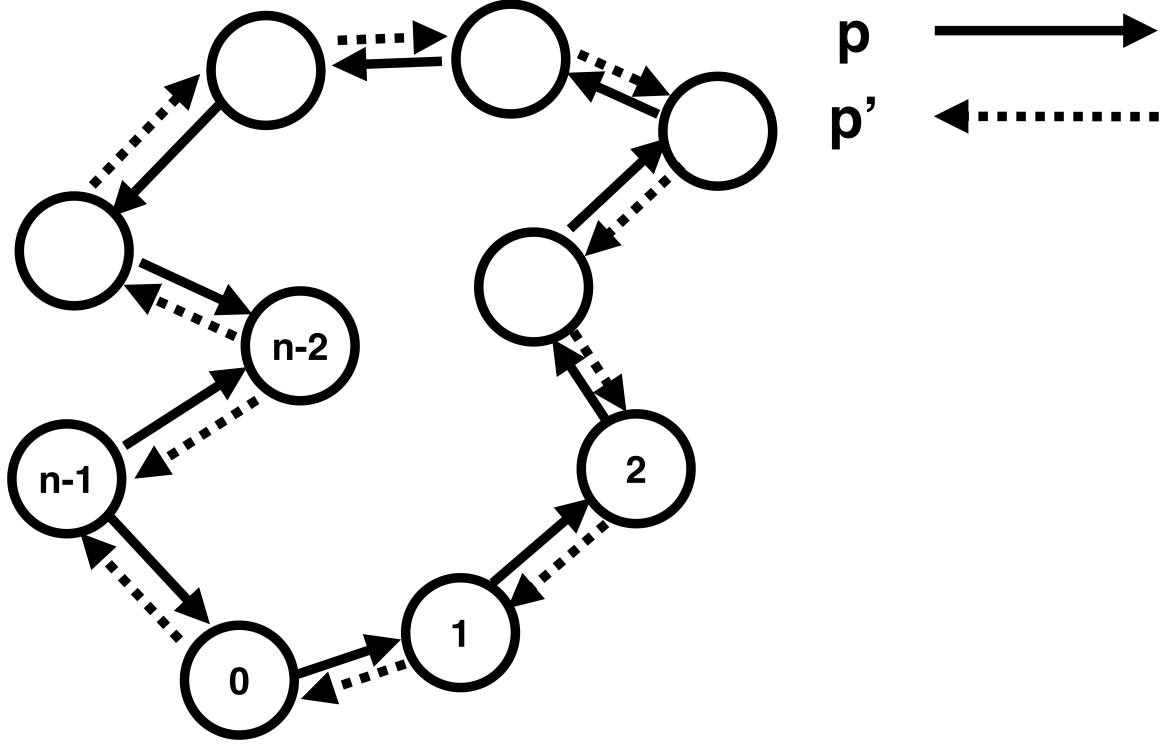


Figure 1.2.1: Two symmetrical loops starting from node 0.

doubled from the interference. This leads to the decrease of overall conductance.

As we can see, coherent scattering plays a central role here for the weak localization to happen. It needs to be more frequent than inelastic scattering where the electron loses coherence phase. Thus, the condition for weak localization is $\tau_\varphi \gg \tau$, where τ_φ and τ are the inelastic and elastic scattering time intervals, respectively. Or equivalently,

$$L_\varphi \approx \sqrt{\tau_\varphi / \tau} \gg l \quad (1.2.5)$$

where L_φ is the phase breaking length and l is the mean free path.

Our interest is on the two dimensional case. The conductance correction from weak localization can be explicitly calculated as [56],

$$\Delta G_{2d} = - \left(\frac{e^2}{2\pi^2 \hbar} \right) \ln \left(\frac{\tau_\varphi}{\tau} \right) \sim \ln(T) \quad (1.2.6)$$

It has weaker dependence on temperature than the strong localization. With increasing amount of disorder, the system will be strongly localized. The crossover takes place at $G \approx G_{00}$ where $G_{00} = \frac{e^2}{2\pi^2\hbar} = 1/81k\Omega$ [57].

In weak localization, two symmetrical paths interfere constructively. The situation can be reversed with spin-orbit coupling. The coupling strength $\langle L \cdot S \rangle$ is proportional to Z^4 , and the spin-flip time $\tau_{SO} \propto Z^{-4}$. Here Z is the atomic number. Thus, for heavy metals, when $\tau_{SO} \ll \tau_\phi$, we need to include the spin term into the interference calculation. The result can be destructive and the conductance is enhanced from the quantum correction [58]. This effect is called weak antilocalization. The magnetoresistance (MR) can be used to separate weak localization and weak antilocalization. In magnetic field, the electron gains a random phase when traveling along the path. It breaks the symmetry between the two paths (see Fig. 1.2.1), which weakens the interference effect. Thus, for weak localization, the system shows negative MR while it is positive for weak antilocalization.

1.3 Superconductor Insulator Transition

The study of the superconductor insulator transition borrows a lot of ideas from metal insulator transition. Moreover, it adds in the pairing interaction, making the phenomena more complicated and more interesting. It is also one of the best examples of a quantum phase transition, in which the transition from one ground state to another is tuned by the parameters of the Hamiltonian. Strictly speaking, the transition takes place only at $T = 0$, which is unreachable in experiment. However, at finite temperature, we can observe the "tails" of the transition that indicate the quantum critical point (QCP) at zero temperature [59]. Specifically, for the SIT, the most interesting platform is the two dimensional system. The controlling parameters include disorder, magnetic field, charge density and magnetic impurity

[42, 60, 61]. Among them, disorder can be further divided into several different sources, including thickness disorder [62], compositional disorder [63], or more recently discussed gauge disorder in magnetic field [64].

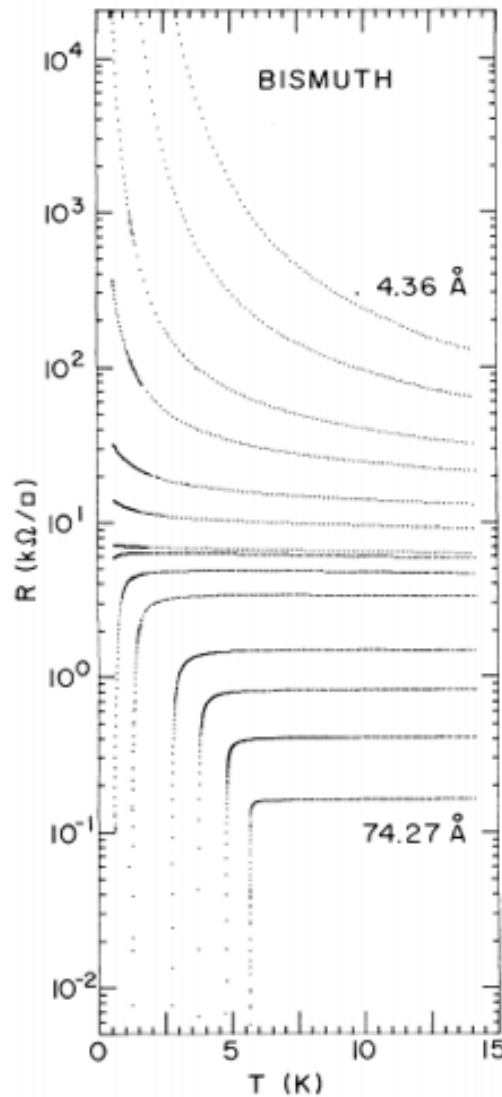


Figure 1.3.1: $R(T)$ for a-Bi films with varying thicknesses [62].

Fig. 1.3.1 shows a typical thickness tuned SIT (d-SIT). The Bi films were quench condensed onto a Ge underlayer. They were considered to be amorphous and homogeneous. The superconducting state is characterized by $dR/dT > 0$ while the insulating side is characterized by $dR/dT < 0$. In the vicinity of the transition, the $R(T)$ curve becomes very flat. Thus, with increasing Bi thickness, the film

undergoes an insulator superconductor transition. Another salient feature of this transition is the critical resistance at the QCP. The normal resistance decreases with successive depositions. The separatrix of the superconducting phase and insulating phase occurs very close to the quantum resistance for 2 electrons: $R_Q = h/4e^2 = 6.45 \text{ k}\Omega$.

1.3.1 Experimental Platform

SIT experiments are performed in many different systems. Here we only focus on two dimensional thin films, but it is still possible in 3D materials [65, 66]. The behavior strongly depends on the morphology of the film. The systems can be generally divided into two groups, granular films and homogeneous films.

Granular Films

A granular film consists of large grains with electron properties similar to bulk materials. It is usually made by directly evaporating metals (like Pb[67], Sn[68]) onto the substrate without wetting layers. Below the bulk critical temperature T_c , superconductivity is established in the grains. The SIT is tuned by the coupling between the grains. On the superconducting side, the coupling is strong enough to enable coherent tunneling of Cooper pairs. With decreasing coupling, the inter-grain repulsive Coulomb interaction builds a large charging energy that creates phase fluctuation. Thus the long range phase coherence is broken and the film turns into the insulating state.

Fig. 1.3.2 shows an example of an SIT on granular Pb films. It is tuned by decreasing film thickness that reduces the inter-grain coupling. The transition is broadened near the SIT critical point. Note that in the weak superconducting phase and insulating phase, the temperature that corresponds to the onset of superconductivity is almost the same as the T_c on the thickest film. This observation indicates the superconductivity inside the grain is unaffected, which is a distinctive

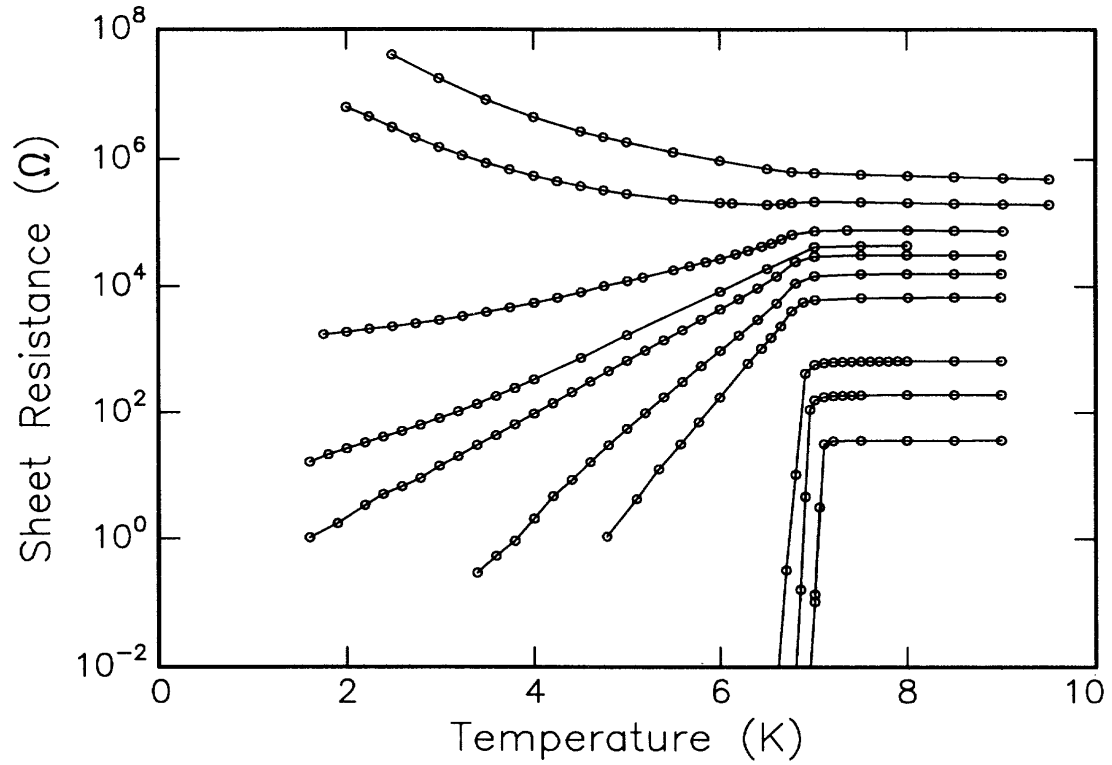


Figure 1.3.2: $R(T)$ curves for a series of Pb films quenched condensed on flat glass substrates [67].

feature for granular films.

Homogeneous Films

Homogeneous films show uniform structure down to the atomic scale. Experimentally, this can be realized in many systems with various film making techniques, such as quench condensation, sputtering or etching. The most common materials under study include Bi/Ge[62], PbBi/Sb[69], Pb/Ge[70], InO[71], TiN[72], Ta[73], MoGe[74]. Note that Pb or Bi films are made homogeneous by depositing a layer of Ge or Sb as an intermediate layer. Those materials could wet the substrate which prevents grain formation.

Fig. 1.3.1 shows the thickness tuned SIT in a homogeneous system. In contrast to the granular case, T_c on the superconducting side is reduced with decreasing thickness. This behavior indicates that the suppression of the amplitude of the

order parameter becomes important.

Unlike the granular system, the picture for the SIT in this category is far more complicated. The experiment results in different systems are sometimes contradicting with each other although they all show the same uniform structure. For example, the electron tunneling measurement on Bi/Sb film [75] shows the superconducting gap reaches zero at the transition, which contradicts the STM measurement on InO film [76] that shows that the gap persists into the insulating state.

1.3.2 Theoretical Studies

The crucial question to answer in SIT studies regards the nature of insulating phase. There are generally two distinct frameworks. One considers the suppression of the superconducting gap and the other one focuses on the phase fluctuations.

Fermionic Picture for SIT

In this scenario, disorder and Coulomb interactions play an important role. They are responsible for driving the pairing amplitude and critical temperature to zero at the transition. On the superconducting side, the superconductivity is gradually suppressed toward the transition and disappears at the boundary. In Finkel'stein's work [77], they treated the system using a diagrammatic renormalization approach. This theory suggests that the critical temperature changes as

$$\frac{T_c}{T_{c0}} = \exp(-1/\gamma) \left[\left(1 + \frac{(t/2)^{1/2}}{\gamma - t/4} \right) \times \left(1 - \frac{(t/2)^{1/2}}{\gamma - t/4} \right)^{-1} \right]^{1/\sqrt{2}t} \quad (1.3.1)$$

where $\gamma = 1/\ln T_{c0}\tau$, τ is the mean free path time. $t = (e^2/2\pi^2\hbar)R$ is the dimensionless resistance. The equation fits very well to the experiment data (see Fig. 1.3.3).

Eq. 1.3.1 provides the mechanism for the suppression of T_c . Tunneling mea-

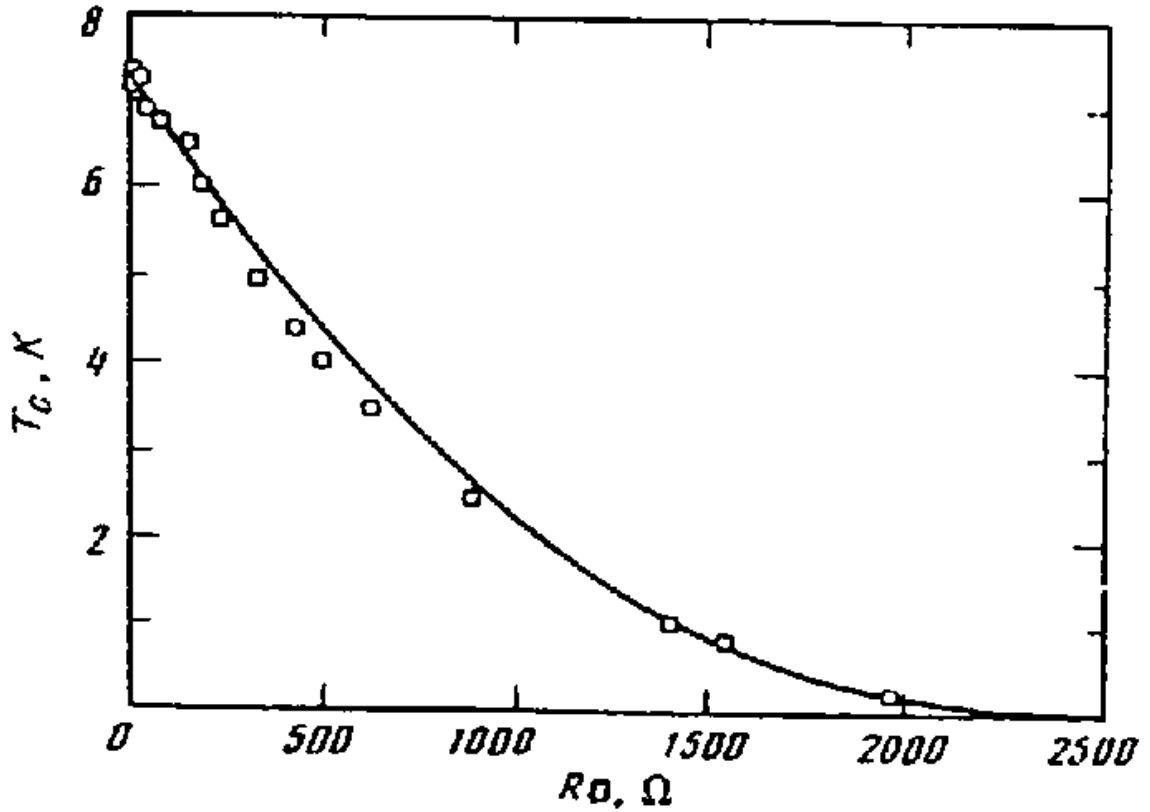


Figure 1.3.3: Suppression of T_c in a-MoGe film. The solid curve is a fit with Eq. 1.3.1.

measurements can directly show how the superconducting gap changes near the critical point. Valles et al [26, 75] conducted electron tunneling measurement on amorphous Pb and Sn films by making Al/oxide/disordered film junctions. The superconducting gap decreases at the same rate as T_c . As T_c goes to zero at the transition, the gap also closes (see Fig. 1.3.4).

Bosonic Picture for SIT

The Fermionic picture is not always valid. There is extensive experimental evidence that shows the existence of preformed Cooper pairs on the insulating side of the transition (see Fig.1.3.5). In this scenario, the superconducting gap remains finite across the transition and the Cooper pairs are localized by strong phase fluctuation.

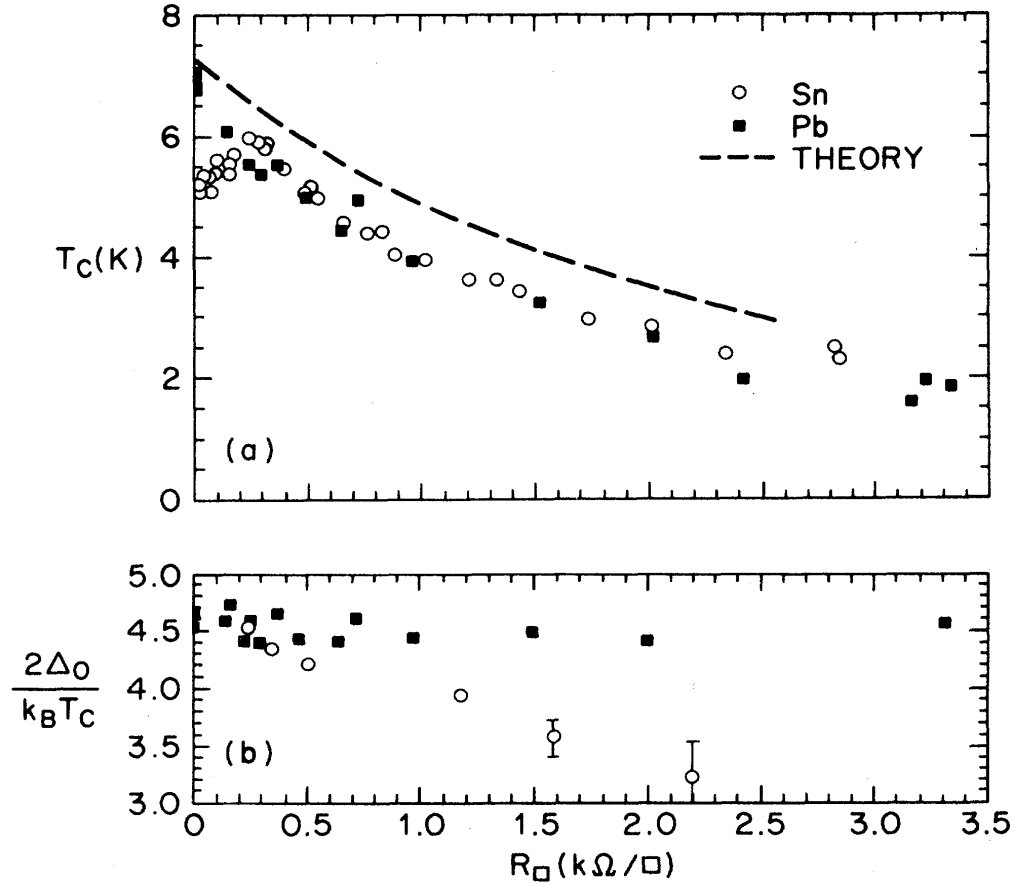


Figure 1.3.4: Tunneling measurements on Sn (open circle) and Pb (closed square) samples. The superconducting gap to critical temperature ratio remains a constant with increasing disorder.

In the early 1970s, Kosterlitz et al [80] did a theoretical study of 2d phase transition based on the topological degree of the system. In this framework, the superconducting state and insulating state are dual to each other. On the superconducting side, the Cooper pairs are condensed and vortices are localized, while on the insulating side of the transition, Cooper pairs are localized and vortices are condensed. The movement of vortices gives rise to the resistivity at finite temperature.

Mean field theory is widely used in condensed matter physics. According to the Ginzburg criterion, it requires that the fluctuation in the order parameter is much smaller than the actual value of the order parameter, i.e. $\langle(\delta\Phi)^2\rangle \ll \langle(\Phi)^2\rangle$. This condition does not hold near the transition. In this case, scaling theory is a useful

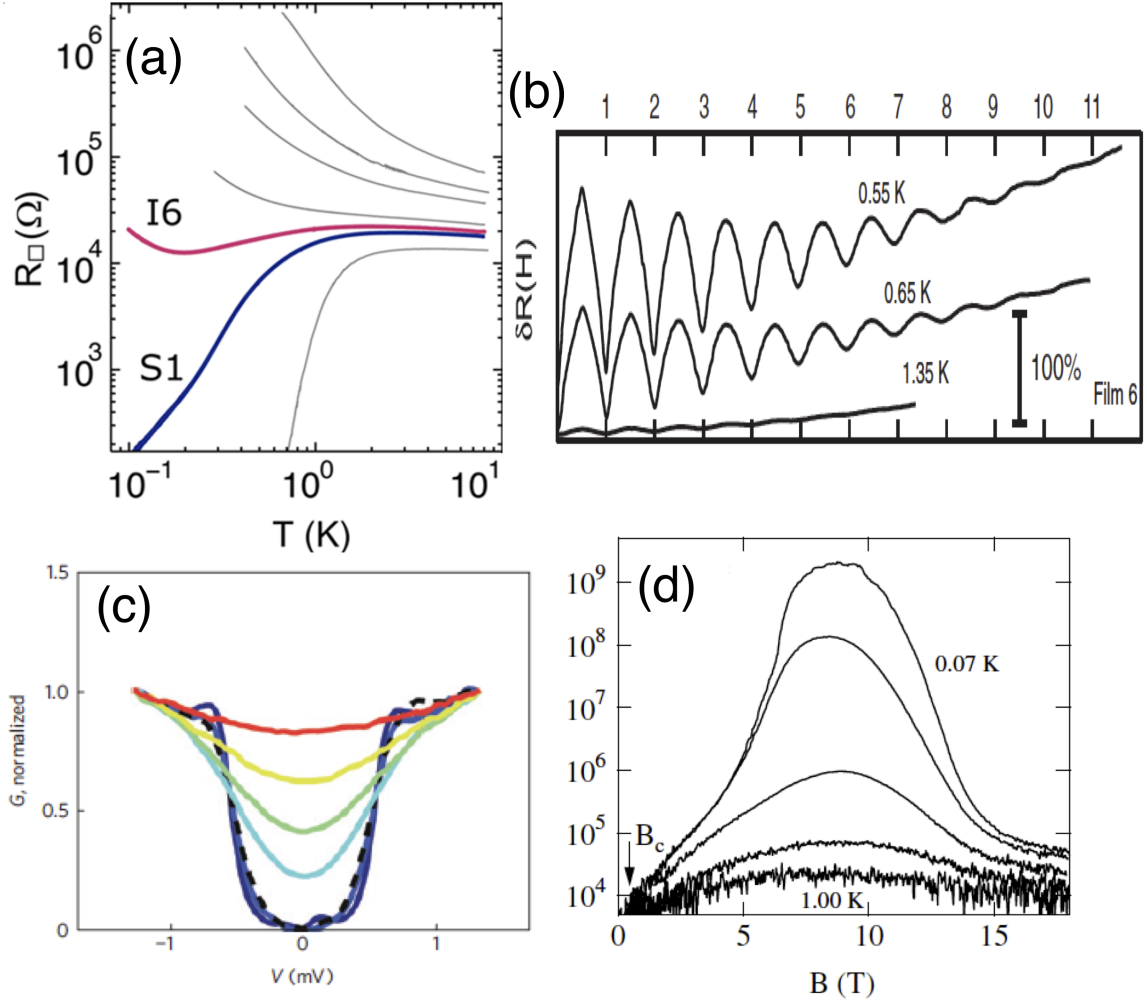


Figure 1.3.5: Experimental evidences that show the onset of superconductivity on the insulating side of the transition. (a) Resistance reentrance with lowering temperature [78]. (b) Little-Parks oscillations [20]. (c) STM measurement of the superconductivity gap [76]. (d) Positive magnetoresistance resistance and giant MR peak [79].

tool to study continuous phase transitions. The idea is that some quantities are scale-invariant at the critical point. For a quantum phase transition, $\hbar\omega_c/T$ is scale-invariant. Here $\hbar\omega_c \sim \xi_{\tau}^{-1}$ is the characteristic energy scale. From the correlation length $\xi = \xi_0|\delta|^{-\nu}$ and the correlation time $\xi_{\tau} \sim \xi^z \sim |\delta|^{-\nu z}$, we can see $|\delta|^{\nu z}/T$ is scale invariant. νz is a constant that determines the universality class of the transition and $|\delta|$ is the distance to the critical point. Fisher et al [81] did finite size scaling analysis for an SIT based on the dirt-boson model, which produces an

electronically inhomogeneous insulating state. He pointed out that the resistance should be a function of the scale invariant quantity in 2d system. Thus,

$$R = R_c F\left(\frac{|\delta|}{T^{1/vz}}\right) \quad (1.3.2)$$

In addition, he predicted a universal resistance at the transition $R_Q = h/4e^2 = 6.45 \text{ k}\Omega$, which was verified by various experiments (see Fig. 1.3.6).

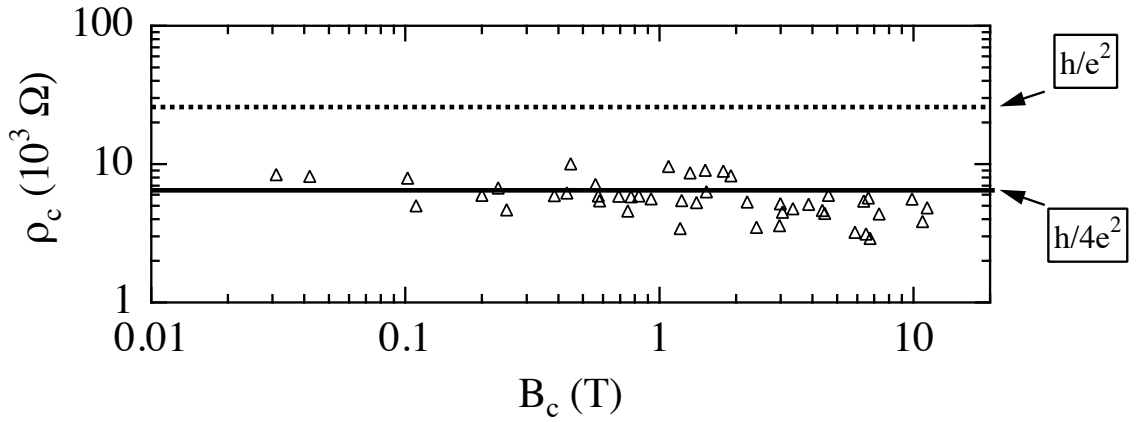


Figure 1.3.6: Critical resistance for various InO samples [82].

Another theoretical approach to study the Bosonic SIT is by numerical simulation, primarily quantum monte carlo simulation. This method involves writing down the Hamiltonian of the system, generating random parameters that correspond to the amount of disorder and solve the Hamiltonian using numerical techniques. The widely used Hamiltonian is the 2D+1 XY model [83], which borrows the idea from Josephson junction array (JJA) model.

$$H = E_c \sum_i n_i^2 - E_J \sum_{ij} \cos(\theta_i - \theta_j - A_{ij}) \quad (1.3.3)$$

The first term is the coulomb blockade and the second term is the nearest neighbor Josephson coupling. The transition is tuned by the relative size of the two terms

similar to the granular scenario.

Obviously, the Bosonic picture assumes local superconductivity survives at the transition and the film is inhomogeneous. A question is how is that possible for geometrically homogeneous films. The Bogoliubov-de Gennes (BdG) analysis by Ghosal et al [84] shows that with increasing disorder, the pairing amplitude becomes spatially inhomogeneous. The large Δ areas remain superconducting in the insulating side of the transition. As a result, it behaves like superconducting islands embedded in the insulating matrix.

1.4 Study of SIT on AAO Substrate

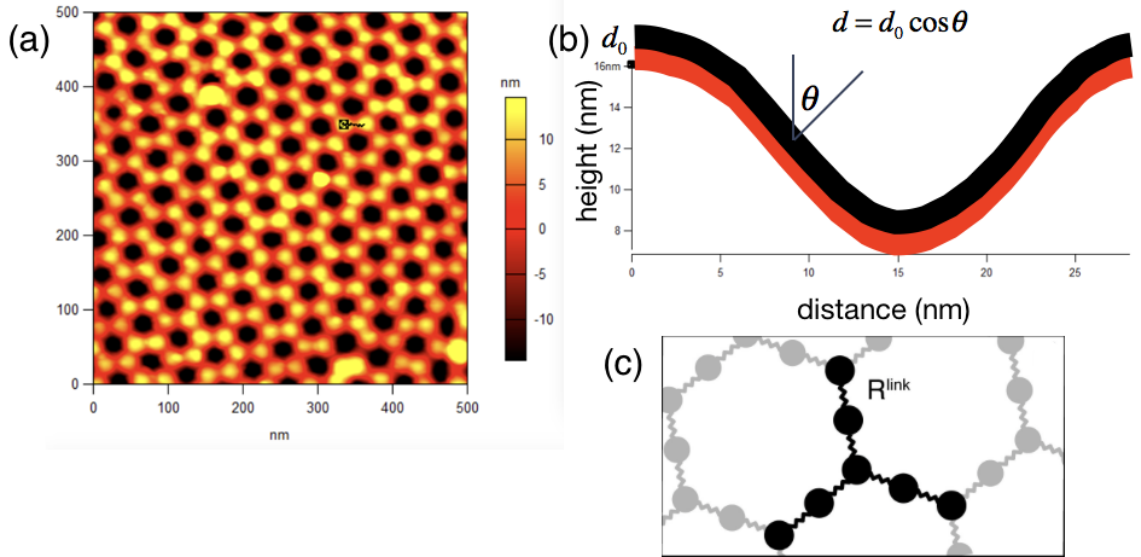


Figure 1.4.1: Morphology of film deposited onto AAO. (a) Atomic force microscope (AFM) image of the substrate. (b) Thickness variation in the film deposited onto AAO. (c) Superconducting island model. The black dots represent robust superconductors connected by resistive links.

Studies of the SIT using films on AAO provided the first direct evidence of Cooper pairs on the insulating side of the transition [20]. Films deposited on AAO cannot be simply categorized as homogeneous or granular. Fig. 1.4.1 shows the morphology of AAO and a film deposited on it. The AAO substrate has ordered

hexagonal nano-pore arrays with six peaks and six valleys around each pore. In quench condensation, the film thickness is uniform along the evaporating direction. For electron transport, however, the height in the direction perpendicular to the surface is the most crucial factor, which is proportional to $\cos \theta$ as shown in Fig. 1.4.1(b). Thus, the normal thicknesses at the peak and the valley are higher than the thickness on the slope. The superconducting critical temperature depends on film thickness as [85],

$$T_c = T_c^{bulk}(1 - d_c/d) \quad (1.4.1)$$

Thus, the thicker areas shows stronger superconductivity. The general model for this system is shown in Fig. 1.4.1(c), where there are twelve superconducting islands. They are connected by resistive links. This system provides a good example for the Josephson junction array model (see Eq. 1.3.3) where the inter-island links control the Josephson coupling. In this section, I will present some main results from SIT study. Some additional features are discussed in Chapter five and Chapter six where I will show the magnetic impurity doping experiments on AAO.

1.4.1 Little-Parks Oscillation

Because of the ordered nano-pore structure, Little-Parks oscillation appears when Cooper pairs are formed and the localization length is greater than the pore size. Fig.1.3.5(b) shows the $h/2e$ oscillations at low fields. The size of the oscillation depends on the temperature. It increases with decreasing temperature as thermal fluctuations tends to reduce the supercurrent around the pores. The period of the oscillation corresponds to one flux quantum,

$$H_M = \Phi_0/S \quad (1.4.2)$$

where s is the unit cell area. For substrates with 100 nm inter-pore spacing, $H_M = 0.21$ T. The field frustration is defined as $f = H/H_M$.

The number of oscillations depends on the ordering of the pores. Assume that the unit cells have an area distribution with standard deviation δS . It creates a gauge disorder [64, 86] in the vector potential A_{ij} (see Eq. 1.3.3). δA is proportional to $f\delta S$. The result can be simply modeled using a Gaussian distribution. The frustration term becomes $\cos(2\pi f) \exp(-(2\pi f D)^2)$, where D represents plaquette area disorder. Thus, we can see the oscillation weakens at higher f , and D determines the decrease rate.

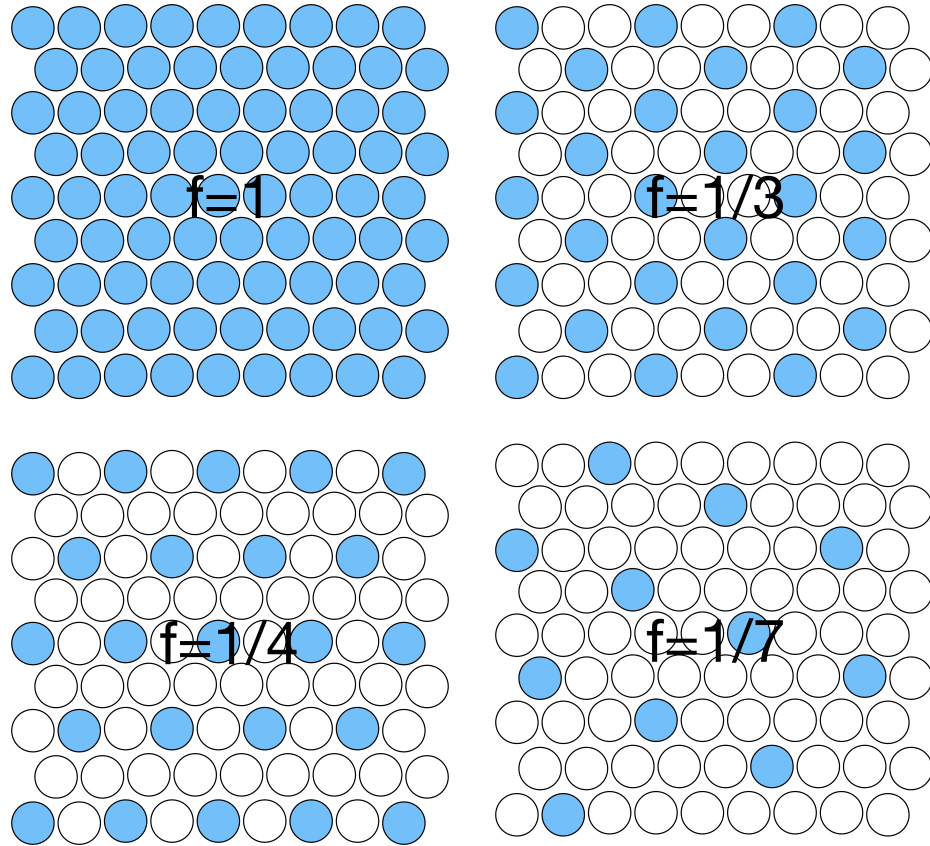


Figure 1.4.2: Vortices configuration for $f = 1, 1/3, 1/4$ and $1/7$ in nanohoneycomb. The blue filled circles represent the locations of the vortices.

Ideally the resistance should also oscillate at fractional frustration [87]. This phenomenon can be explained in terms of the configuration of the vortices. Vortices exert repulsive forces on one from another, forming Abrikosov vortex lattice.

When they are in stable equilibrium configuration, the resistance reaches a minimum. Fig. 1.4.2 shows four stable configurations corresponding to fractional frustrations. To observe those effect, the AAO substrate needs to be highly ordered and the superconductivity needs to be strong. Fig. 1.4.3 shows the first two oscillations on an insulating film in Jan2017 experiment. The kink structure may indicate the fractional frustration effect, although it is a little bit hard to tell whether it corresponds to $f = 1/3$ or $f = 1/4$.

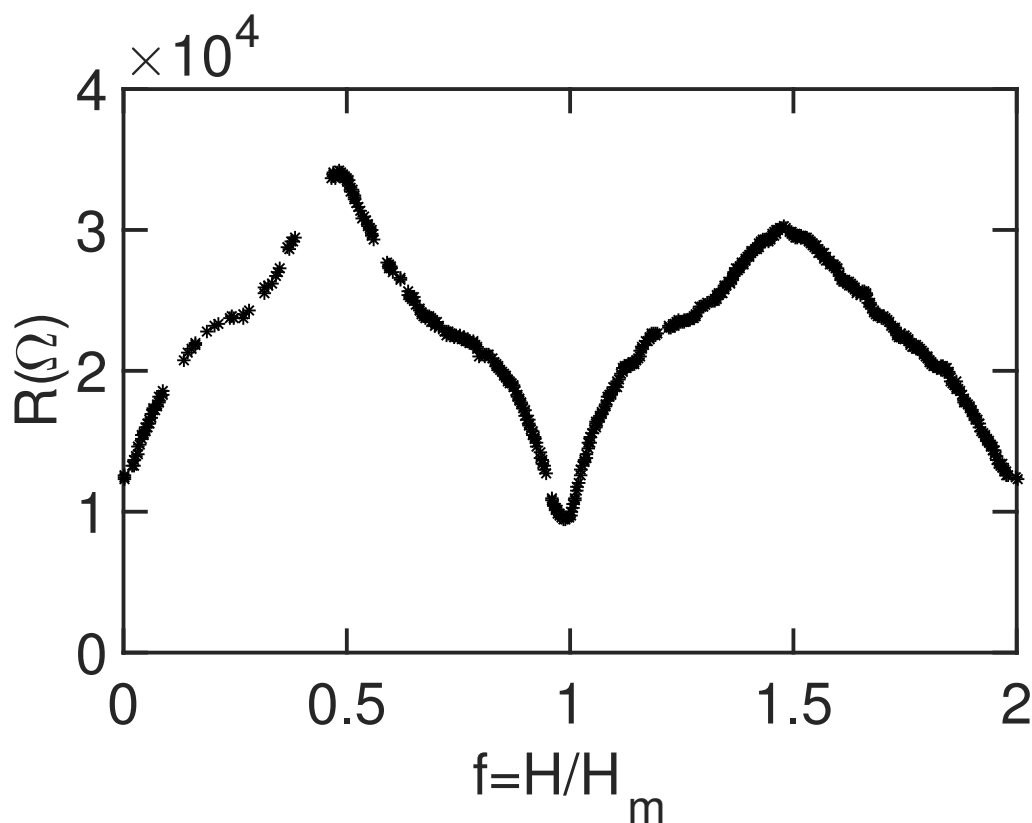


Figure 1.4.3: Resistance oscillation in Jan2017 experiment. Notice the kink on the halfway between the minimum and the maximum.

The period of the oscillation implies that the carriers are Cooper pairs. Thus, the MR oscillations are a probe to detect local Cooper pairs through an easy transport measurement. The facts that we have not observed the oscillation deep in the insulating state or in high magnetic fields are consistent with the expectation that superconductivity is destroyed in those regimes. The more thing interesting

is whether the thickness variation is crucial to localize the Cooper pairs. Experiments on a nano-patterned Si substrate [88] do not show any sign of oscillations on the insulating side of their SIT (see Fig. 1.4.4). Unlike the AAO substrate, the Si substrate is flat, thus the films on it have uniform thickness. The transition tends to be fermionic with no sign of preformed Cooper pairs on the insulating side. It raises another question that how much inhomogeneity is necessary to have a bosonic transition. Several other experiments on substrates, with roughness between 100 nm AAO and Si, are performed to answer this question. The result shows the oscillation still appears on the insulating side but it is much weaker [89].

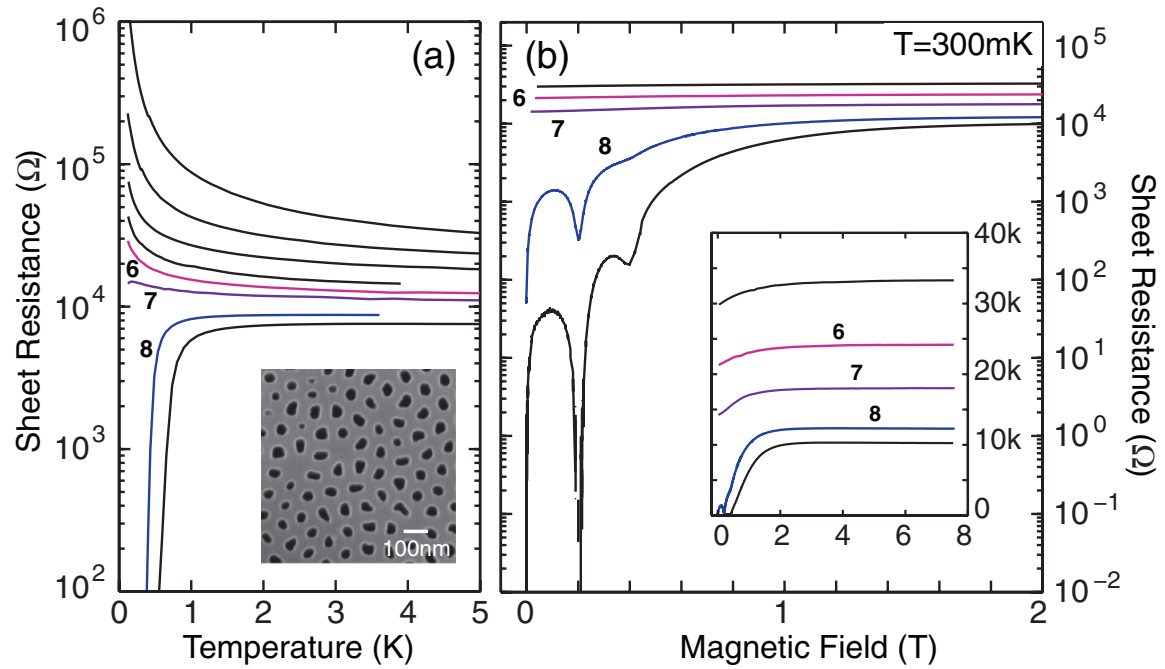


Figure 1.4.4: a-Bi film deposited on flat nano-patterned Si substrate. (a) $R(T)$ with increasing film thickness. No resistance reentrance behavior observed on the insulating side. (b) Isotherms in field sweeps. Note only the superconducting films show Little-Parks oscillations.

1.4.2 Giant Magnetoresistance

Another outstanding feature is the giant MR observed in the insulating phase. The first giant MR was observed on a-InO film by Gantmakher et al [90]. Nguyen et al [78] studied the magnetoresistance on films deposited onto AAO (see Fig. 1.4.5). The MR peak emerges on the insulating side of the transition and grows from zero field. With increasing thickness, the peak becomes larger and also moves to a higher field. The insulating film shown in Fig. 1.4.5 is very close to the transition and the resistance at the peak is one order magnitude higher than the resistance at zero field when the temperature is kept at 100 mK. The position of the peak, B^{peak} , weakly depends on the temperature. With lowering T, the magnitude of the peak goes up and concomitantly, B^{peak} moves to lower value.

The origin of the peak seems to be related to the breaking of Cooper pairs, which reduces E_j in Eq. 1.3.3. With increasing thickness, the superconducting binding energy increases. Then it needs higher pair breaking effect to destroy the superconductivity. As a result, B_{peak} increases as shown in fig. 1.4.6.

Since the peak is a result of Cooper pair transport, bosonic picture can be distinguished from fermionic picture by whether peak appears or not. The film deposited on flat Si substrate (see Fig. 1.4.4) does not show positive MR and resistance peak on the insulating side. More details about the magnetoresistance will be discussed in Chapter six where we use magnetic impurity to study the evolution of the peak.

1.4.3 Activated Transport

Film deposited on AAO shows simply activated transport behavior,

$$R = R_0 \exp(T_0/T) \quad (1.4.3)$$

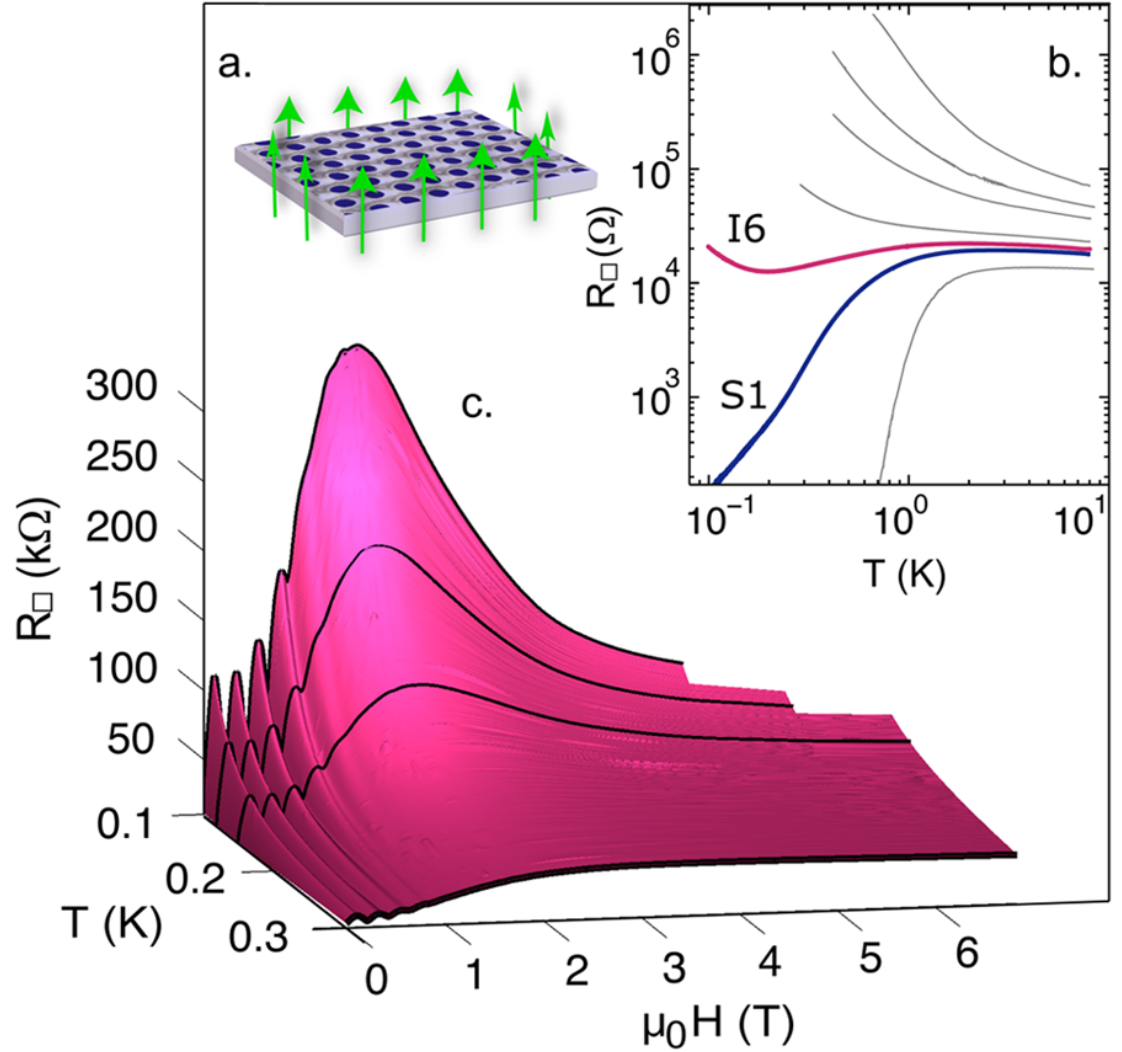


Figure 1.4.5: Surface plot of $R(T,H)$ for the last insulating film. Note the Little-Parks oscillations at low fields and the giant MR peak near 1.5 T.

where the activation energy T_0 is the energy barrier for Cooper pair transport and the prefactor R_0 is a measure of disorder. If we plot of R versus $1/T$ on semi-log scale, the linear fit in the low temperature region indicates the activation energy (see Fig. 1.4.7 (a)).

T_0 is also the vanishing energy scale on the insulating side of the transition as shown in Fig.1.4.7 (b). Deep in the insulating state, T_0 is very high. In fact, that regime is dominated by quasiparticle transport. With increasing thick-

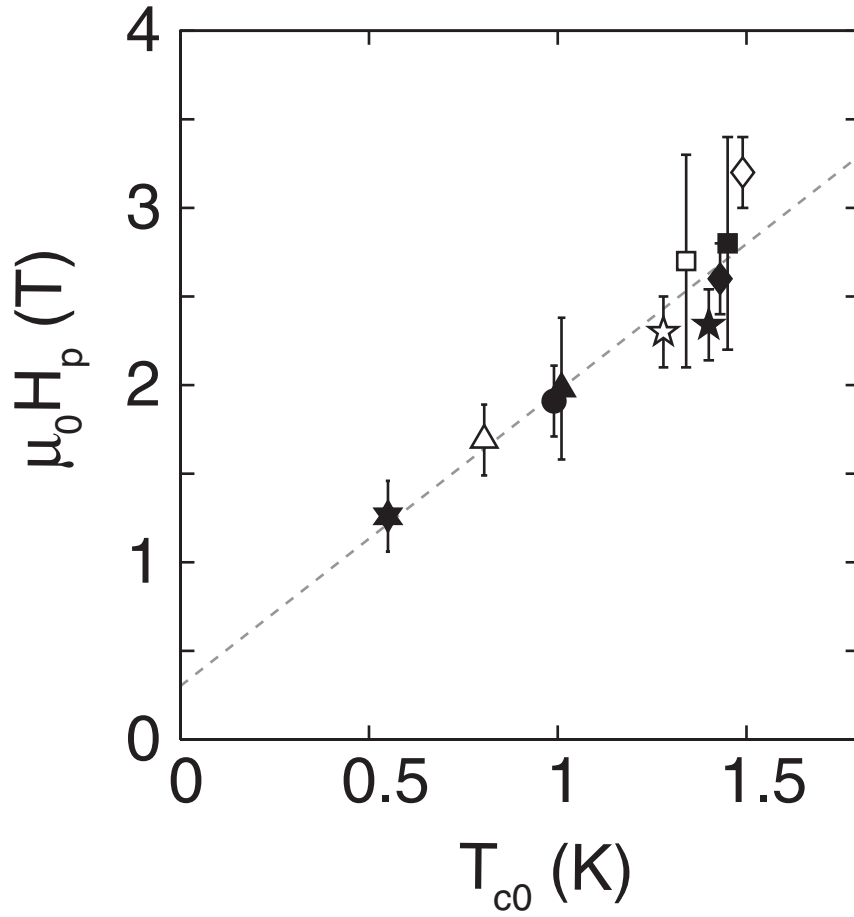


Figure 1.4.6: The peak moves to higher fields with increasing superconducting pairing temperature.

ness, T_0 decreases. There is a crossover from fermion insulator to boson insulator where Little-Parks oscillation and positive magnetoresistance appear. With further increase of the thickness, T_0 decreases approximately linearly to zero with thickness. Thus, it is the characteristic energy scale on the insulating side of SIT while T_c is the characteristic energy scale on the superconducting side. We will have more discussions about the activation energy in Chapter Five where we try to understand the microscopic origin of T_0 .

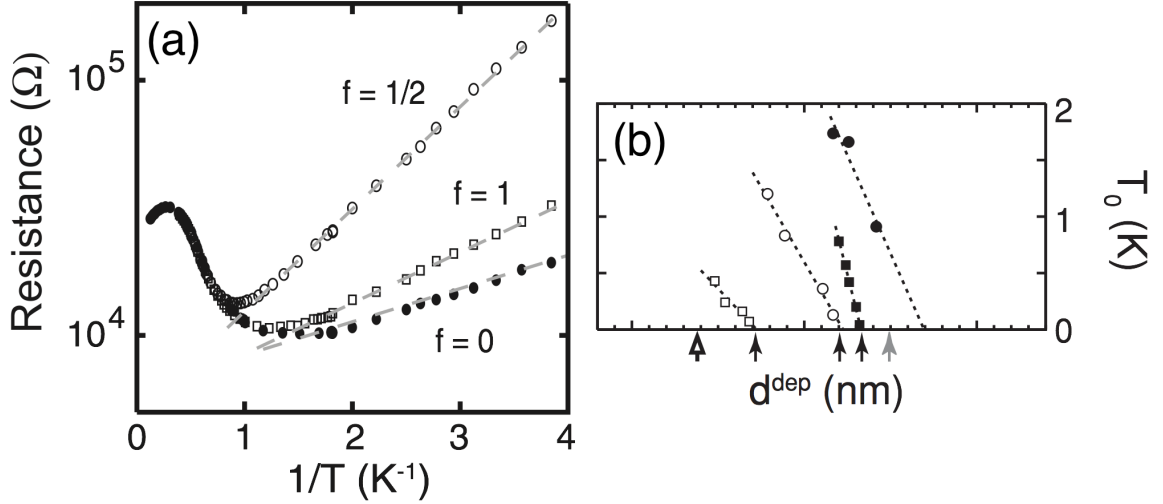


Figure 1.4.7: Activated transport. (a) R versus $1/T$ for $f = 0, 1/2, 1$, respectively [20]. (b) T_0 decreases to zero at the critical point. Data are from different experiments [85].

1.5 Outline of the Remaining Chapters

This thesis aims to describe two projects I have done. One is a study of film growth on AAO substrates. The experiments were performed at room temperature and above. Lots of microscope and image analysis techniques are used. The second project is an investigation of the Cooper Pair Insulator (CPI) phase using magnetic impurity doping. Specifically, we studied the origin of the activated transport behavior and revealed that fermionic degrees of freedom play a role in Cooper pair transport. In addition, doping experiments gave further insight into the magnetoresistance behaviors, especially the emergence of MR peak.

For the following chapters, Chapter Two introduces AAO and its fabrication process. Chapter Three talks about the film growth experiments and discusses how temperature influences the film morphology. Chapter Four is a description about our experimental equipment and techniques for low temperature transport measurement. Chapter Five and Six present the magnetic impurity doping experiments along with theoretical explanations. The last chapter is a summary of the results

and a discussion of some possible future experiments.

Bibliography

- [1] H Kamerlingh Onnes. The resistance of pure mercury at helium temperatures. *Commun. Phys. Lab. Univ. Leiden, b*, 120, 1911.
- [2] Dirk Van Delft and Peter Kes. The discovery of superconductivity. *Physics Today*, 63(9):38–43, 2010.
- [3] Walther Meissner and Robert Ochsenfeld. Ein neuer effekt bei eintritt der supraleitfähigkeit. *Naturwissenschaften*, 21(44):787–788, 1933.
- [4] Alexei A Abrikosov. On the magnetic properties of superconductors of the second group. *Sov. Phys. JETP*, 5:1174–1182, 1957.
- [5] Fritz London and Heinz London. The electromagnetic equations of the superconductor. *Proc. R. Soc. Lond. A*, 149(866):71–88, 1935.
- [6] AB Pippard. Ab pippard, proc. roy. soc.(london) a216, 547 (1953). *Proc. Roy. Soc.(London)*, 216:547, 1953.
- [7] V.L. Ginzburg and L.D. Landau. *Zh. Eksp. Teor. Fiz.*, 20:1064, 1950.
- [8] John Bardeen, Leon N Cooper, and John Robert Schrieffer. Theory of superconductivity. *Physical Review*, 108(5):1175, 1957.
- [9] M Tinkham. Introduction to Superconductivity. *The McGraw-Hill Companies, Inc.*, 1996.
- [10] John Bardeen, Leon N Cooper, and J Robert Schrieffer. Microscopic theory of superconductivity. *Physical Review*, 106(1):162, 1957.

- [11] Gilbert S Blevins, Walter Gordy, and William M Fairbank. Superconductivity at millimeter wave frequencies. *Physical Review*, 100(4):1215, 1955.
- [12] WS Corak, BB Goodman, CB Satterthwaite, and A Wexler. Atomic heats of normal and superconducting vanadium. *Physical Review*, 102(3):656, 1956.
- [13] WS Corak and CB Satterthwaite. Atomic heats of normal and superconducting tin between 1.2 and 4.5 k. *Physical Review*, 102(3):662, 1956.
- [14] RE Glover III and M Tinkham. Transmission of superconducting films at millimeter-microwave and far infrared frequencies. *Physical Review*, 104(3):844, 1956.
- [15] Leon N Cooper. Bound electron pairs in a degenerate fermi gas. *Physical Review*, 104(4):1189, 1956.
- [16] NN Bogolyubov, VV Tolmachev, and DV Shirkov. On a new method in the theory of superconductivity. *J. Exp. Theor. Phys*, 34(1):58, 1958.
- [17] JG Valatin. Comments on the theory of superconductivity. *Il Nuovo Cimento (1955-1965)*, 7(6):843–857, 1958.
- [18] DJ Thouless. Strong-coupling limit in the theory of superconductivity. *Physical Review*, 117(5):1256, 1960.
- [19] W A Little and R D Parks. Observation of Quantum Periodicity in the Transition Temperature of a Superconducting Cylinder. *Phys. Rev. Lett.*, 9:9–12, 1962.
- [20] M D Stewart, Aijun Yin, J M Xu, and James M Valles. Superconducting pair correlations in an amorphous insulating nanohoneycomb film. *Science*, 318(5854):1273–1275, nov 2007.

- [21] Doron Gurovich, Konstantin S Tikhonov, Diana Mahalu, and Dan Shahar. Little-Parks oscillations in a single ring in the vicinity of the superconductor-insulator transition. *Physical Review B*, 91(17), 2015.
- [22] Brian David Josephson. Possible new effects in superconductive tunnelling. *Physics letters*, 1(7):251–253, 1962.
- [23] Brian D Josephson. The discovery of tunneling supercurrents. *Science*, 184(4136):527–530, 1974.
- [24] M Iansiti, AT Johnson, Walter F Smith, H Rogalla, CJ Lobb, and M Tinkham. Charging energy and phase delocalization in single very small josephson tunnel junctions. *Physical review letters*, 59(4):489, 1987.
- [25] Michel H Devoret, Andreas Wallraff, and John M Martinis. Superconducting qubits: A short review. *arXiv preprint cond-mat/0411174*, 2004.
- [26] J M Valles, R C Dynes, and J P Garno. Superconductivity and the electronic density of states in disordered two-dimensional metals. *Physical Review B*, 40(10):6680, 1989.
- [27] AF Hebard and AT Fiory. Microstructure, dimensionality, and depression of the transition temperature in disordered superconducting films. *Physical review letters*, 58(11):1131, 1987.
- [28] MSM Minhaj, S Meepagala, JT Chen, and LE Wenger. Thickness dependence on the superconducting properties of thin nb films. *Physical Review B*, 49(21):15235, 1994.
- [29] K Yu Arutyunov, Dmitri S Golubev, and Andrej Dmitievich Zaikin. Superconductivity in one dimension. *Physics Reports*, 464(1-2):1–70, 2008.

- [30] N Giordano. Evidence for macroscopic quantum tunneling in one-dimensional superconductors. *Physical review letters*, 61(18):2137, 1988.
- [31] Maciek Zgirski, Karri-Pekka Riikonen, Vladimir Touboltsev, and Konstantin Arutyunov. Size dependent breakdown of superconductivity in ultranarrow nanowires. *Nano letters*, 5(6):1029–1033, 2005.
- [32] Alexey Bezryadin, CN Lau, and M Tinkham. Quantum suppression of superconductivity in ultrathin nanowires. *Nature*, 404(6781):971, 2000.
- [33] Anthony Travis Bollinger, A Rogachev, and Alexey Bezryadin. Dichotomy in short superconducting nanowires: Thermal phase slippage vs. coulomb blockade. *EPL (Europhysics Letters)*, 76(3):505, 2006.
- [34] F Sharifi, AV Herzog, and RC Dynes. Crossover from two to one dimension in in situ grown wires of pb. *Physical review letters*, 71(3):428, 1993.
- [35] Yang Guo, Yan-Feng Zhang, Xin-Yu Bao, Tie-Zhu Han, Zhe Tang, Li-Xin Zhang, Wen-Guang Zhu, EG Wang, Qian Niu, ZQ Qiu, et al. Superconductivity modulated by quantum size effects. *Science*, 306(5703):1915–1917, 2004.
- [36] James S Langer and Vinay Ambegaokar. Intrinsic resistive transition in narrow superconducting channels. *Physical Review*, 164(2):498, 1967.
- [37] DE McCumber and BI Halperin. Time scale of intrinsic resistive fluctuations in thin superconducting wires. *Physical Review B*, 1(3):1054, 1970.
- [38] Mitrabhanu Sahu, Myung-Ho Bae, Andrey Rogachev, David Pekker, Tzu-Chieh Wei, Nayana Shah, Paul M Goldbart, and Alexey Bezryadin. Individual topological tunnelling events of a quantum field probed through their macroscopic consequences. *Nature Physics*, 5(7):503, 2009.

- [39] JE Mooij and Yu V Nazarov. Superconducting nanowires as quantum phase-slip junctions. *Nature Physics*, 2(3):169, 2006.
- [40] S L Sondhi Girvin, S.M., Carini, J.P. and Shahar, D. Continuous quantum phase transitions. *Rev. Mod. Phys*, 69:315–333, 1997.
- [41] Philip W Anderson. Theory of dirty superconductors. *Journal of Physics and Chemistry of Solids*, 11(1-2):26–30, 1959.
- [42] V F Gantmakher and V T Dolgoplov. Superconductor-insulator quantum phase transition. *Physics-Uspexhi*, 53(1):1–49, 2010.
- [43] B Abeles, Roger W Cohen, and GW Cullen. Enhancement of superconductivity in metal films. *Physical Review Letters*, 17(12):632, 1966.
- [44] Roger W Cohen and B Abeles. Superconductivity in granular aluminum films. *Physical Review*, 168(2):444, 1968.
- [45] Sangita Bose, Pratap Raychaudhuri, Rajarshi Banerjee, Parinda Vasa, and Pushan Ayyub. Mechanism of the size dependence of the superconducting transition of nanostructured nb. *Physical review letters*, 95(14):147003, 2005.
- [46] SANGITA Bose. *Size effects in nanostructured superconductors*. PhD thesis, Citeseer, 2007.
- [47] P W Anderson. Theory of Dirty Superconductors. *J. Phys. Chem. Solids*, 11:26–31, 1959.
- [48] AV Balatsky, I Vekhter, and Jian-Xin Zhu. Impurity-induced states in conventional and unconventional superconductors. *Reviews of Modern Physics*, 78(2):373, 2006.
- [49] AF Ioffe and AR Regel. Non-crystalline, amorphous and liquid electronic semiconductors. *Prog. Semicond*, 4(237):89, 1960.

- [50] Jun Kondo. Resistance minimum in dilute magnetic alloys. *Progress of theoretical physics*, 32(1):37–49, 1964.
- [51] Ai A Abrikosov and L Pr Gor'kov. Contribution to the theory of superconducting alloys with paramagnetic impurities. *Zhur. Eksptl'. i Teoret. Fiz.*, 39, 1960.
- [52] Nevill F Mott. The basis of the electron theory of metals, with special reference to the transition metals. *Proceedings of the Physical Society. Section A*, 62(7):416, 1949.
- [53] John Hubbard. Electron correlations in narrow energy bands. *Proc. R. Soc. Lond. A*, 276(1365):238–257, 1963.
- [54] M P A Fisher, P B Weichman, G Grinstein, and D S Fisher. Boson Localization and the Superfluid-Insulator Transition. *Physical Review B*, 40(1):546–570, 1989.
- [55] Philip W Anderson. Absence of diffusion in certain random lattices. *Physical review*, 109(5):1492, 1958.
- [56] Gerd Bergmann. Weak localization in thin films: a time-of-flight experiment with conduction electrons. *Physics Reports*, 107(1):1–58, 1984.
- [57] Shih-Ying Hsu and JM Valles Jr. Observation of a well defined transition from weak to strong localization in two dimensions. *Physical review letters*, 74(12):2331, 1995.
- [58] V. F. Gantmakher. *Electrons and Disorder in Solids*. Oxford University Press, aug 2007.
- [59] Subir Sachdev. *Quantum phase transitions*. Cambridge university press, 2011.

- [60] Y H Lin, J Nelson, and A M Goldman. Superconductivity of very thin films: The superconductor-insulator transition. *Physica C-Superconductivity and Its Applications*, 514:130–141, 2015.
- [61] AD Caviglia, Stefano Gariglio, Nicolas Reyren, Didier Jaccard, T Schneider, M Gabay, S Thiel, G Hammerl, Jochen Mannhart, and J-M Triscone. Electric field control of the $\text{LaAlO}_3/\text{SrTiO}_3$ interface ground state. *Nature*, 456(7222):624, 2008.
- [62] D B Haviland Liu, Y., and Goldman, A. M. Onset of superconductivity in the two-dimensional limit. *Physical Review Letters*, 62:2180–2183, 1989.
- [63] U Givan and Z Ovadyahu. Compositional disorder and transport peculiarities in the amorphous indium oxides. *Physical Review B*, 86(16), 2012.
- [64] HQ Nguyen, SM Hollen, J Shainline, JM Xu, and JM Valles Jr. Driving a superconductor to insulator transition with random gauge fields. *Scientific reports*, 6:38166, 2016.
- [65] A Gerber, A Milner, G Deutscher, M Karpovsky, and A Gladkikh. Insulator-superconductor transition in 3d granular al-ge films. *Physical review letters*, 78(22):4277, 1997.
- [66] A Larkin. Superconductor-insulator transitions in films and bulk materials. *Annalen der Physik*, 8(7-9):785–794, 1999.
- [67] S.-Y. Hsu and Valles, Jr., J.M. Magnetic-field-induced pair-breaking effects in granular Pb films near the superconductor-to-insulator transition. *Phys. Rev B*, 48:4164–4167, 1993.
- [68] Alice E White, RC Dynes, and JP Garno. Destruction of superconductivity in quench-condensed two-dimensional films. *Physical Review B*, 33(5):3549, 1986.

- [69] Shih-Ying Hsu, JA Chervenak, and JM Valles Jr. Magnetic field enhanced order parameter amplitude fluctuations in ultrathin films near the superconductor-insulator transition. *Physical review letters*, 75(1):132, 1995.
- [70] RC Dynes, AE White, JM Graybeal, and JP Garno. Breakdown of eliashberg theory for two-dimensional superconductivity in the presence of disorder. *Physical review letters*, 57(17):2195, 1986.
- [71] A F Hebard and Paalanen, M.A. Magnetic-field-tuned superconductor-insulator transition in 2-dimensional films. *Physical Review Letters*, 65:927–930, 1990.
- [72] T. I. Baturina, C. Strunk, M. R. Baklanov, and A. Satta. Quantum metallicity on the high-field side of the superconductor-insulator transition. *Physical Review Letters*, 98(12):127003, mar 2007.
- [73] Yongguang Qin, Carlos L Vicente, and Jongsoo Yoon. Magnetically induced metallic phase in superconducting tantalum films. *Physical Review B*, 73(10):100505, 2006.
- [74] Ali Yazdani and Aharon Kapitulnik. Superconducting-insulating transition in two-dimensional a-moge thin films. *Physical review letters*, 74(15):3037, 1995.
- [75] JM Valles Jr, RC Dynes, and JP Garno. Electron tunneling determination of the order-parameter amplitude at the superconductor-insulator transition in 2d. *Physical review letters*, 69(24):3567, 1992.
- [76] B Sacepe, T Dubouchet, C Chapelier, M Sanquer, M Ovadia, D Shahar, M Feigel'man, and L Ioffe. Localization of preformed Cooper pairs in disordered superconductors. *Nature Physics*, 7(3):239–244, 2011.

- [77] AM Finkel'Stein. Suppression of superconductivity in homogeneously disordered systems. *Physica B: Condensed Matter*, 197(1-4):636–648, 1994.
- [78] H. Q. Nguyen, S. M. Hollen, M. D. Stewart, J. Shainline, Aijun Yin, J. M. Xu, and J. M. Valles. Observation of Giant Positive Magnetoresistance in a Cooper Pair Insulator. *Physical Review Letters*, 103(15):1–4, oct 2009.
- [79] G. Sambandamurthy, L. W. Engel, A. Johansson, and D. Shahar. Superconductivity-Related Insulating Behavior. *Physical Review Letters*, 92(10):107005–1, 2004.
- [80] John Michael Kosterlitz and David James Thouless. Ordering, metastability and phase transitions in two-dimensional systems. *Journal of Physics C: Solid State Physics*, 6(7):1181, 1973.
- [81] M P A Fisher. Quantum phase-transitions in disordered two dimensional superconductors. *Phys. Rev. Lett.*, 65:923–926, 1990.
- [82] P G Bjoernsson, Ganapathy Sambandamurthy, K A Moler, E Peled, A Johansson, Dan Shahar, E Peled, Dan Shahar, P G Bjornsson, and K A Moler. Power law resistivity behavior in 2D superconductors across the magnetic field-tuned superconductor-insulator transition. *Europhysics Letters*, 75(4):611–617, 2006.
- [83] K Kim and D Stroud. Quantum Monte Carlo study of a magnetic-field-driven two-dimensional superconductor-insulator transition. *Physical Review B*, 78(17), 2008.
- [84] Amit Ghosal, Mohit Randeria, and Nandini Trivedi. Inhomogeneous pairing in highly disordered s-wave superconductors. *Physical Review B*, 65(1):014501, 2001.

- [85] S. M. Hollen, H. Q. Nguyen, E. Rudisaile, M. D. Stewart, J. Shainline, J. M. Xu, and J. M. Valles. Cooper-pair insulator phase in superconducting amorphous Bi films induced by nanometer-scale thickness variations. *Physical Review B*, 84(6):064528, aug 2011.
- [86] H. Q. Nguyen, S. M. Hollen, J. M. Valles, J. Shainline, and J. M. Xu. Disorder influences the quantum critical transport at a superconductor-to-insulator transition. *Physical Review B - Condensed Matter and Materials Physics*, 92(14):1–6, 2015.
- [87] Enzo Granato. Superconductor-insulator transition of Josephson-junction arrays on a honeycomb lattice in a magnetic field. *European Physical Journal B*, 89(3):1–8, 2016.
- [88] S. M. Hollen, G. E. Fernandes, J. M. Xu, and J. M. Valles. Collapse of the Cooper pair phase coherence length at a superconductor-to-insulator transition. *Physical Review B - Condensed Matter and Materials Physics*, 87(5):11–14, 2013.
- [89] James Joy. *Studies on the Bose Insulator to Fermi Insulator Crossover Near the Two-Dimensional Superconductor-Insulator Transition*. PhD thesis, Brown University, 2017.
- [90] V F Gantmakher, M V Golubkov, V T Dolgoplov, A A Shashkin, and G E Tsydynzhapov. Observation of the parallel-magnetic-field-induced superconductor-insulator transition in thin amorphous InO films. *Jetp Letters*, 71(11):473–476, 2000.

Chapter 2

AAO substrate fabrication and characterization

Porous AAO templates can be fabricated through electrochemical methods. Self-assembled nano-pores form on the surface of Aluminum with specific combinations of anodizing voltage, acidic electrolyte, concentration and temperature. This material has attracted increasing attention in recent years due to its wide application to create ordered nano-crystal arrays, nano-tube with tunable diameters and high density magnetic recording, etc [1, 2, 3]. Moreover, the straightforward fabrication process and low cost make it preferable to lithography for large scale industry use. In this chapter, I will discuss the fabrication process for AAO with different parameters. I will show scanning electron microscope(SEM) and atomic force microscope(AFM) images to characterize those templates.

2.1 Introduction

The method of surface oxidization has a long history of being used to create a protection layer. The commercial use of Aluminium oxide can be dated back to as early as 1923 [4]. In 1953, Keller, et al. [5] reported the formation of nano-pores by anodizing aluminum in acidic electrolyte. Masuda et al. further developed this method by using a two-step anodization. They successfully fabricated highly ordered AAO with 100 nm pore spacing using 0.3M oxalic acid and applying 40 V constant voltage. Later on, various methods based on two-step anodization have been employed to make highly ordered AAO with pore spacing ranging from 30nm to 500nm [6, 7, 8, 9].

Table 2.1: Conventional Two-step Anodization

Electrolytes	Concentration	Voltage	Temperature	Time	Spacing	Porosity
H_2SO_4	0.3 M	25V	10°C	7.5h	60nm	~ 10%
$C_2H_2O_4$	0.3 M	40V	10°C	16h	100nm	~ 10%
H_3PO_4	0.3 M	195V	0°C	16h	500nm	~ 10%

The three most commonly used acidic electrolytes are sulfuric acid, oxalic acid and phosphoric acid. The corresponding anodizing conditions and AAO pore spacings are listed in Table 2.1. The porosity is a measure of pore area relative to the surface area, and it can be calculated as

$$P = \frac{2\pi}{\sqrt{3}}(r/D_{int})^2 \quad (2.1.1)$$

where r is pore radius and D_{int} is inter-pore spacing. As we can see in the table, the porosity is approximately independent of the specific anodization conditions ("10% porosity rule").

Another important parameter of AAO is the inter-pore spacing. For conventional two-step anodization, the inter-pore spacings increases linearly with the anodic voltage (see Fig. 2.3.2) with roughly $d = 2.5U_a$. This formula agrees well with the

numbers in Table 2.1.

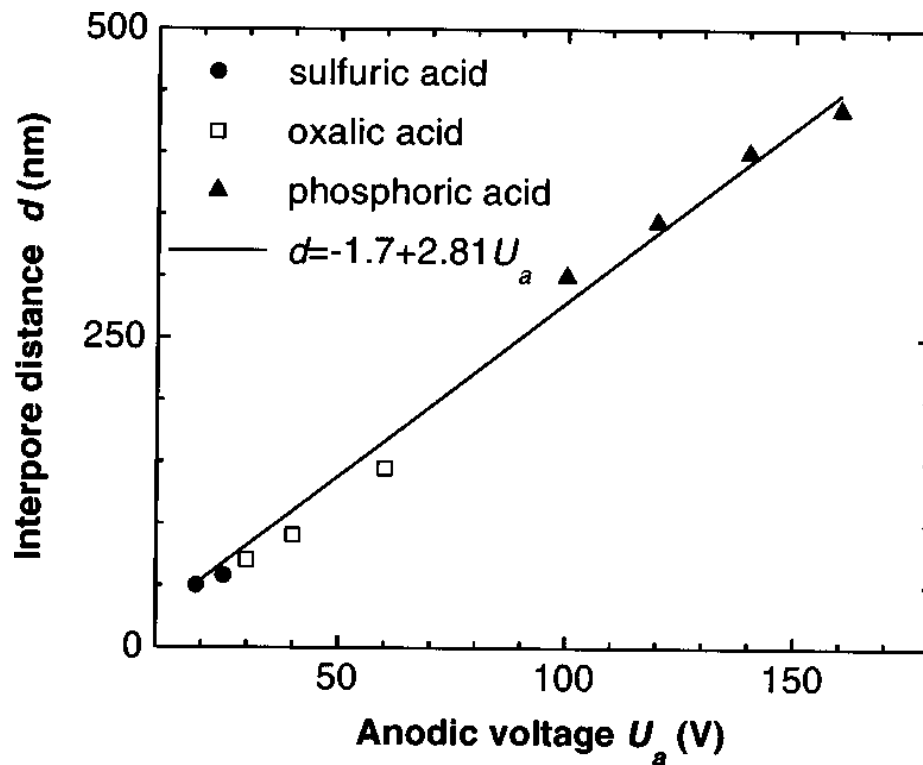


Figure 2.1.1: Inter-pore spacing increases linearly with voltage in different anodizing conditions for sulfuric, oxalic, and phosphoric acid. [7]

A significant drawback of conventional two-step anodization (also called Mild Anodization) is the slow oxide growth rate, which is usually around $1 \sim 2 \mu\text{m}/\text{h}$. To get ordered nano-pore structures, it usually requires at least 10 hours. WOO LEE et al. developed a method anodizing at much higher voltage than the values in Table 2.1, calling it Hard Anodization [10]. For oxalic acid, they found a highly ordered regime at $110 \sim 150\text{V}$ instead of the conventional 40V voltage. Because of the additional heat generated by high current and voltage, this method requires lower temperature and more efficient heat dissipation. The oxide growth rate was increased to $50 \sim 70 \mu\text{m}/\text{h}$ depending on the exact voltage applied, and the porosity is around 3%, which is smaller than the result in mild anodization.

2.2 Fabrication Process

The general processes for conventional two-step anodization are the same although the specific conditions differ for different electrolytes (see Fig. 2.2.1). I will take oxalic acid as an example below. For other types of mild anodization, we only need to replace the electrolyte, change the corresponding temperature and time as shown in Table 2.1. After each step, the aluminum strip should be ultrasonically cleaned to avoid contamination of the solution from the previous step.

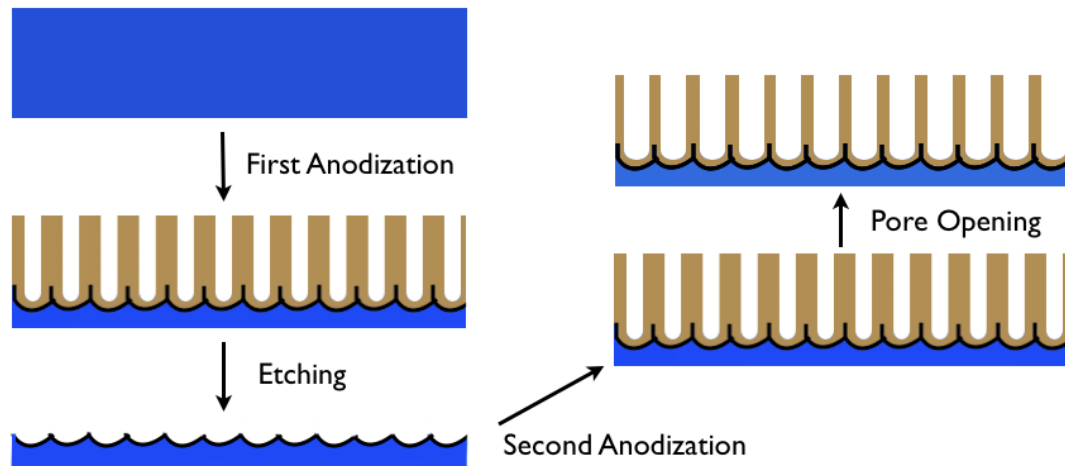


Figure 2.2.1: General procedures for two-step anodization. Cleaning before and after each step is not shown.

- Pre-cleaning. High purity aluminum sheet (0.5" by 2", 5N purity) is ultrasonically degreased and cleaned in acetone, methanol and distilled water, respectively.
- Annealing. Insert the pre-cleaned aluminum sheet into a CVD furnace and anneal it under Nitrogen or Argon ambient at 400°C for 3 hours to remove mechanical stress.

- Electropolishing. Hang the sheet in a mixture of perchloric acid and ethanol(1:5) and maintain the solution temperature at $T = 0^{\circ}C$. Apply 15V voltage for 15 minutes.
- First anodization. Hang the sheet in a 0.3 M oxalic acid at $T = 10^{\circ}C$. Apply 40V DC voltage for 16 hours. Keep the magnetic stir running to dissipate extra heat. Initially at this stage, the pores are disordered in terms of size and location. As the anodizing time increases, the deeper part of the oxide layer becomes more and more ordered.
- Etching. The first oxide layer is etched away in a mixture of 6% phosphoric acid and 1.8% chromic oxide at $T = 60^{\circ}C$. This step takes at least 3 hours, leaving ordered nano-patterned shallow pores on the aluminum surface. Those notches provide the nucleation for oxide layer growth in the second anodization.
- Second anodization. The aluminum sheet is anodized again under the same conditions as the first time. The anodization time depends on how much depth of the oxide layer we need.
- Separation of oxide layer. Depending on the purpose for the AAO, the oxide layer can be removed from the aluminum base using mercuric chloride($HgCl_2$) solution. This step is skipped in our research for the ease of handling the template.
- Pore opening. If necessary, the pore size can be adjusted by submerging it in 5wt% phosphoric acid at $T = 30^{\circ}C$.

Hard anodization is similar but more tricky to deal with because we need to be extremely careful about heat dissipation. The magnetic stir needs to be set at the maximum speed and the temperature should preferably be set below $0^{\circ}C$ ($-1^{\circ}C$ in

my experiments). Before the first anodization, regular 40 V voltage is applied for 30 minutes to build a protective layer. This oxide layer helps prevent instant burning when the voltage increases. Next, the voltage is slowly increased to 110 ~ 150 V but stopped if the current jumps up. Some oxygen and hydrogen bubbles can appear at the two electrodes. That must be allowed away. Since the oxide growth rate is much higher, 2 hours is sufficient to grow an ordered oxide layer.

2.3 AAO Characterization

Key parameters of AAO include the inter-pore spacing, pore diameter, ordering and roughness. Oxide layer thickness can be estimated using the growth rate ($1 \sim 2 \mu\text{m}/h$) or exactly measured using cross-sectional SEM images, but it is less relevant to our research so I will skip the discussion of that.

2.3.1 Inter-pore Spacing

We fabricated AAO by both mild anodization and hard anodization with varying voltages and electrolytes. As shown in the SEM images in Fig. 2.3.1, the inter-pore spacing significantly increases as we increase the anodizing voltage and change the corresponding type of electrolyte. The inter-pore spacings can be estimated by counting the number of pores in each image, or more quantitatively, using an autocorrelation technique. In signal processing, autocorrelation is the correlation with the signal itself but with a time delay. In our context, it can be defined as,

$$Corr(r) = E[\rho(R)\rho(R - r)] \quad (2.3.1)$$

The expectation is calculated as the average over the whole image and r is averaged over all directions. When r equals one period of the images, the correlation

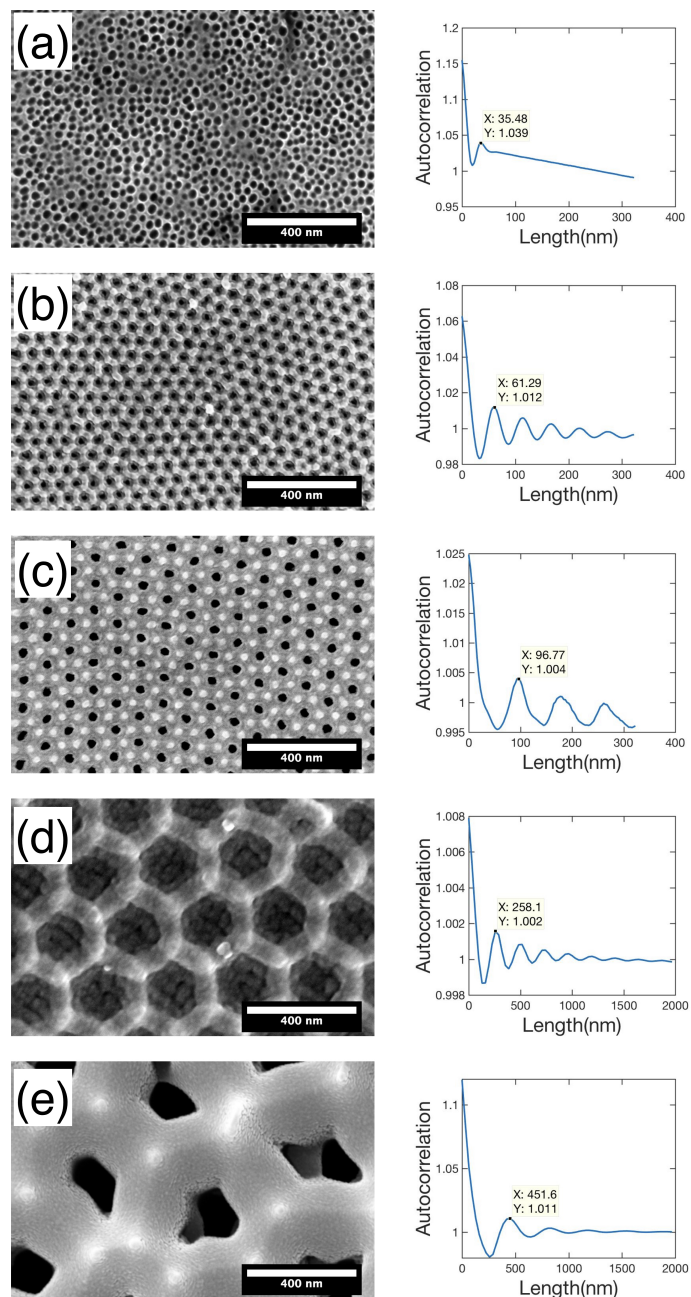


Figure 2.3.1: AAO substrates with various inter-pore spacings. They are coated with 1nm Germanium(Ge) and 10nm Silver(Ag) to avoid blurring in the SEM images. (a) 12V in 8M H_2SO_4 at 40°C for 1 min, following the procedures in Ref. [11]. (b) 25V in 0.3M H_2SO_4 at 10°C. (c) 40V in 0.3M $C_2H_2O_4$ at 10°C. (d) 120V in 0.3M $C_2H_2O_4$ at -1°C (Hard Anodization). (e) 165V in 0.3M H_3PO_4 at 0°C. The right panels are the autocorrelation calculations which show the inter-pore spacing. See the text for details.

is expected to have a local maximum. By the Wiener-Khinchin theorem[12], the autocorrelation is equal to the inverse Fourier transform of the power spectral density(PSD), which is the square magnitude of Fourier transform of the original signal. Therefore, it can be simply calculated as $Corr = \text{ifft}(\text{abs}(\text{fft}(x))^2)$, where fft is the 2 dimensional Fast Fourier transform and ifft is the inverse FFT. Then, since we need to take the average of all directions in r , it is more convenient to use a polar coordinate system and calculate the average over all angles at a specific r .

The right panels in Fig. 2.3.1 show the autocorrelations calculated for the corresponding AAO templates. Please note the images used for calculation have lower magnification than the left ones so that we can see larger scale correlation. The peaks correspond to the multiples of the periods. The data cursor indicates the inter-pore spacing for each substrate. For well ordered substrates, e.g. (b,c,d), we can observe multiple peaks, while the other two only have one or two peaks. For Fig. 2.3.1(a), both the acid concentration and temperature are very high and the anodizing time is only 1 min, making the whole process hard to control. For Fig. 2.3.1(d), as we can see in Table 2.1, the ideal anodizing voltage is 195V, but it requires highly efficient heat dissipation. We can only reach 165V without burning the Aluminum strip in our lab, making it less ordered.

As we discussed in the last section, the inter-pore spacing increases linearly with anodic voltage. Fig 2.3.2 shows the relation between inter-pore spacing calculated using autocorrelation function and voltage applied. It agrees well with the generally accepted value 2.5 nm/V [5, 13, 14] for mild anodization. As reported in Ref.[10], the coefficient for hard anodization is closer to 2 nm/V due to the reduced voltage dependence of the pore diameter and the barrier layer thickness of anodic alumina under high current density.

Another method for characterizing the inter-pore spacing is the Fourier transform(FT) of the original image. For images with periodicity, the signal peaks in

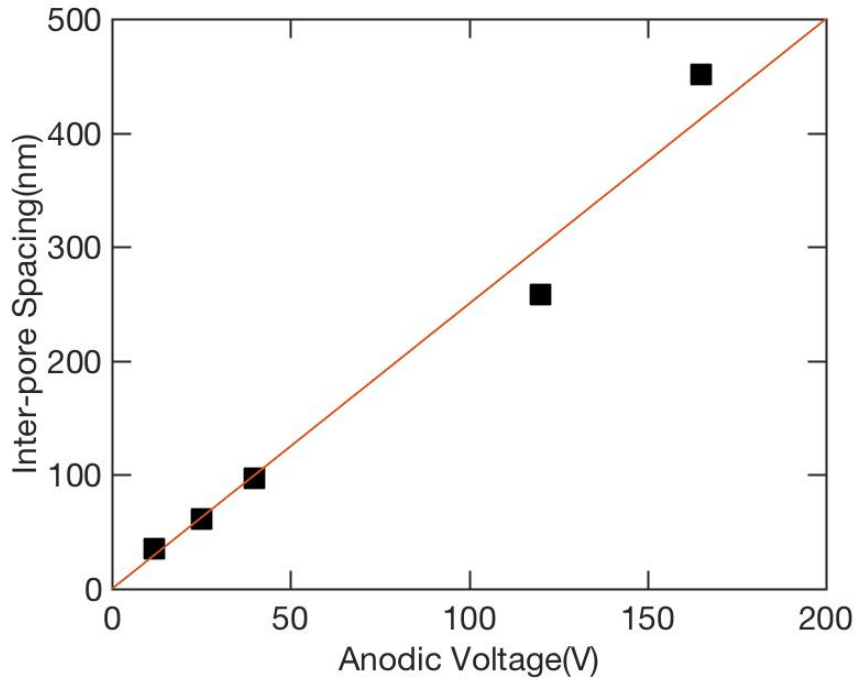


Figure 2.3.2: Inter-pore spacing increases linearly with anodic voltage. The error is smaller than the marker size. The solid line is $d = 2.5U_a$.

Fourier space. The first peak corresponds to the inverse period in real space. Fig. 2.3.3 uses two substrates with significantly different inter-pore spacings as examples to show how the FT works. Both show rim structures in Fourier space, and the periods agree with the values found using autocorrelation technique. Due to the high ordering in Fig. 2.3.3(a), we can even see hexagonal structure. Since the hexagonal lattice is dual to itself in FT, we can prove that the original lattice is hexagonal (although it is obvious). In contrast, Fig. 2.3.3(b) is less ordered and the rim is vague, making the relative estimated error high. The disordering smears the inhomogeneity in different directions, resulting in circular rims.

2.3.2 Pore Diameter

To locate the pores, it is necessary to first convert the original image to binary format. Otsu's method[15] is applied to find the threshold for conversion. The

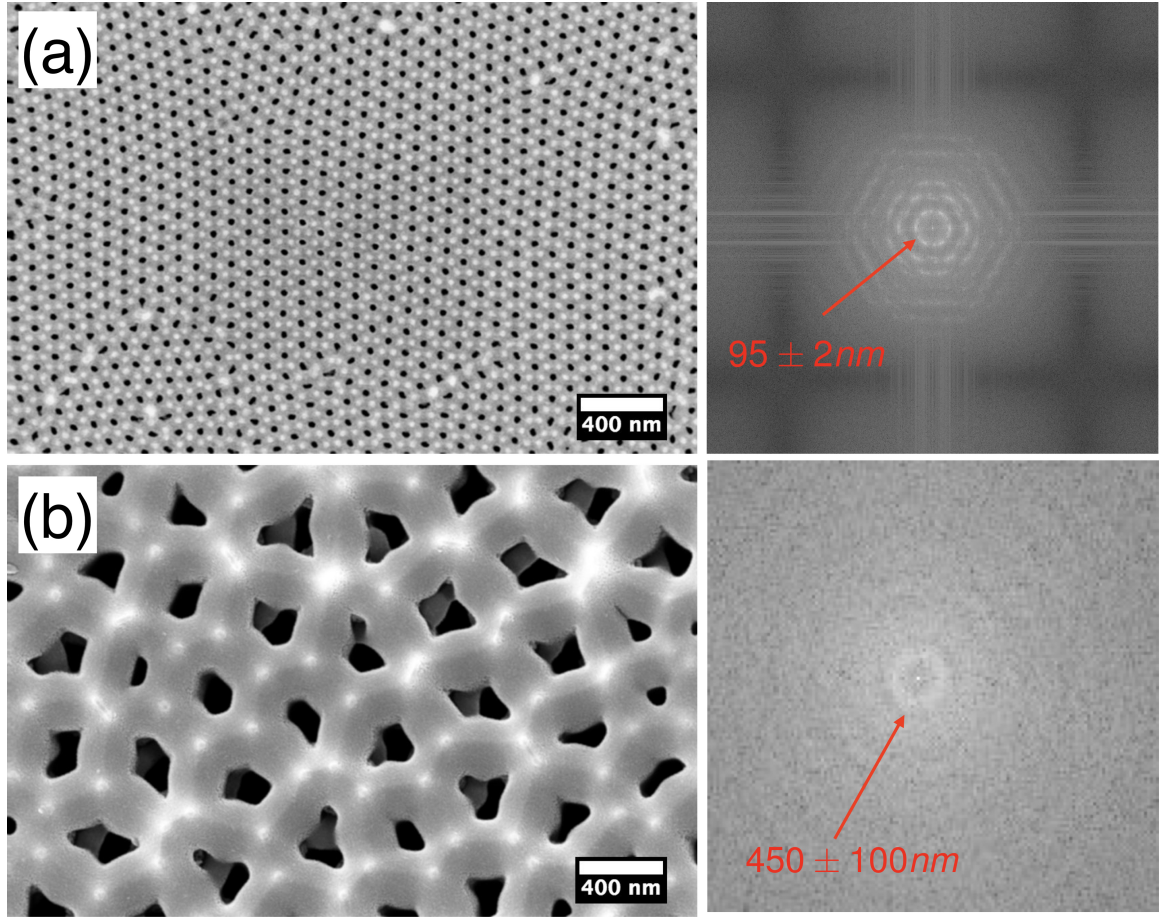


Figure 2.3.3: Fast Fourier Transform(FFT) of the SEM images corresponding to a (a) 100 nm and (b) 450 nm inter-pore spacing AAO. Those are the same substrates as in 2.3.1(c, e) except the magnification is lower. The inner rim of the FFT image indicates the periodicity. The inter-pore spacing of the upper one is $95 \pm 2nm$ and the lower one is $450 \pm 100nm$.

threshold is chosen to minimize the variance within the class ($\sigma^2(t) = \omega_0(t)\sigma_0^2(t) + \omega_1(t)\sigma_1^2(t)$, where σ_0^2 and σ_1^2 are the variance of black and white regions. ω_0 and ω_1 are their corresponding weights). The pores are separated as black regions('0') in white background('1'). Then the goal is to find the distribution of the black regions. Fig 2.3.4(b) plots circles with equivalent area at each recognized pore. The diameters show an approximate Gaussian distribution with $27.4 \pm 1.2nm$. The relative error is only 4%, indicating highly ordered pore sizes. Plugging those values into Eq.2.1.1, the porosity equals 7%.

The pore diameter can be changed by the extra "pore opening" step. The AAO

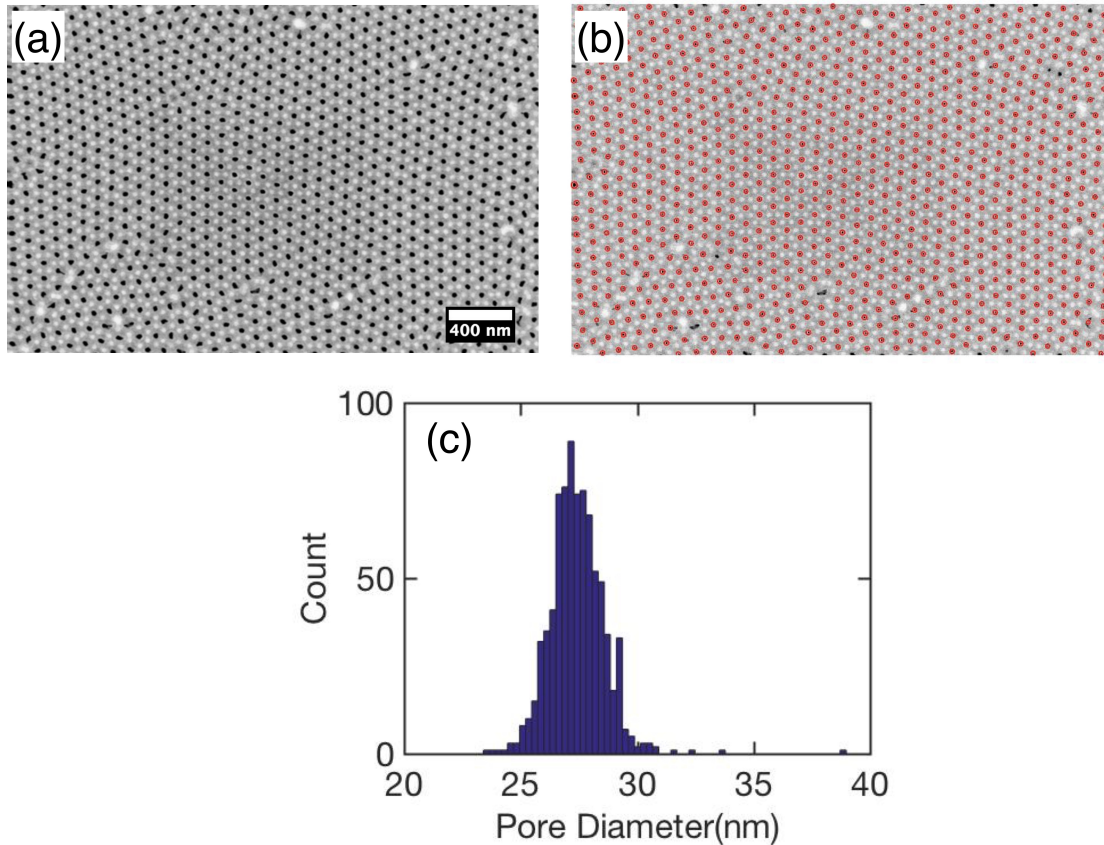


Figure 2.3.4: Pore size distribution. (a) Original 100nm AAO substrate used for analysis. (b) Pore recognition using MATLAB built-in functions. See the text for details. (c) Pore diameter distribution with mean value $27.4nm$ and standard deviation of $1.2nm$.

is submerged in 5wt% phosphoric acid at $30^{\circ}C$. The final pore size depends on the etching time. For substrate shown in Fig. 2.3.5, it takes 50 min. Using the same method discussed above, we found that the enlarged pore size is $83.1 \pm 3.1nm$. The relative error is still around 4%, but the porosity has significantly increased to 66%. This process makes AAO highly versatile for making nano-wires or nano-tubes with tunable diameters [16, 17, 18].

2.3.3 Ordering

The ordering of the nano-pore structure can be quantified using the pore size distribution shown above. However, for many application on the surface, e.g. the

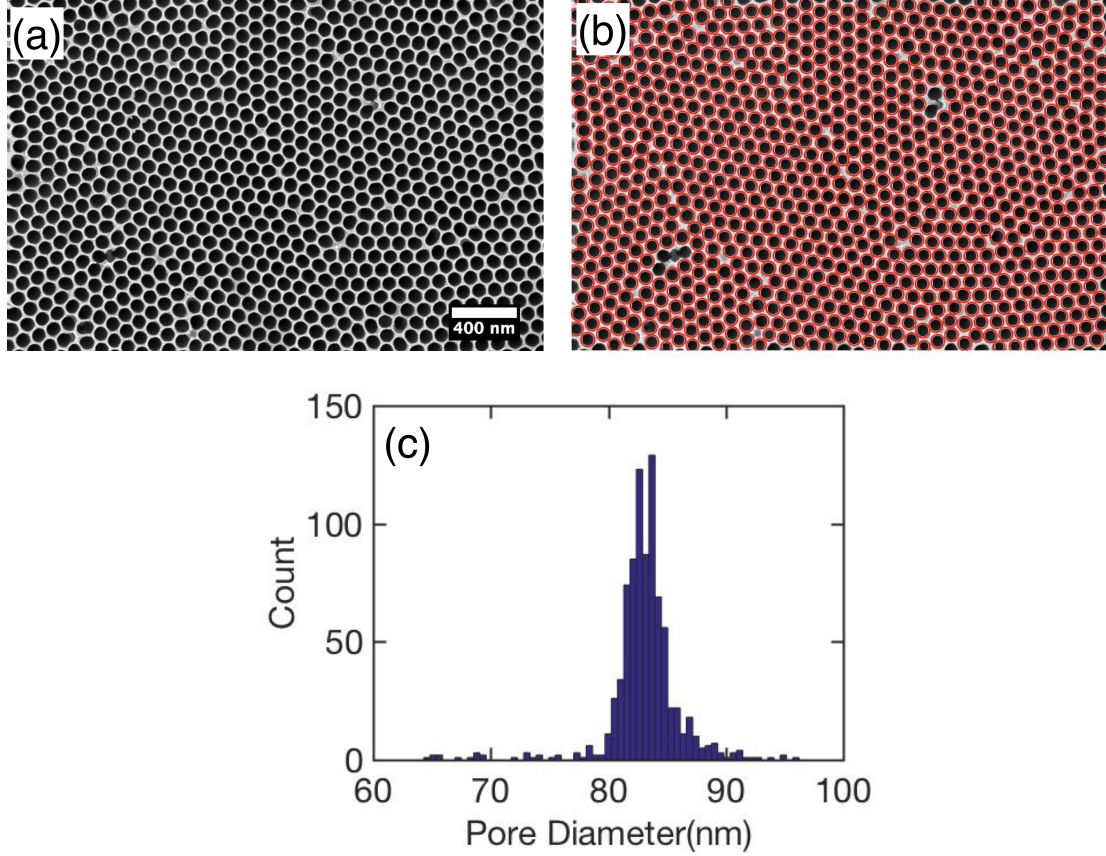


Figure 2.3.5: Pore size distribution after 50 min pore opening process. (a) 100nm AAO substrate with enlarged pores. (b) Pore recognition marked by red circles. (c) Pore diameter distribution with mean value $83.1nm$ and standard deviation of $3.1nm$.

electron transport measurements and gauge disorder experiments[19], the unit cell distribution is more relevant. In essence, it is a measure of pore displacement while the previous one is a measure of pore size disorder. Therefore, the ordering in this context is solely dependent on the location or the centroids of the pores.

To find the unit cell size distribution, the first step is to identify of centroids of pores. We can use the same trick as before. Again, we need to convert the original image to binary format and find the centroids for each black region. The next step is to partition the whole area by those centroids. We employ a Voronoi diagram for partitioning. Each subset area contains exact one pore center and every point in that subset is closer to the pore center contained than any other pore centers. The

last step is to calculate the area for each subset.

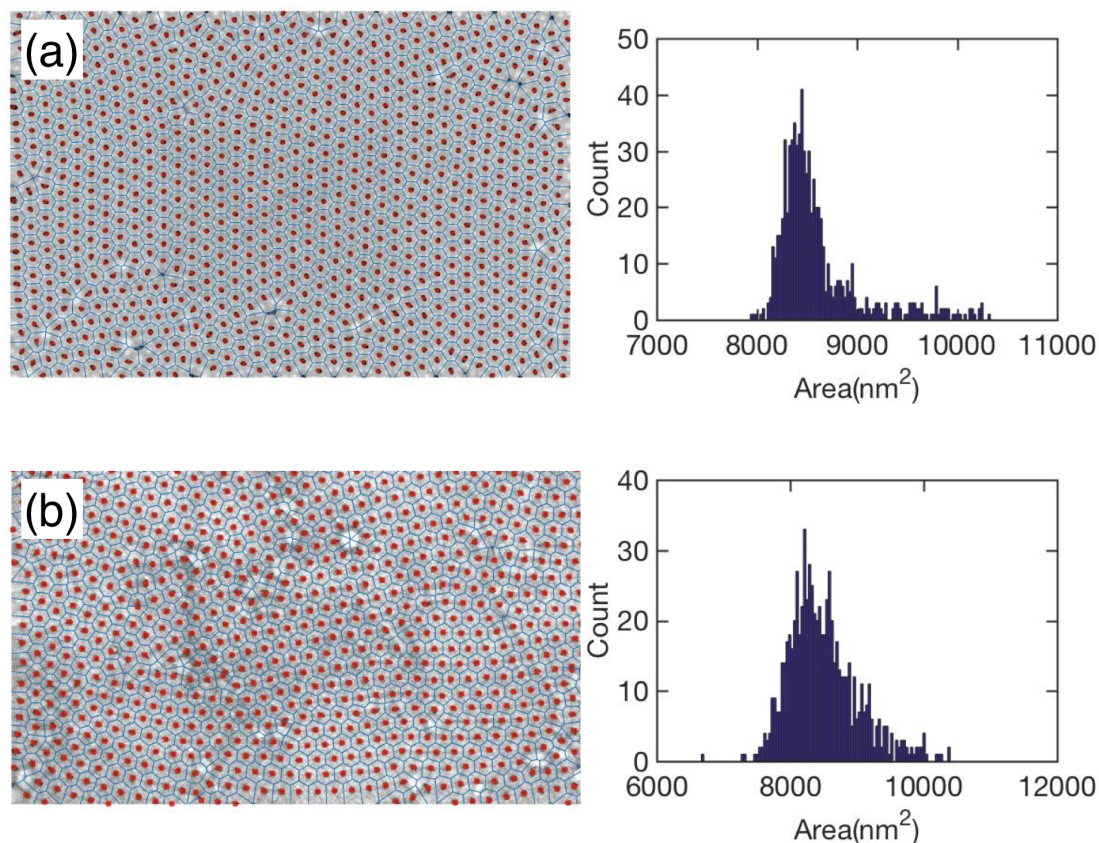


Figure 2.3.6: Unit cell size distribution of (a) highly ordered and (b) less ordered substrates. The red dots indicate the centers of pores. The whole area is partitioned using Voronoi diagram. The right panels show the area distribution of the cells. For (a), the mean is 8600nm^2 and the standard deviation is 430nm while the less ordered sample has a mean of 8500nm^2 with standard deviation of 530nm .

As shown in Fig. 2.3.6, both of the samples have unit cell area around 8600nm^2 . The highly ordered sample has a slightly smaller relative error of 5% while the other one has an error of 6%. If we consider it as close-packing hexagonal array, the nearest center-to-center distance can be calculated as $\sqrt{\frac{2\text{Area}}{\sqrt{3}}} = 100\text{nm}$. This agrees very well with our previous analysis.

2.3.4 Roughness

The surface of AAO is not smooth. As we can see in the SEM images, especially in Fig. 2.3.1(c), there are ordered bright dots around each pore. The principle of SEM is detecting secondary electrons or back-scattered electrons. For the same material, brighter parts usually indicate closer to detector and thus at high position. In that sense, we can roughly conclude there are six peaks around each pore. Actually, this roughness is crucial for the formation of superconducting islands in our research[20, 21].

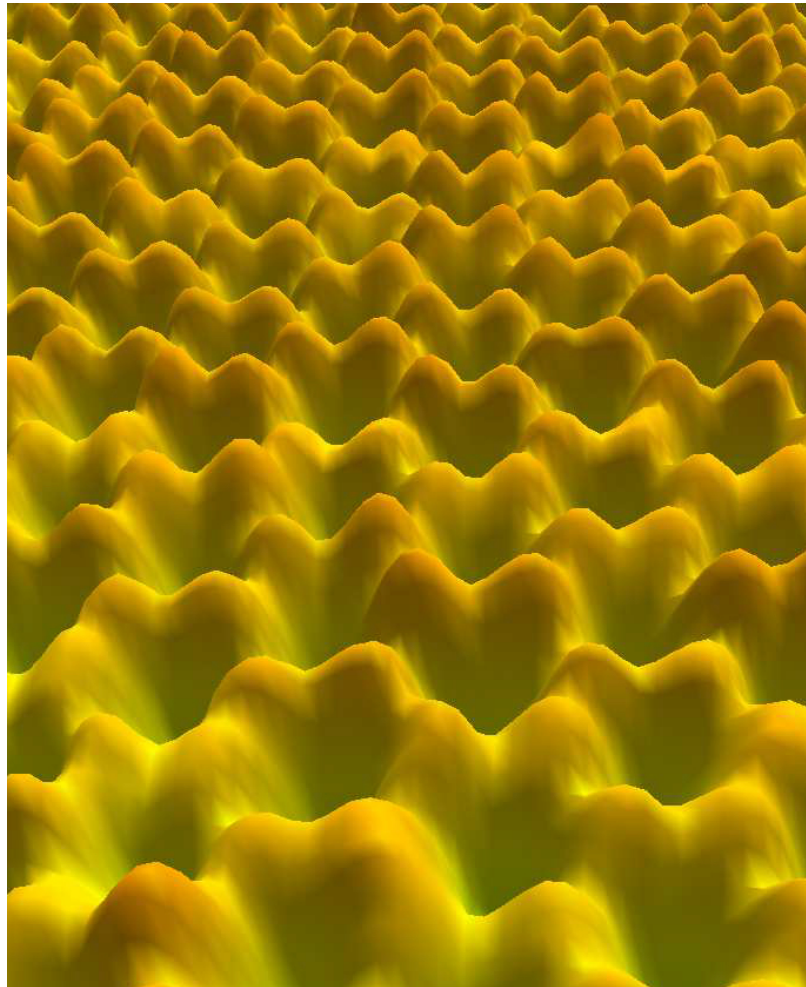


Figure 2.3.7: Viewing the substrate with an angle. It is a snapshot of a 3d AFM image.

Although the brightness of SEM images can act as a clue to show that the

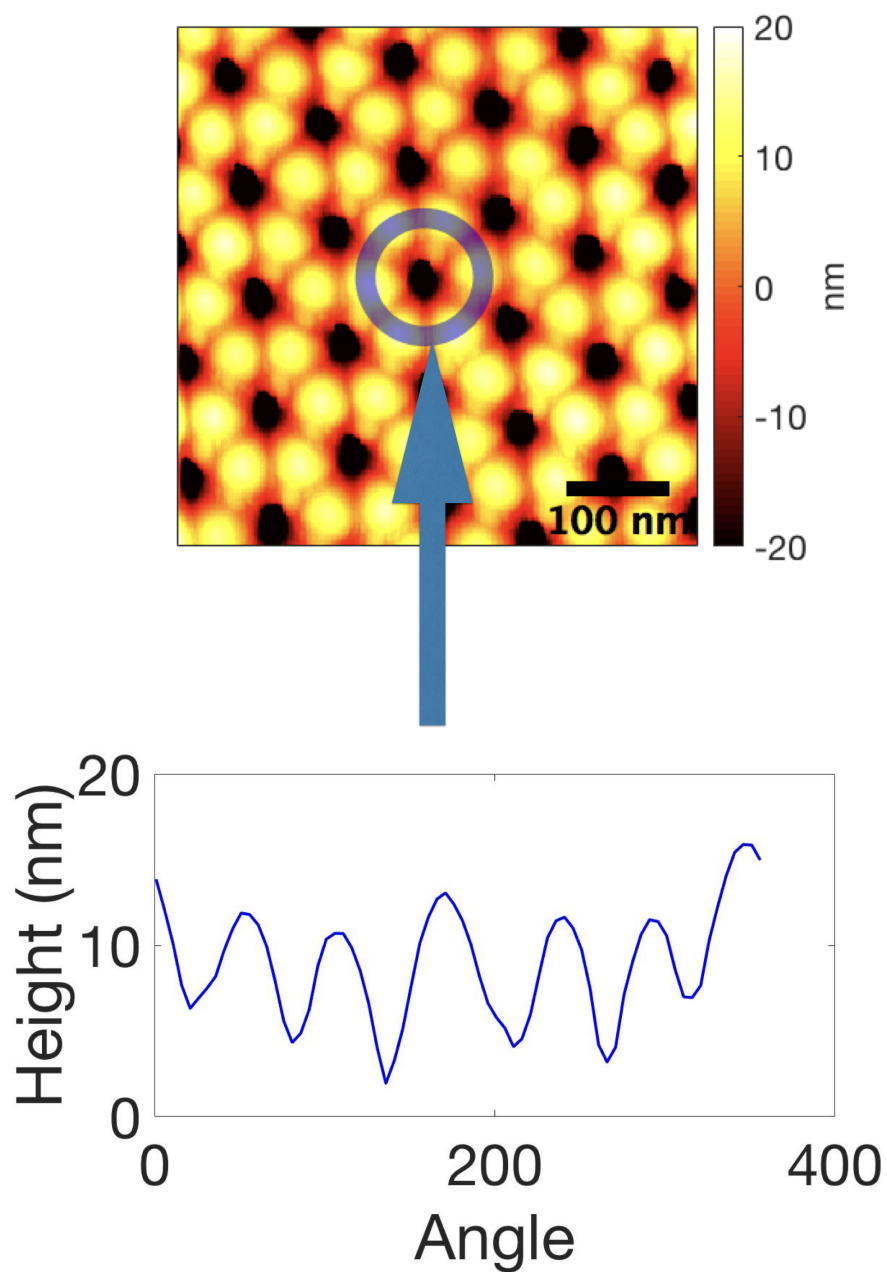


Figure 2.3.8: Linescan around the pore. The x axis is the angular distance in polar coordinate system. At each specific angle, the height is calculated as the mean value along the rim.

surface is not smooth, it is not reliable to quantify the roughness. AFM data gives us the extra dimension to reveal height change on the surface. We usually use the 'AC Air' mode with scanning rate set to 0.5 Hz or 1 Hz. The scanning area ranges from $1\mu m$ down to $300nm$, and the resolution is set to 256 or 512 points.

Fig. 2.3.7 shows the AFM image of a typical 100nm substrate. The roughness has been exaggerated to have a clear view of the six peaks and valleys around each pore. The cells form a close-packed hexagonal array and each peak is shared by three nearby pores. Another thing to note is that the pore walls are tapered near the upper surface. Using the etched sample as an example, a pore tapers down from about 80 nm diameter at the upper surface to less than 50 nm diameter below the upper surface [22].

Fig. 2.3.8 shows the line scan around the pore. For the 100nm AAO in the example, the peak to valley difference is around 10nm. That is across a distance of $50/\sqrt{3}$ nm, so the average angle is $\arctan(\sqrt{3}/5) = 20^\circ$. The angle at the steepest part, however, can be around 45° . We have used the pore opening process. It has little effect on the surface roughness, which is surprising to us.

For other inter-pore spacings, the roughness can be quite different. See Fig. 2.3.9 for the results. First, the ranges in x directions are different. The length between the two nearest peaks equals $D_{int}/\sqrt{3}$, where D_{int} is the inter-pore spacing as shown in the previous discussions. Those values are consistent with each other. Second, the peak-valley height differs a lot for different substrates. It is around 5nm on 60nm AAO, 10nm on 100nm AAO, 35nm on 250nm AAO and 65nm on 450nm AAO. The corresponding average angles are $\theta(60nm) = 16^\circ$, $\theta(100nm) = 20^\circ$, $\theta(250nm) = 26^\circ$, and $\theta(450nm) = 27^\circ$. Those values come from a very rough calculation. Better estimates require calculation for all the peak-valley pairs. But from what we observed, there is a general trend that AAO with larger inter-pore spacing is rougher than the ones with lower inter-pore spacings. The

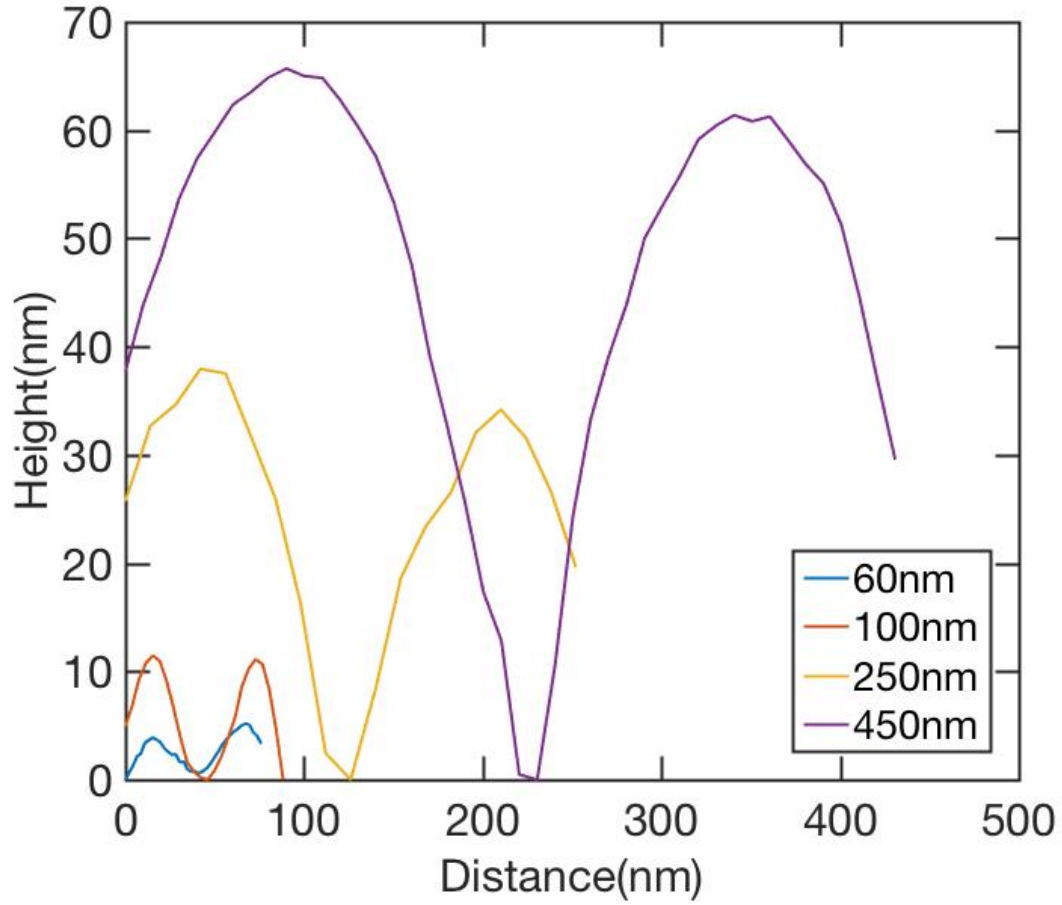


Figure 2.3.9: Linescans of AFM images for different substrates. The curves are labeled with their inter-pore spacings. Refer to Fig.2.3.1. The two peaks correspond to two nearest peaks on the surface.

reason behind this variation still remains a mystery.

In quench condensation, the thickness undulation depends on the surface height variation of the substrate [23]. The thickness of the film is given by,

$$d(x) = d^{\text{dep}} \cos \theta = \frac{d^{\text{dep}}}{\sqrt{1 + (\nabla h(x))^2}} \quad (2.3.2)$$

where $\nabla h(x)$ is the surface gradient. Fig. 2.3.10 shows the thickness maps. As expected, the substrate with larger inter-pore spacing shows rougher surface structure. Since the slope is zero at the peaks and the valleys. There are twelve islands formed around each pore.

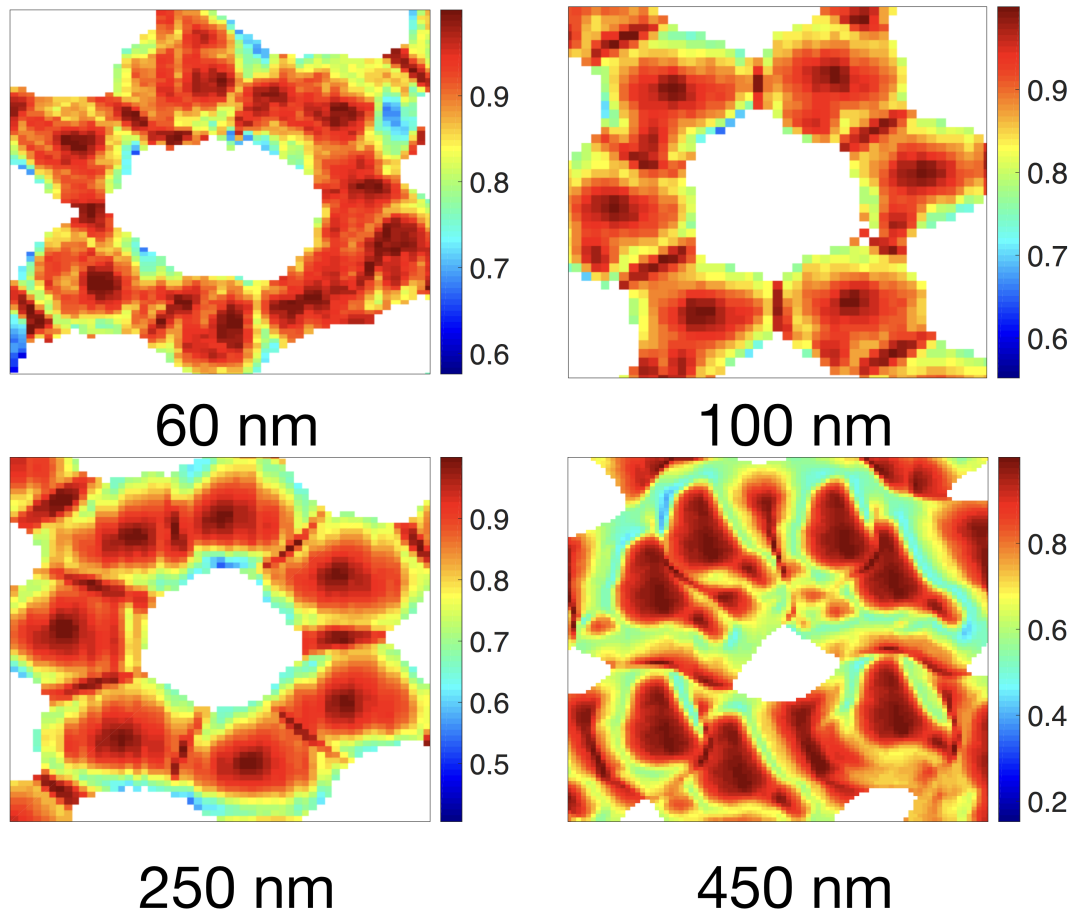


Figure 2.3.10: Thickness maps for films deposited on the substrate using quench condensation.

2.4 Conclusion

We have shown different methods, including mild and hard anodization, to make AAO substrates with various inter-pore spacings. The inter-pore spacing grows linearly with increasing anodizing voltage. One thing needs to mention is that we skipped the discussion about the chemical reaction behind those fabrication processes. That is beyond the scope of this thesis and there are still many unsolved questions. We also discussed various techniques to characterize the substrates, including SEM and AFM image analysis. Those substrates show different inter-pore spacings, pore sizes, ordering and roughness. Those parameters may be

related to the anodizing conditions, including temperature, electrolyte type, concentration, anodizing time, etc. To fully understand those questions, more systematic study is needed.

Bibliography

- [1] Shouheng Sun, C. B. Murray, Dieter Weller, Liesl Folks, and Andreas Moser. Monodisperse fept nanoparticles and ferromagnetic fept nanocrystal superlattices. *Science*, 287(5460):1989–1992, 2000.
- [2] Brian O'Regan and Michael Gratzel. A low-cost, high-efficiency solar cell based on dye-sensitized. *nature*, 353(6346):737–740, 1991.
- [3] Philippe Serp, Massimiliano Corrias, and Philippe Kalck. Carbon nanotubes and nanofibers in catalysis. *Applied Catalysis A: General*, 253(2):337 – 358, 2003.
- [4] G. D. Bengough and J. M. Stuart, 1923.
- [5] F Keller, MS Hunter, and DL Robinson. Structural features of oxide coatings on aluminum. *Journal of the Electrochemical Society*, 100(9):411–419, 1953.
- [6] Hideki Masuda, Fumio Hasegwa, and Sachiko Ono. Self-ordering of cell arrangement of anodic porous alumina formed in sulfuric acid solution. *Journal of the electrochemical society*, 144(5):L127–L130, 1997.
- [7] AP Li, F Müller, A Birner, K Nielsch, and U Gösele. Hexagonal pore arrays with a 50–420 nm interpore distance formed by self-organization in anodic alumina. *Journal of applied physics*, 84(11):6023–6026, 1998.
- [8] Feiyue Li, Lan Zhang, and Robert M Metzger. On the growth of highly ordered pores in anodized aluminum oxide. *Chemistry of materials*, 10(9):2470–2480, 1998.

- [9] Hideki Masuda, Kouichi Yada, and Atsushi Osaka. Self-ordering of cell configuration of anodic porous alumina with large-size pores in phosphoric acid solution. *Japanese Journal of Applied Physics*, 37(11A):L1340, 1998.
- [10] Woo Lee, Ran Ji, Ulrich Gösele, and Kornelius Nielsch. Fast fabrication of long-range ordered porous alumina membranes by hard anodization. *Nature materials*, 5(9):741, 2006.
- [11] Hideki Masuda, Kensuke Takenaka, Tomohiro Ishii, and Kazuyuki Nishio. Long-range-ordered anodic porous alumina with less-than-30 nm hole interval. *Japanese journal of applied physics*, 45(11L):L1165, 2006.
- [12] Norbert Wiener, Norbert Wiener, Cyberneticist Mathematician, Norbert Wiener, Norbert Wiener, and Cybernéticien Mathématicien. Extrapolation, interpolation, and smoothing of stationary time series: with engineering applications. 1949.
- [13] JP O'sullivan and GC Wood. The morphology and mechanism of formation of porous anodic films on aluminium. *Proc. R. Soc. Lond. A*, 317(1531):511–543, 1970.
- [14] K Ebihara, H Takahashi, and M Nagayama. Structure and density of anodic oxide films formed on aluminium in oxalic acid solutions. *J. Met. Finish. Soc. Jpn*, 34(11):548–553, 1983.
- [15] Mehmet Sezgin and Bülent Sankur. Survey over image thresholding techniques and quantitative performance evaluation. *Journal of Electronic imaging*, 13(1):146–166, 2004.
- [16] Changli Li, Maojun Zheng, Ming Li, Changqing Zhu, Li Ma, Xianghu Wang, Zhengping Li, and Wenzhong Shen. Template-based sputtering method for

vertically aligned tin nanotube arrays: From fabrication to superconductivity. *Thin Solid Films*, 542:14–20, 2013.

- [17] Guowen Meng, Yung Joon Jung, Anyuan Cao, Robert Vajtai, and Pulickel M Ajayan. Controlled fabrication of hierarchically branched nanopores, nanotubes, and nanowires. *Proceedings of the National Academy of Sciences of the United States of America*, 102(20):7074–7078, 2005.
- [18] J Li, C Papadopoulos, JM Xu, and M Moskovits. Highly-ordered carbon nanotube arrays for electronics applications. *Applied physics letters*, 75(3):367–369, 1999.
- [19] H. Q. Nguyen, S. M. Hollen, J. M. Valles, J. Shainline, and J. M. Xu. Disorder influences the quantum critical transport at a superconductor-to-insulator transition. *Physical Review B - Condensed Matter and Materials Physics*, 92(14):1–6, 2015.
- [20] S. M. Hollen, G. E. Fernandes, J. M. Xu, and J. M. Valles. Collapse of the Cooper pair phase coherence length at a superconductor-to-insulator transition. *Physical Review B - Condensed Matter and Materials Physics*, 87(5):11–14, 2013.
- [21] S M Hollen, G E Fernandes, J M Xu, and J M Valles. Fate of the Bose insulator in the limit of strong localization and low Cooper-pair density in ultrathin films. *Physical Review B*, 90(14), 2014.
- [22] Xue Zhang, James C Joy, Chenwei Zhao, Jin Ho Kim, Gustavo Fernandes, JM Xu, and James M Valles Jr. Evaporating metal nanocrystal arrays. *Nanotechnology*, 28(10):105302, 2017.
- [23] S. M. Hollen, H. Q. Nguyen, E. Rudisaile, M. D. Stewart, J. Shainline, J. M. Xu, and J. M. Valles. Cooper-pair insulator phase in superconducting amorphous

Bi films induced by nanometer-scale thickness variations. *Physical Review B*, 84(6):064528, aug 2011.

Chapter 3

Evaporating Metal Nanocrystal Arrays

In this chapter, I will discuss an application of Anodic aluminum oxide (AAO) templates to make nano-scale materials, especially nanocrystal arrays in my research. The content of this chapter has been published in Ref. [1]. AAO substrates with a self-ordered triangular array of nanopores provide the means to fabricate multiple forms of nano materials, such as nanowires and nanoparticles. This study focuses on nanostructures that emerge in thin films of metals thermally evaporated onto the surface of AAO. Previous work showed that films of different evaporated metals assume dramatically different structures, e.g. an ordered triangular array of nearly monodisperse nanoparticles forms for Lead(Pb) while a polycrystalline nanohoneycomb structure forms for Silver(Ag). Here, we present investigations of the effects of substrate temperature and deposition angle that reveal the processes controlling the nano particle array formation. Our findings indicate that arrays form provided the grain nucleation density exceeds the pore density and the atomic mobility is high enough to promote grain coalescence. They introduce a method for producing films with anisotropic grain array structure. The results provide insight into the influence of substrate nano-morphology on thin film growth energetics and kinetics that can be harnessed for creating films with other novel nano-structures.

3.1 Introduction

Materials formed with nanoscale dimensions, such as nanoparticles, nanowires, nanotubes and nanorods, have been used in many applications because of their novel properties. They have been employed for high density magnetic recording,[2] efficient photovoltaic devices,[3], and as effective catalysts and catalyst supports.[4] Approaches to nanomanufacturing are characterized as "top down" and "bottom up". Within those methods, self-assembly on nano patterned templates is one of the facile and inexpensive synthetic "bottom up" strategies for producing nanostructures of well controlled size, shape and arrangement.[5, 6, 7] Anodic aluminum oxide(AAO) is a commonly used template due to its high degree of ordering and straightforward fabrication process. Its structure is characterized by a triangular array of nanoscale pores (Figs. 3.1.1a and b) that individually taper down from about 80 nm diameter at the upper surface to less than 50 nm diameter below the upper surface. Each pore is surrounded by a hilly surface with six peaks and six valleys. Demonstrations of the growth of carbon nanotubes,[8] Tin nanotube arrays[9] and Ni nanowires[10] inside the pores, and Gold nanoparticles [11] on the surface are examples of AAO's usefulness for the synthesis of nano structured materials with tunable dimensions. Of particular relevance here is the creation of nanostructure through the deposition of thin films onto AAO substrates.[12, 13, 14, 15, 16, 17, 18, 19, 20, 21] Some show particular promise for Surface Enhanced Raman Scattering applications[12, 13, 14, 15, 16] and others for investigating quantum phase transitions in superconductors.[19, 20, 21]

Previously, we reported that some metals deposited on AAO substrates spontaneously form an ordered array of uniformly sized nanoparticles that align with the underlying pore arrangement.[22] Fig. 3.1.1c and d compares scanning electron microscope(SEM) images of equivalent Pb film depositions on an AAO and a flat

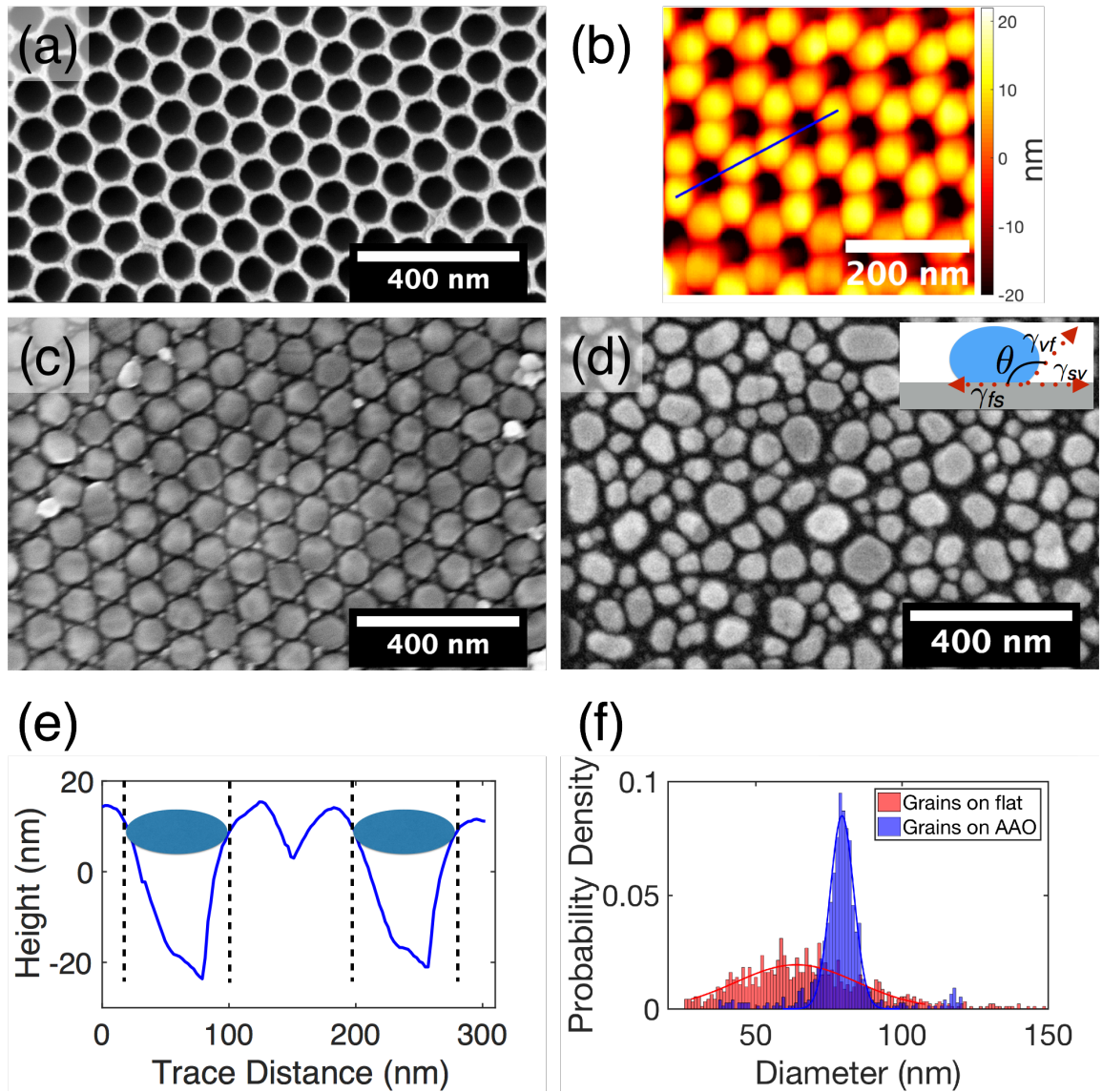


Figure 3.1.1: (a) AAO template fabricated using two-step anodization followed by pore opening by acid etching. The template was coated with a thin Ag/Ge conducting layer (see Materials and Methods) to prevent blurring of the SEM image due to charging effects. The inter-pore spacing is 97 ± 4 nm. (b) Atomic-force microscopy (AFM) image of the substrate. 15 nm Pb films were deposited on (c) an AAO substrate and (d) a flat alumina substrate. (e) Line scan of the AFM image shows around 10 nm height variations on the upper AAO surface (e.g. between the dashed lines at 100 and 200 nm). The line scan becomes inaccurate toward the middle of the pores due to the finite width of the AFM tip. The dashed lines indicate the relative locations of pore boundaries on the SEM image. The position of grains are also drawn. (f) Normalized size distribution of Pb grains. For Pb on the flat substrate, the mean diameter is 68 nm and the standard deviation is 22 nm, while on AAO, the mean diameter is 80 nm and the standard deviation is 12 nm.

alumina substrate. While both films have granular structures, the grain diameter distribution on AAO is narrower by a factor of 4 to 5 compared to the distribution on the flat substrate. Also, the mean diameter of the Pb grains on AAO is very close to the pore size and much larger than the mean diameter of Pb grains on the flat substrate. This observation strongly suggests that the AAO pores constrain the grain growth to produce grains with lateral dimensions comparable to the size of the pore openings. We previously speculated that surface energies drive the grains into this registry with the pores.[22] Here we present measurements that provide a more detailed view of this process. We propose a model for the nanostructure formation that we test by exploring the influence of deposition angle and temperature on the film structure.

3.2 Materials and Methods

The AAO templates were fabricated using the well established two-step anodization procedure[23, 24, 25, 26, 27, 28]. See the previous chapter for more details. To begin, an ultrapure aluminum sheet is cleaned and electropolished to a mirror finish before the first anodization. It is anodized subsequently in 0.3 M oxalic acid kept at 10 °C under a constant voltage of 40 V. Next, the oxide layer is removed using a mixture of phosphoric acid and chromic oxide. A second anodization is then performed under the same condition as the first one. Finally, the sheet is rinsed in 5wt% phosphoric acid at 30 °C to open the pores. Fig. 3.1.1a shows the template used in these studies. The standard deviation of the inter-pore spacings is about 4% of the mean value, and the pore arrays are well ordered over many lattice spacings. Those qualities enable the production of highly ordered nano patterned films on the surfaces.[29]

To produce the granular films various chemical elements were thermally evap-

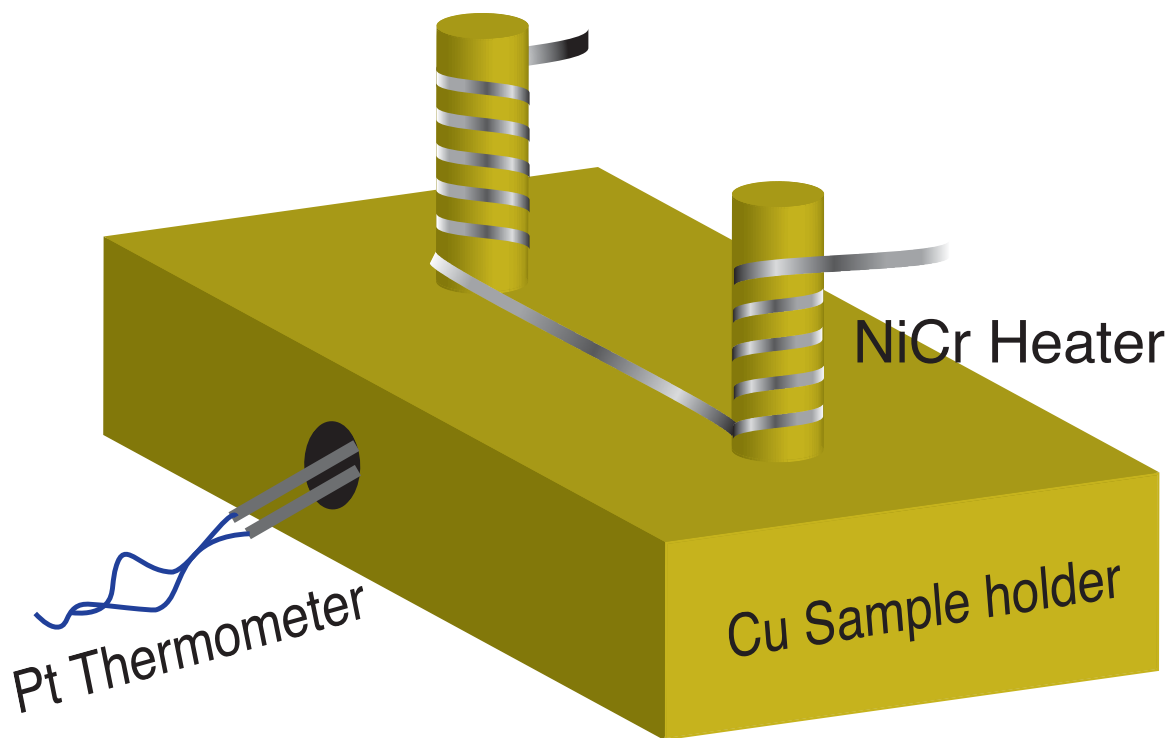


Figure 3.2.1: Homemade sample holder with a NiCr heater and a Pt thermometer installed

orated onto the AAO substrates in a vacuum chamber pumped down to 10^{-6} Torr. The evaporation rate was kept near $1 \text{ \AA/sec}$ to eliminate the influence of variations in evaporation rate on the film structure. The nominal thickness was monitored by a quartz crystal microbalance *in situ*. To explore the effect of substrate temperature, T_s , a homemade heater using Nichrome wires and a Platinum resistance thermometer(see Fig. 3.2.1) were installed on the sample holder right above the substrate. The sample was held at the same temperature for several minutes after each evaporation and then slowly cooled to room temperature in vacuum to avoid effects from sudden temperature changes. To prepare the bare templates for scanning electron microscopy imaging they were coated by a thin conducting layer. The layer was deposited by thermal evaporation of a 10 nm film of Ag on top of a 1 nm film of Ge that promoted wetting of the Ag.

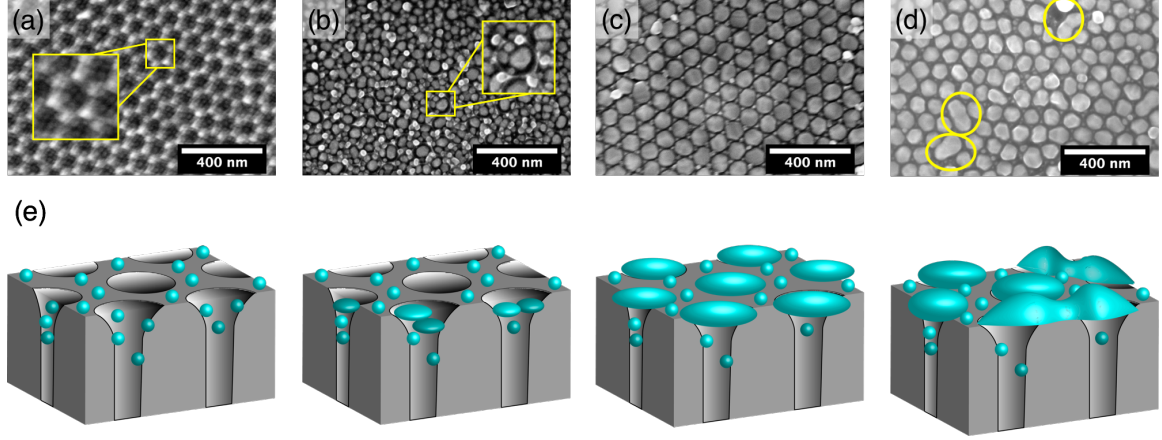


Figure 3.2.2: SEM of Pb films with thicknesses (a) 5nm, (b) 10nm, (c) 15nm, (d) 25nm. The AAO substrates were held at room temperature. In addition to the big grains centered at each pore, there are also six small bright dots at the 'peak' positions around each of them. (e) Proposed mechanism for film growth. Each cartoon corresponds to each of the SEM images on the top.

3.3 Results and Analysis

3.3.1 Model Description

To present these studies it is helpful to first review the prevailing model of the early stages of film growth on flat inert substrates that has been verified through extensive studies.[30, 31, 32, 33] The parameters that control grain formation include the surface energies, the rate of deposition from the vapor, the diffusion of adatoms along the substrate and grain surfaces, and the desorption of atoms from the substrate. Consider an isolated grain on the surface in equilibrium. According to Young's equation, the contact angle between the grain and the surface is determined by the surface energies[34] $\gamma_{sv} = \gamma_{fs} + \gamma_{vf} \cos \theta$ (see the inset of Fig. 3.1.1d). Here γ_{sv} , γ_{fs} and γ_{vf} are the surface energies of substrate-vapor, film-substrate and vapor-substrate interfaces, respectively. For grain growth to occur the deposited films must not wet the substrate. In other words, the contact angle θ must be larger than zero, namely $\gamma_{sv} < \gamma_{fs} + \gamma_{vf}$. [22] Pb films deposited at room temperature satisfy this requirement. The adatom mobility and deposition rate con-

trols the density of grain nuclei. The nuclei form through the collision of adatoms. The higher the adatom mobility, the greater the distance an adatom moves before colliding with a partner. Thus, the nuclei density decreases with increasing adatom mobility. Once nuclei have formed, they grow as adatoms collide with them or evaporated atoms hit them directly. These grains grow independently until they come in contact with neighbors. This contact can lead to grain growth through coalescence provided the mobility of the atoms on grains is sufficiently large. It is important to point out that this model presumes that atoms remain bound to grains once they join them. This presumption can break down at higher substrate temperatures and lead to grain growth through Ostwald ripening processes.[32] The randomness of the nucleation and coalescence processes produce a broad distribution of grain sizes that shifts to larger scales with increasing deposition amounts.

Now, we turn to our investigation of how the film structure is modified by deposition onto AAO substrates. Fig. 3.2.2 shows SEM images of films made of various amounts of Pb deposited onto an AAO substrate held at room temperature. Tin(Sn) source depositions exhibit similar behavior. The growth process can be characterized by four stages. Fig. 3.2.2e displays cartoons of these stages.

Stage 1: Nucleation. Grains nucleate on the pore walls as well as the upper surface of the AAO. It gives a measure of the density of nuclei. The number of nuclei is at least 3 to 4 per pore. That sets a lower bound for the nucleation density of $1/\bar{r}^2$, where $\bar{r}$ is the average pore radius. The tendency for the grains to nucleate primarily on the rim and inner surface of the individual pores is similar to the behavior of InAs grown on GaAs substrates patterned with an array of nanopores.[35] In the latter work, it was suggested that the kinetics of the nucleation process was strongly influenced by the nanoscale geometry.

Stage 2: Growth of nuclei. The grains in and around the pores grow. The magnified view of a pore in Fig. 3.2.2b shows some smaller grains that appear to be in contact with the pore wall. This "side view" of grains suggests that the contact angle between Pb and the AAO pore wall exceeds $\pi/2$. Their size distribution is non-uniform. This growth occurs either through the direct condensation of atoms from the vapor onto the nuclei or the collision of diffusing adatoms with the nuclei as described above. Because of shadowing effects, the upper grains are more likely to capture incoming vapor, making them larger than the lower grains in the pores.

Stage 3: Intra-pore grain coalescence. As the grains grow, they touch and coalesce into larger grains that fill the pore openings. Surface energies presumably drive the coalescence as the larger grains have lower surface curvature. The tendency for these coalesced grains to reside at the pore openings results probably from two factors: an energetic factor and a kinetic factor. Energetically, the surface curvature of the pore wall makes the van der Waals interactions between the nuclei and the substrate stronger compared to a flat surface. The kinetics favors growth within the pores because of the constraints imposed by their geometry. The pore constrains adatom motion to enhance the adatom-nuclei collision rate and the curvature of the walls promotes grain touching that leads to coalescence. The coalescence process continues until a single grain with radius comparable to the pore radius forms at the top of each pore. The result is an array of nearly equal sized grains that is as well ordered as the underlying pore array.

Stage 4: Inter-pore grain coalescence. With subsequent deposition, the grains grow out of the pores, make contact with grains in neighboring pores and coalesce with them into larger grains that span pores.

Interestingly, throughout the 4 growth stages, there are six small grains around each pore (see Fig. 3.1.1b in particular). They appear on local high points or apices of the hilly structure located at the vertices of the upper substrate surface (see Fig. 3.1.1b). As shown by the figures below, these grains appear for Sn and Ag depositions as well. We discuss them separately near the end of this chapter.

3.3.2 Evaporation on Tilted Substrate

The four stage scenario described above suggests that tilting the substrate relative to the deposition flux vector ought to render the grain array structure anisotropic. In the scenario, a key to the development of the isotropic ordered array of grains in registry with the pore array is the high nucleation density. The grains form centered on the pores because they emerge from the coalescence of multiple small grains that nucleate in and around the rims of each pore. With this in mind, we tilted the substrates at an angle to create a higher density of nuclei on one side of the pores. We expected that this bias would induce the large grains to form off the center of the pore on the side of the higher density of nuclei. Fig. 3.3.1 shows SEM images of Pb depositions on substrates tilted 60° from normal to the evaporation flux. The tendency for the largest grains to form off the pore center appears most clearly in Figs. 3.3.1a and b. The largest grains do not fill the pore openings leaving open pore area toward the bottom of the images. This bias in grain position makes the larger grains more closely spaced along lines of pores that are nearly perpendicular to the deposition flux vector. It appears to lead to coalescence preferentially along lines perpendicular to the deposition flux vector as shown for the 50 nm deposition in Fig. 3.3.1c.

Fourier transforms (FT) of the tilted films are consistent with the anisotropic real space structure proposed above. Fig. 3.3.2 displays FTs of the tilted films as well

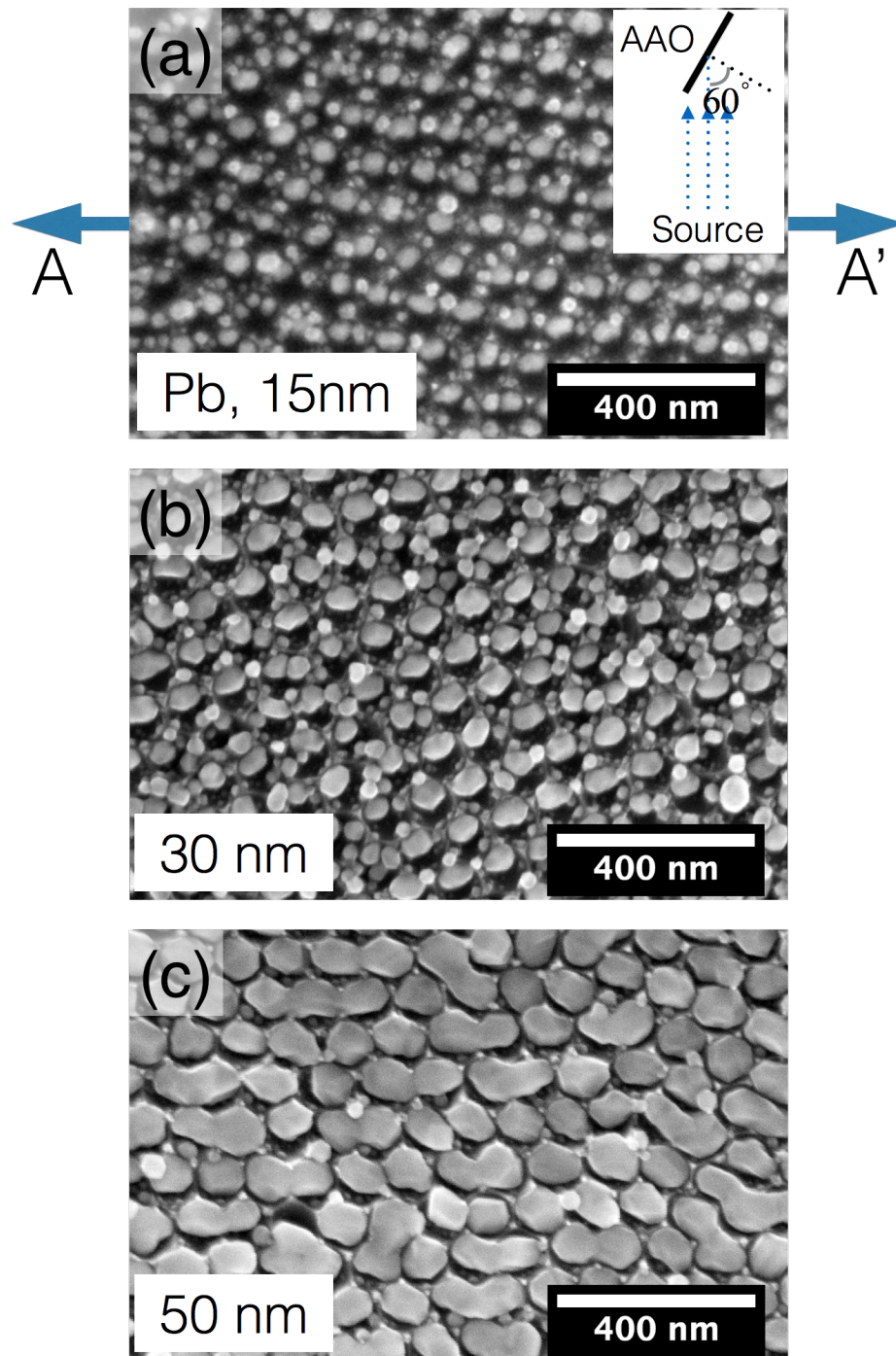


Figure 3.3.1: Nano-array formation onto tilted substrates. Substrates were tilted 60 degrees from normal and held at room temperature. SEMs of Pb films with nominal deposition thicknesses of (a) 15nm, (b) 30nm, and (c) 50nm are shown. Since the substrate is held at 60 degrees, the actual thicknesses correspond to one half the nominal thicknesses. Insert: Experimental configuration for deposition.

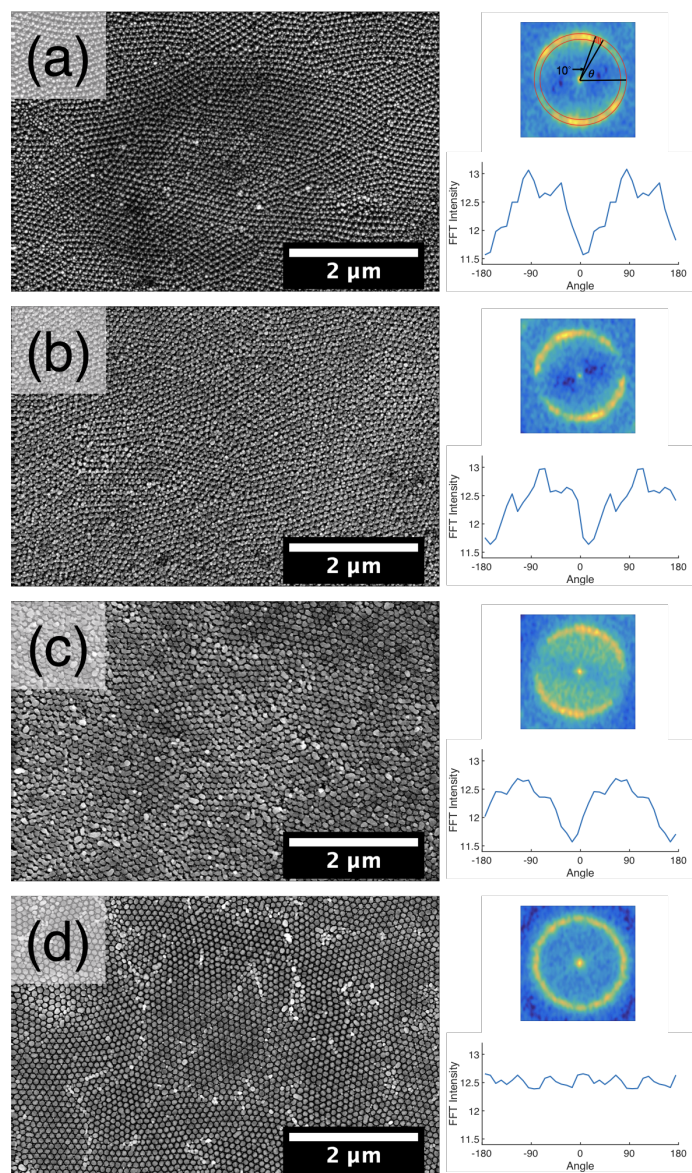


Figure 3.3.2: Fourier transforms analysis of (a) 15nm tilted, (b) 30nm tilted, (c) 50nm tilted and (d) 15nm untilted Pb films. The left column is the original large area SEM images used for analysis. The right column is the Fourier transforms intensity shown in logarithmic scale and the averaged profile scans along the rings. The yellow rings, which correspond to peaks in the FT have radii at the wavenumber corresponding to the inter-pore spacing. The x-axis is the counterclockwise angle measured from the positive x-axis in the FT map. Each value is the average intensity over a 10 degree wide region shown as the shadowed area in the top right image.

as of an untilted 15 nm film in large scale. The bright rings (i.e. peaks) in the FT's are at the wavevector corresponding to the inverse hole spacing. The intensity of the untilted film's ring is continuous and nearly constant as a function of angle. This behavior is as expected for an isotropic grain arrangement ordered by the pores. One thing needs to mention is that, substrate has domain structure with size of $1\mu m$, so do the grains forming on the top of it. Although within each domain, the grains form hexagonal structure, it is smeared in larger scale, resulting in a simple circular rim in the FT map. In contrast, the rings for all of the tilted images have breaks in them that align roughly along the direction of the tilt axis and thus, the lines of grains. Moreover, the intensity on the rings is maximum along the directions perpendicular to the breaks. This anisotropy in the FT is consistent with a weaker modulation of image intensity along lines of grains and a stronger modulation of image intensity across the lines of grains.

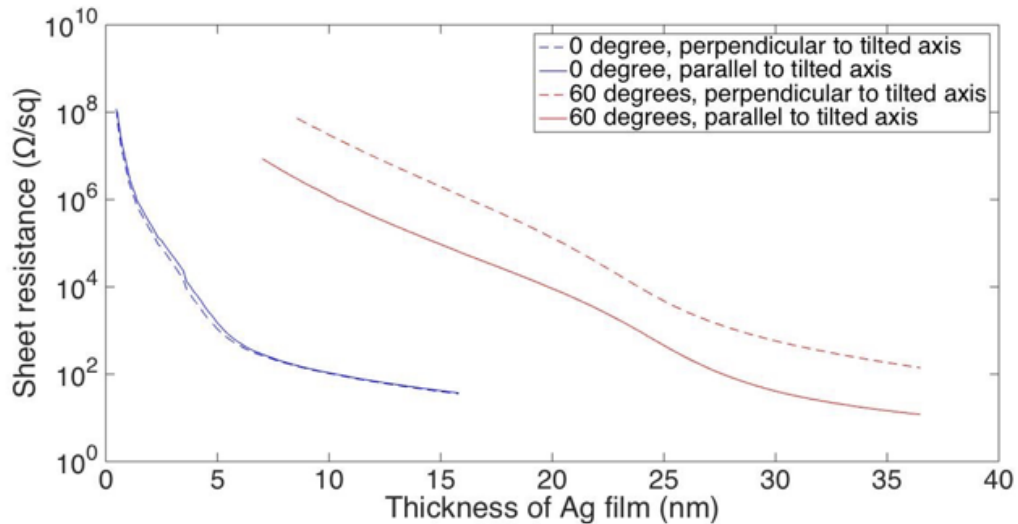


Figure 3.3.3: Resistance measurement for Ag films on untilted substrate(blue) and tilted substrate(red). The solid lines are parallel to the tilted axis and dashed lines are perpendicular to that.

We also performed electrical transport measurement on Ag films evaporated onto both untilted and tilted substrates. As we can see in Fig.3.3.3, the film on untilted substrate is uniform in both directions. However, on substrate with 60

degrees angle, the resistance in the direction perpendicular to the tilted axis is around 10 times larger than the resistance on the other side. This phenomenon further shows film is more closely spaced along the direction perpendicular to the deposition flux vector. Another thing to note is the critical thickness to conduct. Since, the angle is 60 degrees, the average thickness on tilted substrate is only half of the thickness on the other substrate. That is the reason why it starts to conduct at much higher thickness.

3.3.3 Effect of Substrate Temperature

Another key factor controlling the ordered array formation within the model is the atomic mobility. Diffusion along the substrate determines the nucleation density and initial grain growth, while diffusion of adatoms along the grain surfaces controls the coalescence that dominates the last two stages of array formation. The variation of these mobilities can account for why some elements do not form grain arrays when deposited onto room temperature substrates. For example, if the nucleation density is lower than the pore density then grains will form and grow in random pores. Consequently, the grain arrangements will not align well with the AAO template.

The importance of the diffusion of the adatoms along the grains is provided by the example of Ag. As illustrated by the SEM in Fig. 4a, a Ag film deposited on room temperature AAO consists of small grains that closely pack to follow the template of the AAO substrate upper surface. While neighboring grains touch, they do not coalesce. Prior observations of electron beam deposited Ag films [36] shows that this lack of coalescence persists in even much thicker, ≥ 80 nm, films in which the grains are taller than their width. Pb films can also assume a close packed grain structure without coalescence when they are formed by quench condensing Pb onto cryogenically cooled substrates.[37, 38] One direct way to control the dif-

fusivity and thus, the coalescence is by changing the substrate temperature(T_s). The diffusivity D depends on the ratio of the substrate temperature T_s to the metal melting temperature T_m as

$$D = D_0 \exp(-CT_m/T_s) \quad (3.3.1)$$

where D_0 and C are constants. Typically, the temperature must exceed about $0.3T_m$ for grain formation and coalescence. [39, 40, 41] This relation holds true for Pb and Sn at room temperature. Ag, on the other hand, has a higher melting point. It is expected to show large grains only for $T_s > 370\text{K}$. Thus, it is reasonable to expect to induce coalescence and large grain formation in Ag by increasing T_s . There are caveats. Raising the temperature can also promote desorption that causes grains to shrink or Ostwald ripening that causes larger grains to grow through the local evaporation of smaller grains.

SEM images of Ag deposited onto AAO substrates held at different temperatures suggest that raising the temperature promotes grain array formation as for Pb films on room temperature substrates. The nominal thicknesses of the Ag films shown in Fig. 3.3.4 are the same but the structures are quite different. At room temperature, the Ag film conforms to the AAO substrate structure. At higher substrate temperatures that just exceed $0.3T_m$, grains form that fill the pores indicating that intra-pore coalescence is enhanced. The grain shapes are slightly more irregular than the Pb grains in Fig. 3.2.2c. With further increase in substrate temperature, a more ordered array of nanoparticles appears that is quite similar to the Pb film at room temperature shown in Fig. 3.2.2c. This result promises that nano-particle arrays can be made out of a range of elements with either low melting points or high melting points.

Increasing the substrate temperature can also promote inter-pore grain coalescence. To exhibit this effect, the materials must have a relatively low desorption

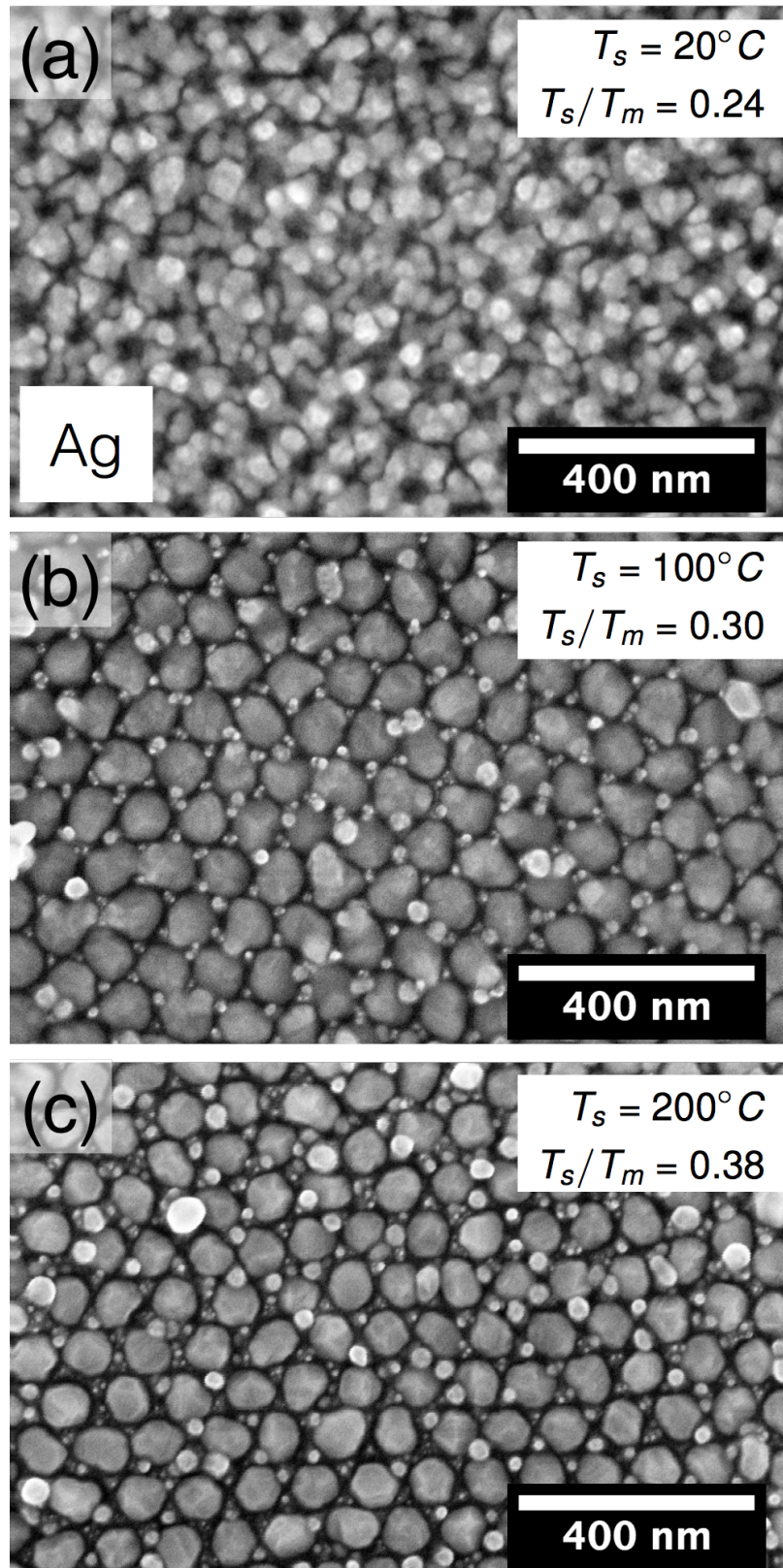


Figure 3.3.4: Effect of substrate temperature on Ag grain structure. SEM images of 15 nm Ag films deposited onto substrates held at the different temperatures indicated in each panel.

rate at the elevated temperatures necessary for promoting coalescence. Sn turns out to be a good candidate. Fig. 3.3.5 shows that at room temperature ($\frac{T_s}{T_m} = 0.58$), Sn grains form an ordered array with all pores occupied. At higher temperatures ($\frac{T_s}{T_m} = 0.74$ and 0.94), the majority of the grains still occupy pores but some larger grains become apparent. The larger grains are brighter and reside next to pores that appear nearly empty. We presume that these larger grains form through the coalescence of grains in two or more neighboring pores. The coalescence produces a large grain centered on one pore next to a pore or pores from which grains have been drawn out in the process. We speculate that the coalescence is mediated by the small grains on the upper surface, especially those that nucleated around the rim of each pore and at the apices. These upper grains provide the connection between the grains in neighboring pores. This connection is the first step in the coalescence process. Interestingly, some of the "empty" pores show very small grains inside (see Fig. 5d in particular). These grains resemble those apparent in the nucleation stage of film growth shown in Fig. 3.2.2a. This observation suggests that after the grains leave the pores, the film restarts the four-stage growth process within the empty pores.

We deem the above coalescence phenomenon for Sn "high temperature" coalescence as it differs from that shown for Pb in Fig. 3.2.2d and Fig. 3.3.1d at lower relative substrate temperatures ($\frac{T_s}{T_m} = 0.49$). Those figures show grains coalescing by forming a neck between them without depletion of grains from neighboring pores. The coalescence phenomenon shown for Sn in Fig. 5 can also be observed in Pb films provided the substrate temperature is sufficiently high. Fig. 3.3.6 exhibits the "high temperature" coalescence for a 25 nm Pb film. Note that the nominal thickness of Pb was increased to 25nm to compensate for the strong desorption effect compared with Sn. Those empty pores nearby indicate the mechanism of inter-pore coalescence is Ostwald Ripening or cluster migration, while the

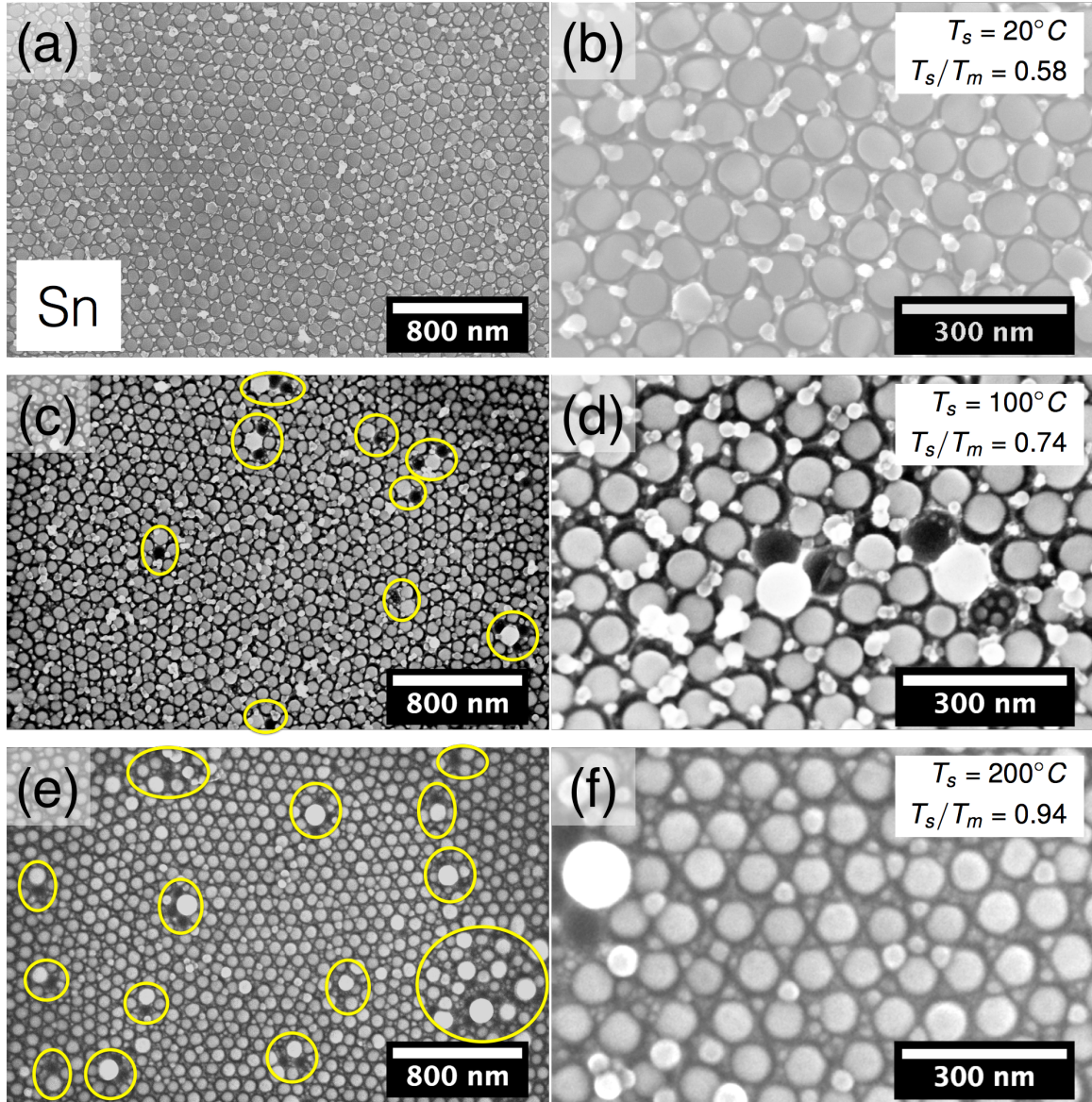


Figure 3.3.5: Effects of substrate temperature on Sn grain structure. SEM images of 15 nm of Sn thermally evaporated onto AAO substrates held at (a,b) room temperature, $T_s/T_m = 0.58$, (c,d) 100 °C, $T_s/T_m = 0.74$, (e,f) 200 °C, $T_s/T_m = 0.94$, respectively. The coalesced grains are marked in yellow circles in the left figures. The right figures are the magnified views of the left ones.

room temperature case is more likely to be sintering.[31]

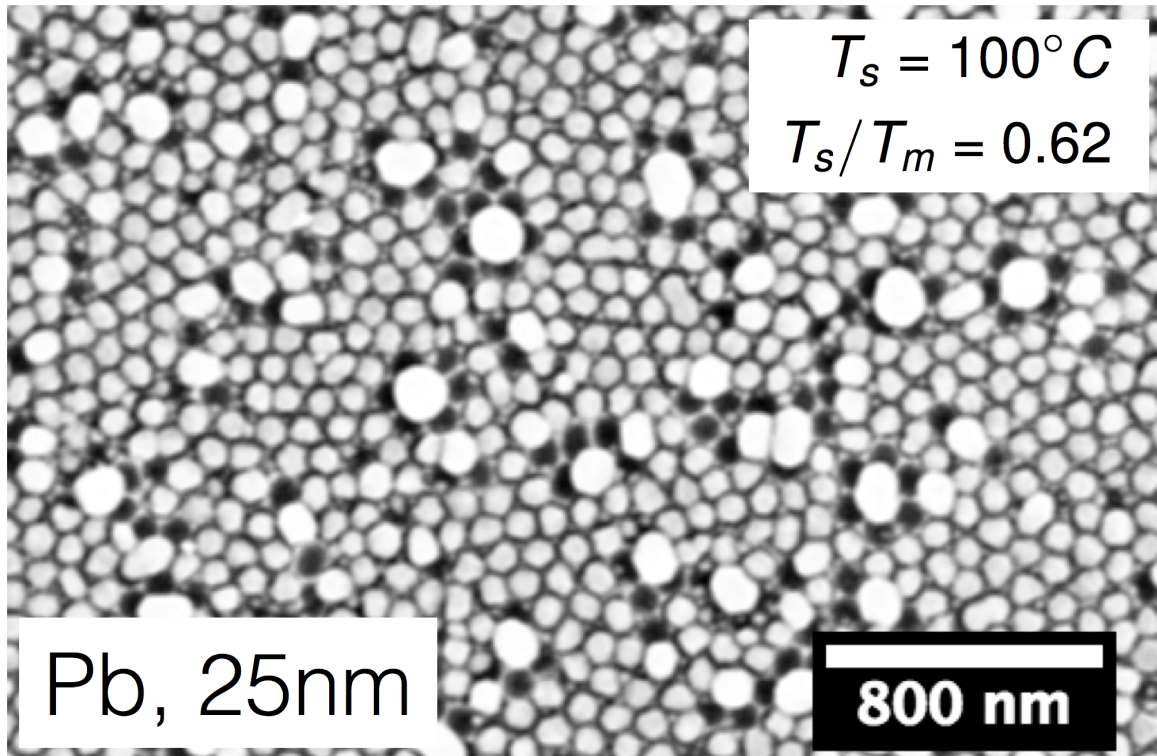


Figure 3.3.6: Pb grain structure on a heated substrate. SEM image of a 25nm Pb deposited onto an AAO substrate held at $100^\circ C$, $T_s/T_m = 0.62$

As shown above, increasing the substrate temperature promotes grain growth through intra-pore and inter-pore coalescence. The latter effect results in less spatially ordered and nonuniform particles. A balance between them must be found in order to produce a highly ordered array for different materials. Moreover, some materials like Pb and Antimony(Sb) showed no film formation on surfaces held at high temperatures, i.e. 200 degrees Celsius(See Fig.3.3.7 and Fig.3.3.8). We believe this phenomenon is the thermal desorption effect alluded to above. We speculate that this desorption is related to the vapor pressure of the material at a specific temperature. Vapor pressure gives a measure of how well bound atoms are to other atoms, i.e. lower vapor pressure indicates stronger binding and vice versa. The vapor pressures of Pb and Sb are orders of magnitude higher than those of Ag and Sn as shown by the Table3.1. The critical temperature for the start

of incomplete condensation of different materials is still unknown and definitely demands further attention.[31, 42, 33, 43]

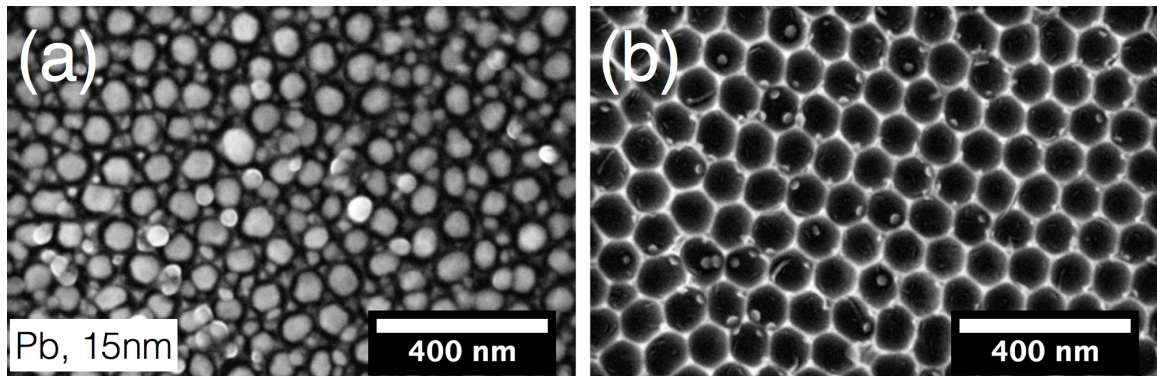


Figure 3.3.7: SEM images of 15nm of Pb thermally evaporated onto AAO substrates held at (a) 100 °C and (b) 200 °C

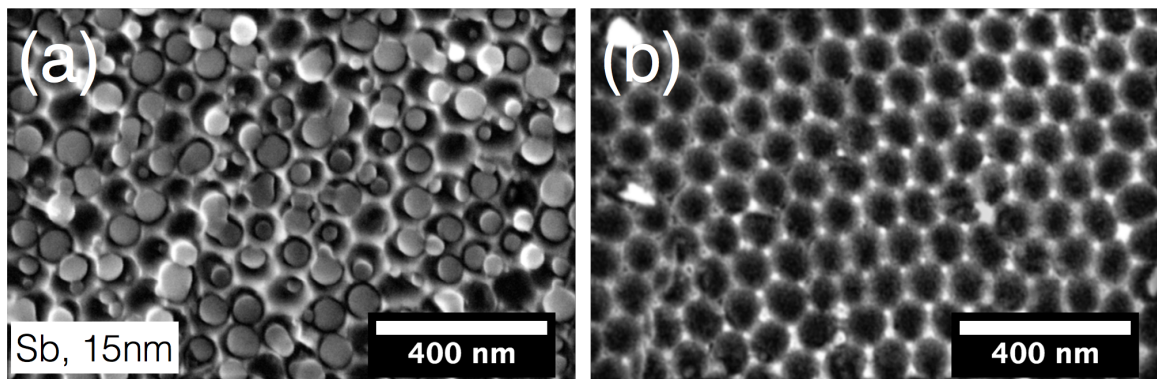


Figure 3.3.8: SEM images of 15nm of Sb thermally evaporated onto AAO substrates held at (a) 100 °C and (b) 200 °C

Table 3.1: Vapor Pressure (Pa) at Specified Temperatures(Alcock, C.B., Itkin, V.P., and Horrigan, M.K., Canadian Metallurgical Quarterly, 23, 309, (1984))

Temperature(K)	473	573	673
Sb	3.87E-11	1.76E-07	6.54E-05
Pb	1.60E-11	8.86E-08	3.78E-05
Ag	2.11E-20	6.21E-15	4.24E-11
Sn	6.74E-23	4.22E-17	5.00E-13

3.3.4 Small Dots Form on the Peak

Returning now to the six small grains that appear around pores in Pb (Fig. 3.2.2b), Ag (Fig. 3.3.4b) and Sn (Fig.3.3.5b). Their persistence through the 4 stages of large grain formation suggests that grains are constantly renucleated in these apical locations. Individual apical grains may be absorbed and removed occasionally by coalescence with a larger grain but a new grain can nucleate to replace it. We first considered whether surface energies make these locations favorable for grain nucleation.

3.3.4.1 Liquid Droplet Model

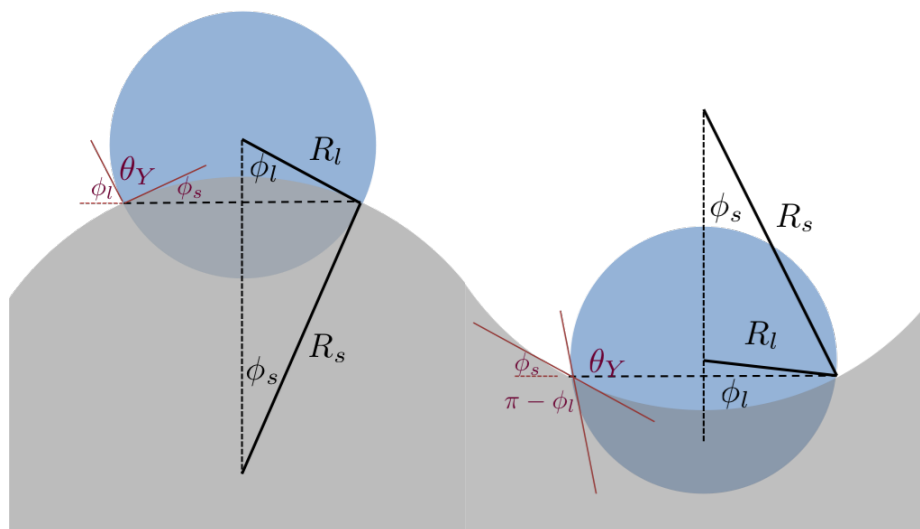


Figure 3.3.9: Droplets (blue) on a convex surface (left) and on a concave surface (right). The phantom penetration of the droplet into the grey surface is shown to emphasize that the droplets' surfaces are spherical sections.

Consider liquid droplets on convex and concave surfaces as shown in Fig. 3.3.9. Because we are assuming a fixed volume droplet, we determine the contribution to the energy by the surfaces. The liquid surfaces are spherically shaped since this ensures a uniform pressure within them. We denote the radii of the liquid and solid substrate surfaces with R_l and R_s , respectively. We denote the angles

subtended in these spheres by the contact region between them as ϕ_l and ϕ_s , respectively. The energy has three surface terms and one volume term:

$$E = \gamma_{ls}A_{ls} + \gamma_s(4\pi R_s^2 - A_{ls}) + \gamma_l A_l \quad (3.3.2)$$

where $A_{ls} = 2\pi R_s^2(1 - \cos \phi_s)$ and $A_l = 4\pi R_l^2 - 2\pi R_l^2(1 - \cos \phi_l)$ are the areas of the liquid-solid interface and γ_l , γ_s and γ_{ls} are the surface energy densities for the liquid vacuum, solid-vacuum, and liquid-solid interfaces, respectively.

Minimization of the surface energy leads to Young's wetting angle condition:

$$\cos \theta_Y = \frac{\gamma_s - \gamma_{ls}}{\gamma_l} \quad (3.3.3)$$

where θ_Y is the angle between tangents to the droplet and substrate surfaces at the contact line for the tangents oriented perpendicular to the contact line. A method to derive this condition, which is well known for flat surfaces, for spherically curved surfaces can be found in *Wetting of Real Surfaces* by Bormashenko (2013). Setting $\gamma_l = 1$ we can rewrite Eq. (1) in terms of θ_Y as:

$$E = A_l - \cos \theta_Y A_{ls} + \gamma_s 4\pi R_s^2 \quad (3.3.4)$$

Determining E for a given R_s , drop volume, V_d , and θ_Y requires finding the angles, ϕ_l and ϕ_s , and the droplet radius, R_l . Note that R_s , V_d and θ_Y are the same for convex and concave substrates. There are three constraints that we can use.

1) The wetting angle is related to the two angles, ϕ_l and ϕ_s , that subtend the droplet substrate contact area from the centers of the droplet and the solid spheres. For the convex substrate:

$$\theta_Y + \phi_l + \phi_s = \pi \quad (3.3.5)$$

For the concave substrate:

$$\theta_Y + \phi_l - \phi_s = \pi \quad (3.3.6)$$

2) The radius of the circle of intersection of the two spherical surfaces can be calculated with the parameters in two ways that must be equivalent:

$$R_l \sin \phi_l = R_s \sin \phi_s \quad (3.3.7)$$

3) The final relation comes from the constraint of the fixed droplet volume. We write it in terms of the angles by breaking the volumes into the spherical caps defined by the intersection of the droplet and substrate spheres (see Fig. 3.3.9). The cap volumes are:

$$V_l^{cap} = \frac{1}{3} \pi R_l^3 (2 - 3 \cos \phi_l + \cos^3 \phi_l) \quad (3.3.8)$$

and

$$V_s^{cap} = \frac{1}{3} \pi R_s^3 (2 - 3 \cos \phi_s + \cos^3 \phi_s) \quad (3.3.9)$$

The relation among the volumes for the convex case of the droplet on a sphere is:

$$V_d = \frac{4\pi}{3} R_l^3 - (V_l^{cap} + V_s^{cap}) \quad (3.3.10)$$

and for the concave case of a droplet on the inside of a spherical shell is:

$$V_d = \frac{4\pi}{3} R_l^3 - (V_l^{cap} - V_s^{cap}) \quad (3.3.11)$$

3.3.4.2 Model Calculation Results

Solutions to the equations above were used to generate cross sectional views of droplets on substrates and surface energies of droplets for different wetting angles

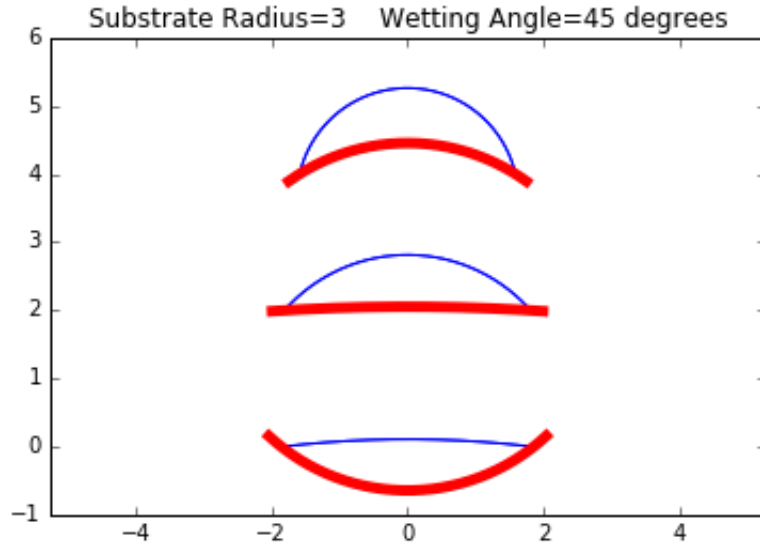


Figure 3.3.10: Cross section of droplets with 45 degree wetting angle on, from top to bottom, convex, nearly flat and concave substrates. The substrate radius is 3 for the convex and concave substrates. The droplet volume is fixed at $v_d = \frac{4\pi}{3}$.

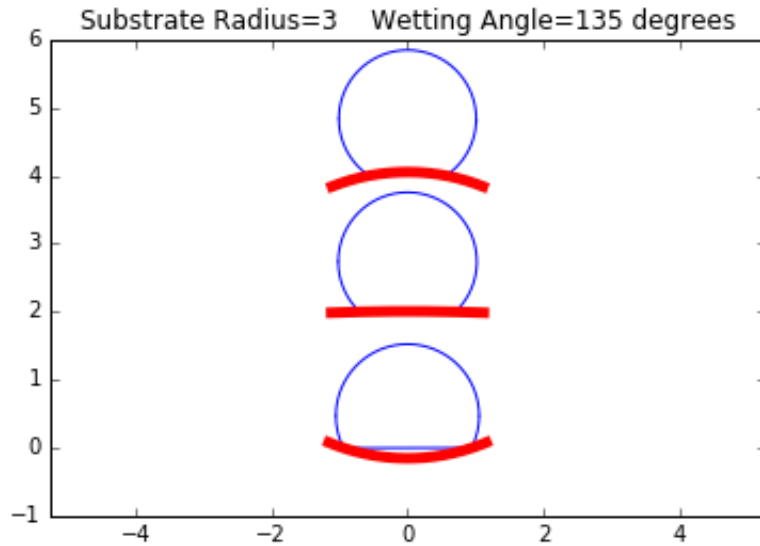


Figure 3.3.11: Cross section of droplets with 135 degree wetting angle on, from top to bottom, convex, nearly flat and concave substrates. The substrate radius is 3 for the convex and concave substrates. The droplet volume is fixed at $v_d = \frac{4\pi}{3}$.

and substrate curvatures. The substrate radii are in units of $(\frac{3v_d}{4\pi})^{1/3}$ where v_d is the droplet volume. Representative views of droplets are shown for the two extremes

of wetting angles considered, 45 (Figure 3.3.10) and 135 (Figure 3.3.11) degrees. The calculated surface energy relative to the flat surface energy (i.e. $r_s = 100$) is shown as a function of substrate radius over the range of wetting angles. The energy of the droplets is lower on the concave surfaces for all wetting angles shown. Thus, droplets with wetting angles in excess of 90 degrees find it more energetically favorable to reside on concave surfaces. This wetting angle limit corresponds to the Pg, Ag and Sn grains.

An alternative way to display the energy is as the binding energy of a droplet to a surface (see Figure 3.3.13). The binding energy is measured relative to the energy of a free droplet, $E_{free} = 4\pi((3v_d)/(4\pi))^{2/3}$. This approach explicitly shows that the droplets are bound to any shape surface.

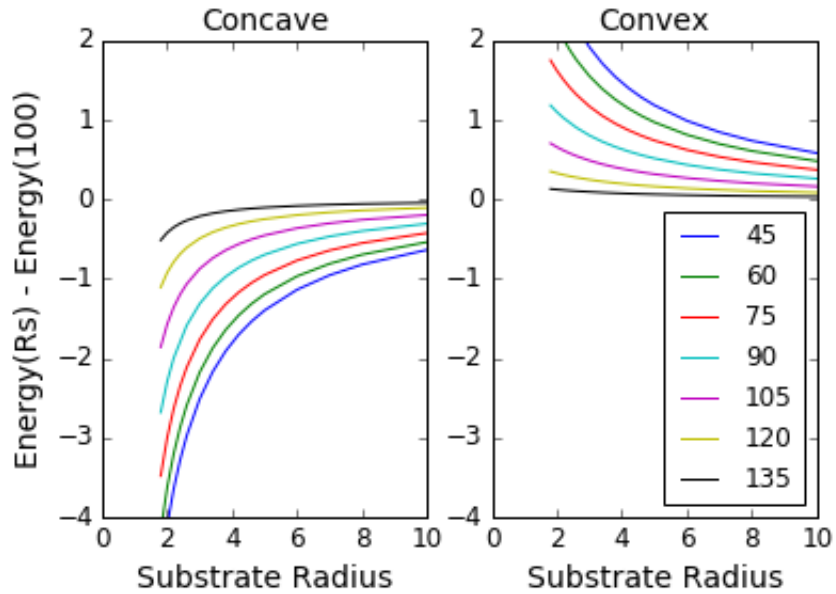


Figure 3.3.12: Surface energy of a liquid droplet as a function of the radius of the spherical substrate surface relative to the flat substrate surface for a range of Young's wetting angles, θ_Y . The droplet volume is fixed at $v_d = \frac{4\pi}{3}$.

In both methods of energy calculation, the model implies that grains have a lower energy on concave surfaces than on convex surfaces. What seems more likely is that kinetic factors determine the location. The grains appear at the intersection of three pore surfaces and the three pore ridges defining the pore open-

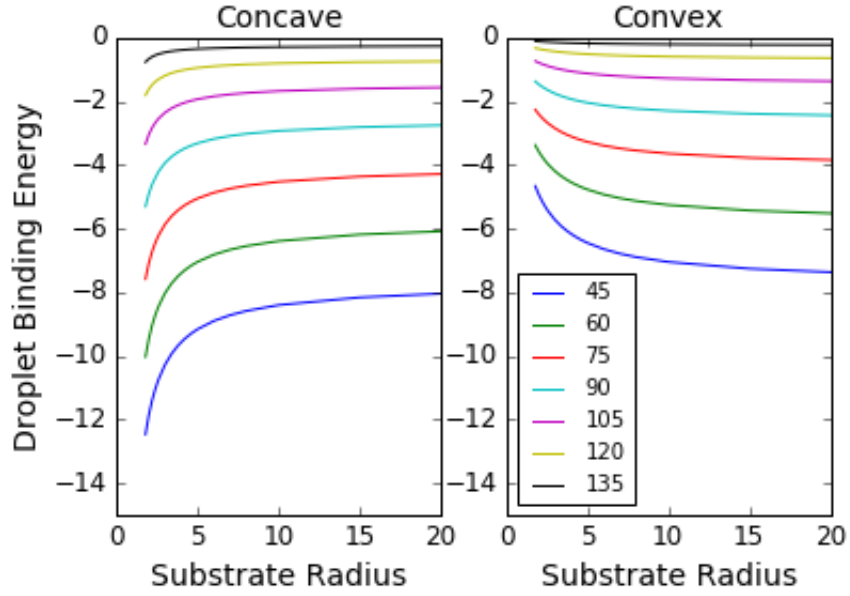


Figure 3.3.13: The binding energy of a liquid droplet as a function of the radius of the spherical substrate surface relative to a free droplet for a range of Young's wetting angles, θ_Y . The droplet volume is fixed at $v_d = \frac{4\pi}{3}$. The binding energy is the energy relative to a free droplet.

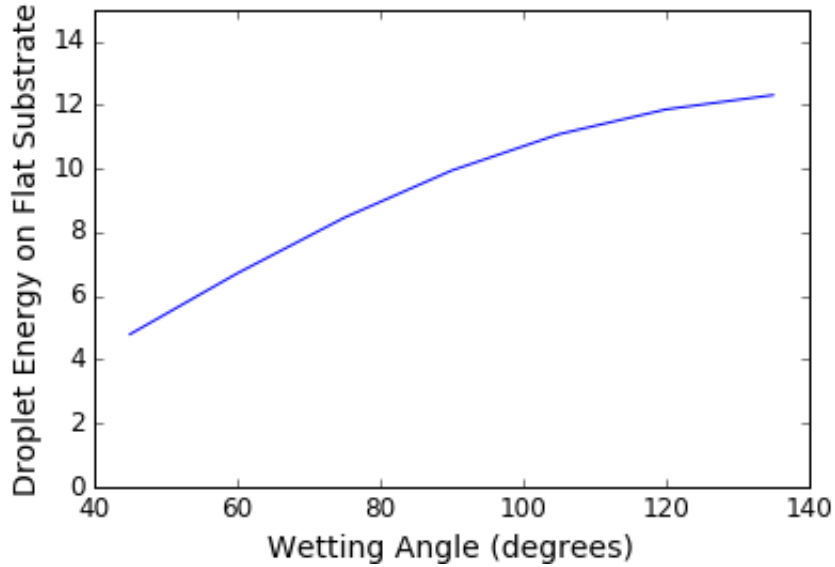


Figure 3.3.14: Surface energy of a liquid droplet in the flat substrate limit as a function of wetting angle, θ_Y . The droplet volume is fixed at $v_d = \frac{4\pi}{3}$.

ings. Thus, diffusing adatoms have a higher probability of colliding at these apices to form nuclei.[44] It is worthwhile to point out that this explanation differs from that

used to account for grains forming at similar locations in dewetting experiments using Fe films on AAO substrates[29] and Au films on nano-patterned substrates[36]. In those, the geometry of the substrate nanostructure controlled the location of the grooves that form in the first step of dewetting of continuous films. Those grooves formed around the vertices between holes trapping grains to form centered on the apical vertices. Even though surface energies drive the dewetting process, they do not lead to grains residing in the lowest energy, concave portions of the substrates.

3.4 Conclusions

Various elements (Pb, Sn, Ag, Sb) have been thermally evaporated onto AAO substrates to study the process that produces an ordered array of uniform grains on these nanostructured surfaces. A four-stage mechanism has been proposed for the process that is based on well established models of thin film growth on flat, unstructured substrates. We tested the mechanism through studies of the effects of changing the angle of the substrate and substrate temperature. The results show that ordered arrays of grains can be made out of a range of elements using AAO substrates. Moreover, the arrays form with an anisotropic structure on tilted substrates. Overall, AAO substrates can promote the formation of ordered arrays of grains provided the number of nuclei per pore is greater than one and the atomic mobility on the grains is sufficiently high to support grain coalescence. More generally, these results highlight how substrate morphology can influence the kinetics and energetics of thin film growth in a manner with potential for new approaches to nano-structure fabrication.

Bibliography

- [1] Xue Zhang, James C Joy, Chenwei Zhao, Jin Ho Kim, Gustavo Fernandes, JM Xu, and James M Valles Jr. Evaporating metal nanocrystal arrays. *Nanotechnology*, 28(10):105302, 2017.
- [2] Shouheng Sun, C. B. Murray, Dieter Weller, Liesl Folks, and Andreas Moser. Monodisperse fept nanoparticles and ferromagnetic fept nanocrystal superlattices. *Science*, 287(5460):1989–1992, 2000.
- [3] Brian O'Regan and Michael Gratzel. A low-cost, high-efficiency solar cell based on dye-sensitized. *nature*, 353(6346):737–740, 1991.
- [4] Philippe Serp, Massimiliano Corrias, and Philippe Kalck. Carbon nanotubes and nanofibers in catalysis. *Applied Catalysis A: General*, 253(2):337 – 358, 2003.
- [5] Yiding Liu, James Goebel, and Yadong Yin. Templated synthesis of nanostructured materials. *Chem. Soc. Rev.*, 42:2610–2653, 2013.
- [6] Yajun Wang, Alexandra S. Angelatos, and Frank Caruso. Template synthesis of nanostructured materials via layer-by-layer assembly. *Chemistry of Materials*, 20(3):848–858, 2008.
- [7] Ganesh K Kannarpady, Khedir R Khedir, Hidetaka Ishihara, Justin Woo, Olu-mide D Oshin, Steve Trigwell, Charles Ryerson, and Alexandru S Biris. Controlled growth of self-organized hexagonal arrays of metallic nanorods using template-assisted glancing angle deposition for superhydrophobic applications. *ACS applied materials & interfaces*, 3(7):2332–2340, 2011.

- [8] J Li, C Papadopoulos, JM Xu, and M Moskovits. Highly-ordered carbon nanotube arrays for electronics applications. *Applied physics letters*, 75(3):367–369, 1999.
- [9] Changli Li, Maojun Zheng, Ming Li, Changqing Zhu, Li Ma, Xianghu Wang, Zhengping Li, and Wenzhong Shen. Template-based sputtering method for vertically aligned tin nanotube arrays: From fabrication to superconductivity. *Thin Solid Films*, 542:14 – 20, 2013.
- [10] AJ Yin, J Li, W Jian, AJ Bennett, and JM Xu. Fabrication of highly ordered metallic nanowire arrays by electrodeposition. *Applied Physics Letters*, 79(7):1039–1041, 2001.
- [11] Hideki Masuda and Masahiro Satoh. Fabrication of gold nanodot array using anodic porous alumina as an evaporation mask. *Japanese Journal of Applied Physics*, 35(1B):L126, 1996.
- [12] Jun Wang, Liqing Huang, Lipeng Zhai, Lin Yuan, Lihua Zhao, Weiwei Zhang, Dongzhi Shan, Aiwen Hao, Xuehong Feng, and Jian Zhu. Hot spots engineering in hierarchical silver nanocap array for surface-enhanced Raman scattering. *Applied Surface Science*, 261:605–609, 2012.
- [13] S. N. Terekhov, P. Mojzes, S. M. Kachan, N. I. Mukhurov, S. P. Zhvavyi, A. Yu. Panarin, I. A. Khodasevich, V. A. Orlovich, A. Thorel, F. Grillon, and P.-Y. Turpin. A comparative study of surface-enhanced Raman scattering from silver-coated anodic aluminum oxide and porous silicon. *Journal of Raman Spectroscopy*, 42(1):12–20, jan 2011.
- [14] Dukhyun Choi, Yeonho Choi, Soongweon Hong, Taewook Kang, and Luke P. Lee. Self-organized hexagonal-nanopore SERS array. *Small*, 6(16):1741–1744, aug 2010.

- [15] Li Dongming, Jia Shuhai, Wang Jun, and Jia Yang. Ordered silver nanoparticle arrays as surface-enhanced Raman spectroscopy substrates for label-free detection of vitamin C in serum. *Sensors and Actuators A: Physical*, 201:416–420, 2013.
- [16] S. N. Terekhov, S. M. Kachan, A. Yu. Panarin, and P. Mojzes. Surface-enhanced Raman scattering on silvered porous alumina templates: role of multipolar surface plasmon resonant modes. *Phys. Chem. Chem. Phys.*, 17(47):31780–31789, 2015.
- [17] Aree Song, Chul Sung Kim, and Taejoon Kouh. Evolution of sheet resistance of thin Ni film deposited on porous anodic alumina substrate. *Applied Physics Letters*, 99(26):263103, 2011.
- [18] Y. Park, H. Ko, I.-B. Shim, C.S. Kim, and T. Kouh. Growth of nanostructured Cu-Al-O film deposited on porous aluminium oxide. *Physica E: Low-dimensional Systems and Nanostructures*, 42(5):1302–1306, 2010.
- [19] M D Stewart, Aijun Yin, J M Xu, and James M Valles. Superconducting pair correlations in an amorphous insulating nanohoneycomb film. *Science (New York, N.Y.)*, 318(5854):1273–5, nov 2007.
- [20] G Kopnov, O Cohen, M Ovadia, K Hong Lee, C C Wong, and D Shahar. Little-Parks Oscillations in an Insulator. *Physical Review Letters*, 109(16), 2012.
- [21] S. M. Hollen, H. Q. Nguyen, E. Rudisaile, M. D. Stewart, J. Shainline, J. M. Xu, and J. M. Valles. Cooper-pair insulator phase in superconducting amorphous Bi films induced by nanometer-scale thickness variations. *Physical Review B*, 84(6):064528, aug 2011.

- [22] Niravun Pavenayotin, MD Stewart Jr, James M Valles Jr, Aijun Yin, and JM Xu. Spontaneous formation of ordered nanocrystal arrays in films evaporated onto nanopore array substrates. *Applied Physics Letters*, 87(19):193111, 2005.
- [23] Hideki Masuda and Kenji Fukuda. Ordered metal nanohole arrays made by a two-step replication of honeycomb structures of anodic alumina. *Science*, 268(5216):1466–1468, 1995.
- [24] Hideki Masuda, Fumio Hasegawa, and Sachiko Ono. Self-ordering of cell arrangement of anodic porous alumina formed in sulfuric acid solution. *Journal of The Electrochemical Society*, 144(5):L127–L130, 1997.
- [25] AP Li, F Müller, A Birner, K Nielsch, and U Gösele. Hexagonal pore arrays with a 50–420 nm interpore distance formed by self-organization in anodic alumina. *Journal of applied physics*, 84(11):6023–6026, 1998.
- [26] Hideki Masuda, Kouichi Yada, and Atsushi Osaka. Self-ordering of cell configuration of anodic porous alumina with large-size pores in phosphoric acid solution. *Japanese Journal of Applied Physics*, 37(11A):L1340, 1998.
- [27] Feiyue Li, Lan Zhang, and Robert M Metzger. On the growth of highly ordered pores in anodized aluminum oxide. *Chemistry of Materials*, 10(9):2470–2480, 1998.
- [28] Kornelius Nielsch, Jinsub Choi, Kathrin Schwirn, Ralf B Wehrspohn, and Ulrich Gösele. Self-ordering regimes of porous alumina: The 10 porosity rule. *Nano Letters*, 2(7):677–680, 2002.
- [29] Eric R. Meshot, Zhouzhou Zhao, Wei Lu, and A. John Hart. Self-ordering of small-diameter metal nanoparticles by dewetting on hexagonal mesh templates. *Nanoscale*, 6:10106–10112, 2014.

- [30] K Reichelt. Nucleation and growth of thin films. *Vacuum*, 38(12):1083 – 1099, 1988.
- [31] Ohring Milton. *Materials science of thin films*. Academic press, 1992.
- [32] J A Venables, G D T Spiller, and M Hanbucken. Nucleation and growth of thin films. *Reports on Progress in Physics*, 47(4):399, 1984.
- [33] C Ratsch and JA Venables. Nucleation theory and the early stages of thin film growth. *Journal of Vacuum Science & Technology A*, 21(5):S96–S109, 2003.
- [34] Thomas Young. An essay on the cohesion of fluids. *Philosophical Transactions of the Royal Society of London*, 95:65–87, 1805.
- [35] Jianyu Liang, Hailin Luo, Rod Beresford, and Jimmy Xu. A growth pathway for highly ordered quantum dot arrays. *Applied physics letters*, 85(24):5974–5976, 2004.
- [36] Dong Wang, Ran Ji, and Peter Schaaf. Formation of precise 2d au particle arrays via thermally induced dewetting on pre-patterned substrates. *Beilstein journal of nanotechnology*, 2(1):318–326, 2011.
- [37] K. L. Ekinici and J. M. Valles. Morphology of quench condensed pb films near the insulator to metal transition. *Phys. Rev. Lett.*, 82:1518–1521, Feb 1999.
- [38] K.L. Ekinici and J.M. Valles Jr. Formation of polycrystalline structure in metallic films in the early stages of zone i growth. *Acta Materialia*, 46(13):4549–4557, 1998.
- [39] H. T. G. Hentzell, C. R. M. Grovenor, and D. A. Smith. Grain structure variation with temperature for evaporated metal films. *Journal of Vacuum Science & Technology A*, 2(2):218–219, 1984.

- [40] C Sürgers, Christoph Strunk, and HV Löhneysen. Effect of substrate temperature on the microstructure of thin niobium films. *Thin Solid Films*, 239(1):51 – 56, 1994.
- [41] I Petrov, PB Barna, Lars Hultman, and JE Greene. Microstructural evolution during film growth. *Journal of Vacuum Science & Technology A*, 21(5):S117–S128, 2003.
- [42] Leon I Maissel and Reinhard Glang. *Handbook of thin film technology*. New York: McGraw-Hill, 1970.
- [43] N. S. Sokolov, S. M. Suturin, B. B. Krichevstov, V. G. Dubrovskii, S. V. Gastev, N. V. Sibirev, D. A. Baranov, V. V. Fedorov, A. A. Sitnikova, A. V. Nashchekin, V. I. Sakharov, I. T. Serenkov, T. Shimada, T. Yanase, and M. Tabuchi. Cobalt epitaxial nanoparticles on $\text{CaF}_2/\text{Si}(111)$: Growth process, morphology, crystal structure, and magnetic properties. *Phys. Rev. B*, 87:125407, Mar 2013.
- [44] X.L. Li, C.X. Wang, and G.W. Yang. Thermodynamic theory of growth of nanostructures. *Progress in Materials Science*, 64:121 – 199, 2014.

Chapter 4

Experimental Apparatus and Techniques

We have seen AAO fabrication and its application to make nano-sized materials. In the following chapters, we will talk about the low temperature experiments in our lab. We will see how AAO can be used to study a 2 dimensional superconductor insulator transition(SIT). In this chapter, I will show the experimental apparatus including substrate fabrication, thermal evaporation setup, low temperature cryostat as well as equipment for transport measurement. We will see the major experimental techniques to calibrate the film thickness, quench condense ultra thin films and measure resistance. In the last part, I will show the detailed experimental workflow.

4.1 Introduction

To study the quantum transport of 2D materials, we need to reach the temperature range well below the superconducting critical temperature. Also, the thermal fluctuations, which are proportional to $k_B T$, have to be much smaller than the energy scale of the ground state. Both of these require conducting the measurements in the sub-Kelvin range. For the film evaporation, in the previous chapter, we learned that high temperature promotes coalescence of grains. Actually, thermally activated process begin to dominate film formation when $T_s > 0.1T_m$ [1, 2], where T_s is the substrate temperature and T_m is the melting point of the material. To make an amorphous film with uniform thickness, we employ the quench condensation method that evaporations are performed *in situ* inside the cryostat with constant substrate temperature $T_s = 8K$ in an ultra high vacuum(UHV) environment. For those reasons, the major challenges in our experiments are making films and maintaining low temperature.

4.2 Experimental Apparatus

4.2.1 Anodization setup

The most important step to make AAO is the anodization as shown in Fig. 4.2.1. The electrolyte cell is surrounded by liquid coolant and a magnetic stirrer helps diffuse the heat. In the case of hard anodization, we need to increase the voltage very slowly. We can set the ramping rate of the programmable DC power supply to be 0.1 V/s. In most cases, 100nm inter-pore spacing AAO is used in low temperature experiments due to its high ordering and optimum roughness. Thus, the bath temperature is set to be $10^\circ C$ and the anodizing voltage is 40V. A thermometer sometimes is put into the cell to make sure the electrolyte is in equilibrium with the

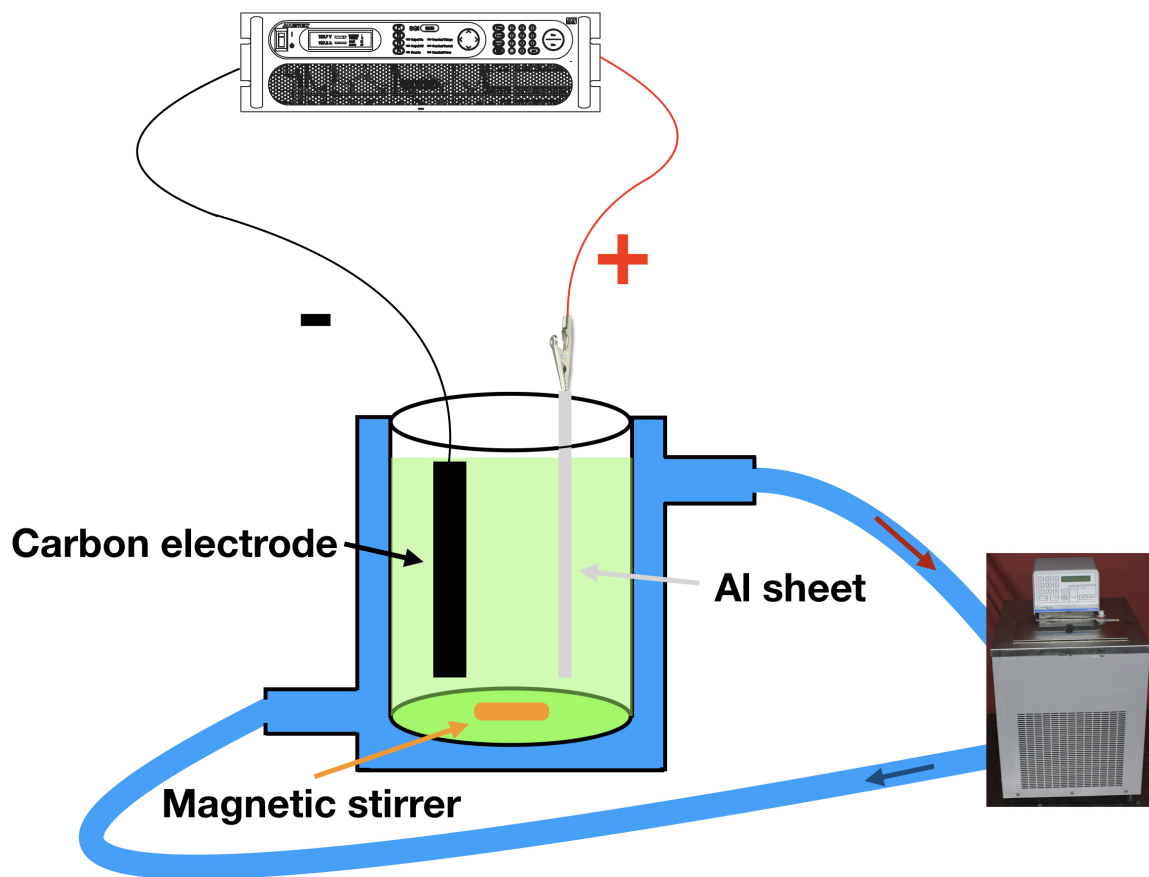


Figure 4.2.1: Anodizing cell for AAO fabrication. The blue liquid is the coolant connect to a refrigerated circulator that is capable of maintaining temperature down to -30°C . The Green liquid represents acidic electrolyte. The aluminum sheet is hanged on the anode that is connected to a programmable DC power supply with 200V maximum voltage.

coolant.

4.2.2 Evaporator

We use the evaporator for multiple purposes. First, we need to melt the source in advance and do quartz crystal microbalance (QCM) calibration. Pre-Melting the source makes it stick to the basket, which lowers the current for evaporation. Also, because of limited space inside the fridge, the QCM is not at the same height as the substrate. We need to know in advance the thickness to frequency ratio for that specific configuration. Those two things can be done at the same time.

Second, we need to use the evaporator to make the Ge wetting layer and electrical contacts(Au) at room temperature before we cool down. Those two evaporations require different masks.

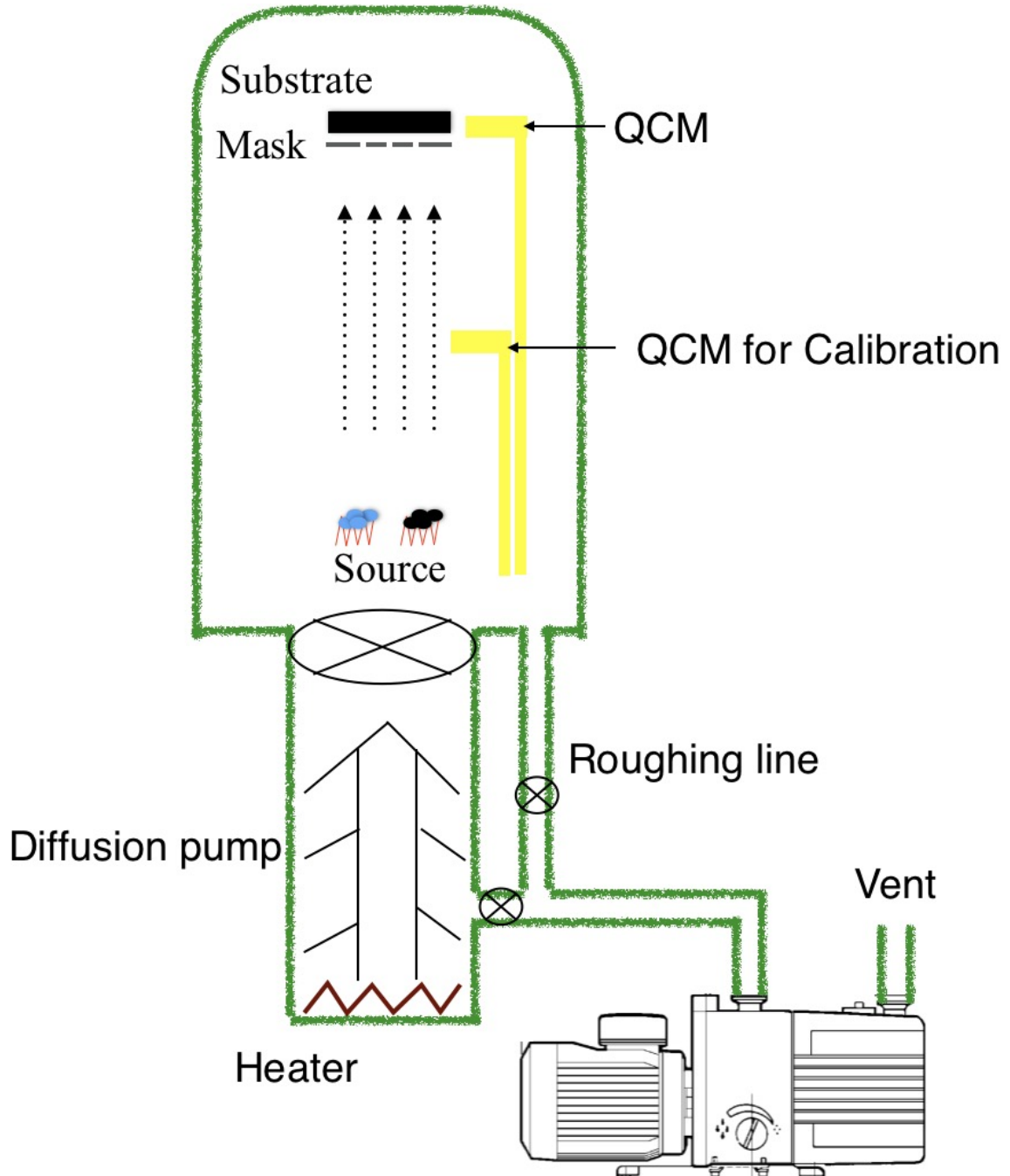


Figure 4.2.2: Evaporator setup. The chamber is evacuated by a mechanical pump and a diffusion pump. There are three valves to control the pumping process. The extra QCM is only needed when doing calibration.

Table 4.1: Crystal calibration

Material	Density(g/cm ³)	$\Delta f/d(\text{Hz}/\text{\AA})$
Ge	5.32	3.85
Ag	10.49	7.87
Au	19.30	14.5
Pb	11.34	8.5
Sn	7.26	5.4
Gd	7.90	5.9
Sb	6.70	5.0
Bi	9.78	7.3

Fig. 4.2.2 shows the evaporation setup at room temperature. In order to have uniform films, the mean free path of the evaporated particles needs to be at least as large as the chamber size. We usually pump it down to 2E-6 mbar before starting evaporation. This is accomplished by two-step pumping. In the first step, we pump it through the roughing line and the pressure drops below 0.1 mbar within 10 min. Then we open the diffusion pump valve and the gas inside the chamber is pushed into the foreline by the heated oil gas in the diffusion pump. The ultimate pressure can be as low as 1E-6 mbar.

To measure the film thickness, the quartz crystal has a characteristic frequency that is proportional to the amount of film evaporated on it. The QCM used in our lab has resonance frequency around 5 MHz. The shift in frequency is related to the mass deposited, δm as,

$$\delta f = \alpha \delta m = \alpha A \rho d \quad (4.2.1)$$

where α is a constant, A is the area of the crystal surface, ρ is the density of the evaporated film and d is the thickness. For the crystal in our lab, $\delta f/d = 7.5 \times 10^7 \text{ Hz/g} \cdot \text{cm}^2 \times \rho$. Based on the density of different materials, the ratios for different elements are shown in Table 4.1.

So the thickness is given by the frequency change. For calibration, the QCM is

placed 13cm away from the source, which is the same as the height of the substrate in the cryostat. An extra QCM is placed around 6cm from the source. That is the one we are going to put into the cryostat. The upper QCM tells us the real thickness deposited on the substrate while the lower one gives us the measured frequency change.

Besides the measurements talked about above, the chamber can also be customized to serve other purposes. We installed a heater and cooling medium on the substrate holder to control the substrate temperature while doing evaporation. Cables outside the chamber are connected to the substrate through the feedthrough so that we can do transport measurement during evaporation.

4.2.3 Dilution Refrigerator

This is the major piece of equipment for our experiments. Ideally, with several cooling stages, it is able to get down below 10 mK [4]. It reaches base temperature around $T=50\text{ mK}$ with the heat loads in our lab. Fig. 4.2.3 draws the sketch of the dilution refrigerator. The whole chamber is pre-cooled in Liquid N_2 ($T=77\text{ K}$). Then it is submerged in Liquid He ($T=4.2\text{ K}$) bath. Below are detailed descriptions of the major components.

4.2.3.1 Source and Sample Stage

This is the primary part in our lab that differs from a normal dilution refrigerator. Since we need to quench condense films at low temperature, the chamber has been extended to make room for evaporation. Fig. 4.2.4 shows the pictures of the sample stage and the sources. On the sample holder, a small piece (14mm by 9.5mm) of AAO substrate is placed side by side with fire polished Glass substrate. The surface of the glass is flat and it is used as a reference film that represents the maximum T_c on AAO at specific thickness [5]. The wetting layer and electri-

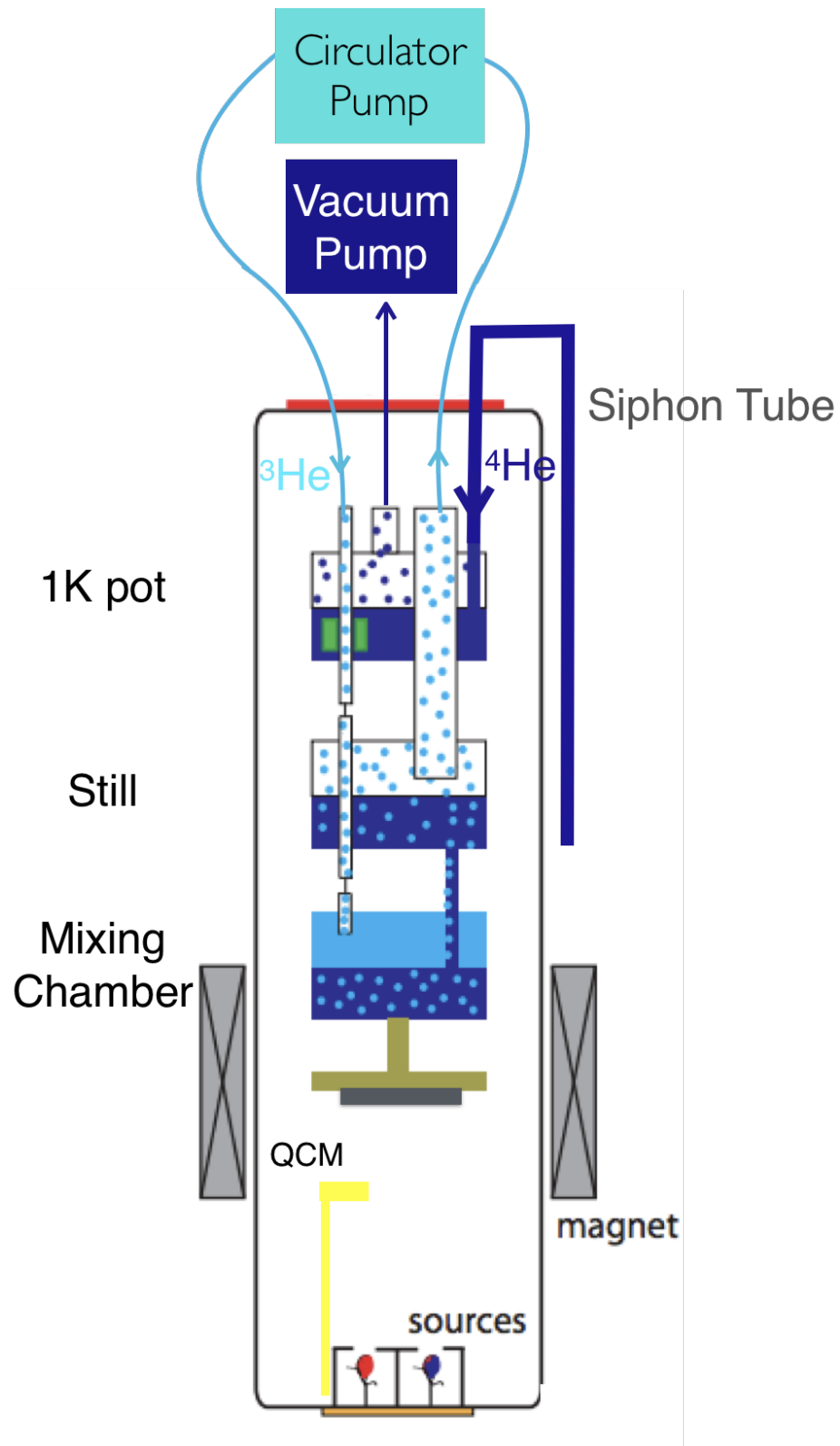


Figure 4.2.3: Dilution refrigerator. Part of the sketch comes from Ref.[3]. The whole chamber is sealed by Cu flange at the bottom and indium wire at the top. It consists of three major cooling stages. $T_{1\text{Kpot}} = 1\text{ K}$, $T_{\text{still}} = 700\text{ mK}$, $T_{\text{MC}} = 50\text{ mK}$. See the text for more details.

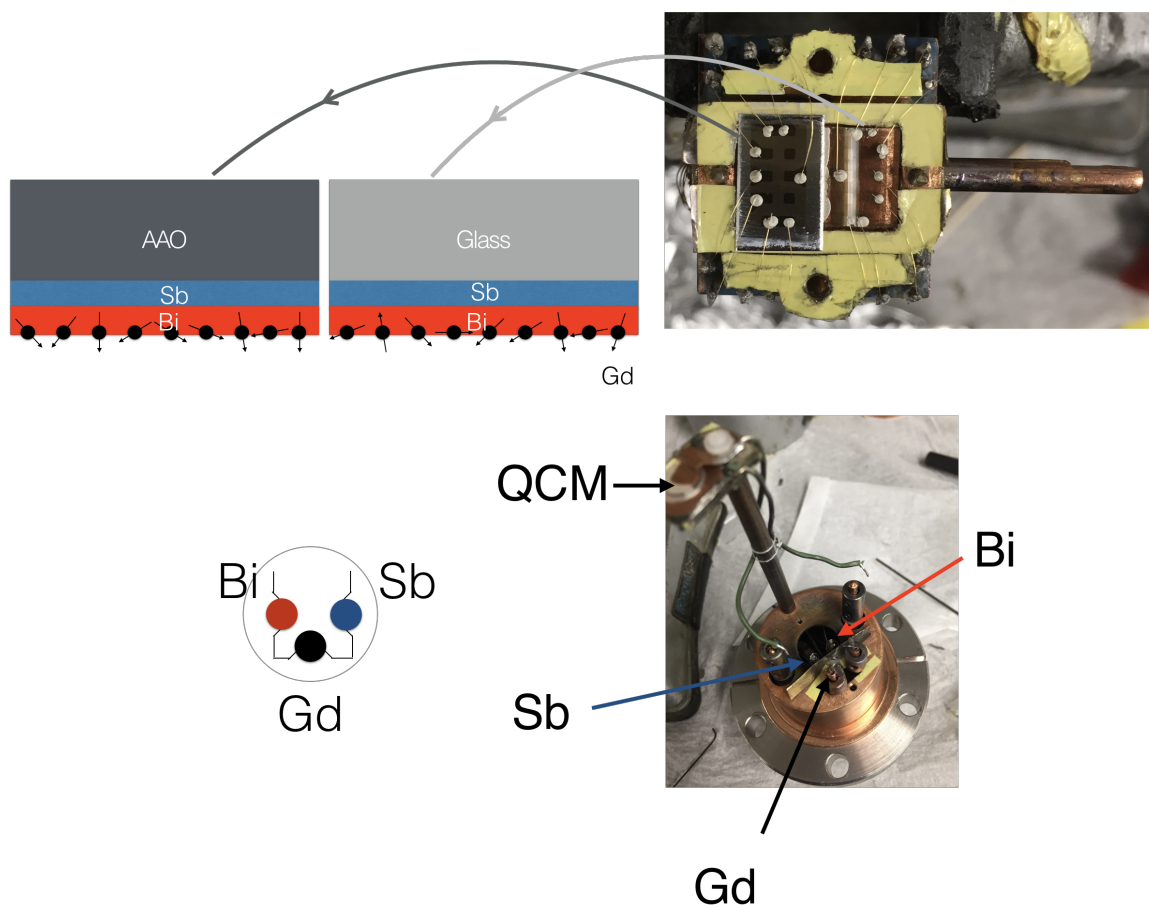


Figure 4.2.4: Sample stage and evaporating sources. The right panels are the real-life images.

cal contacts are made in the evaporator at room temperature. Then it is inserted into the sample stage, which is connected to the mixing chamber through a Cu rod. Good thermal conductivity of Cu ensures that the sample can be cooled to the lowest temperature of the fridge. At the back of the sample holder, there is a homemade heater and resistance thermometer that are connected to a resistance bridge and a temperature controller. The resistance of the thermometer has negative temperature coefficient. By setting the balancing resistance on the bridge, the temperature controller is able to automatically adjust the output power to the heater using feedback circuits. In this way, we are able to stabilize the temperature or ramp the temperature at a given rate. However, those operations are based on constant cooling power. If the mixing chamber is not in equilibrium condition, it is

more tricky to control the temperature of the sample.

In our previous experiments, only two sources, i.e. Bi and Sb, were needed. Since we need to study the effects of magnetic impurity, Gd is added to the evaporation base. With limited feedthroughs on the base, Gd source shares the posts with the other two sources. This method works since we only do one evaporation at a time. Bi and Sb sources sit on baskets that are made of high resistive and high melting point material. Tungsten is a common choice for Bi. We use tantalum wire for Sb because Sb sticks better to Ta. Gd, however, itself has a very high melting point. Also, we only need very tiny amount of Gd. A small piece ($2 \sim 3\text{mm}^2$) of Gd foil is wrapped around the Ta wire and pre-melted in the evaporator. The current for melting is around 7 Amps in my attempts. After melting, it will look like a pellet hanging on the wire. Unlike Bi and Sb, the required amount of Gd is so small that we cannot use the QCM to measure the thickness in quench condensation. As we will see later in this chapter, we can use a timer at room temperature to calibrate the amount evaporated.

4.2.3.2 Superconducting Magnet

The dewar is equipped with an American Magnetics, Inc made superconducting solenoid that can apply magnetic field up to 8 Tesla in the direction perpendicular to the film. The magnet is energized by a Power Ten, Inc made DC power supply which provides current up to 100 amps and voltage up to 10 volts. The current applied to the magnet is controlled by AMI model 420 power programmer, which is capable of communicating with labview with GPIB interface. Those instruments together enable us to apply a programmable magnetic field to our samples.

For a solenoid, the magnitude of field is proportional to the current applied. Thus, the noise in the power supply will also transfer to the magnetic field. Current running on a superconducting loop will decay with a lifetime longer than the age of

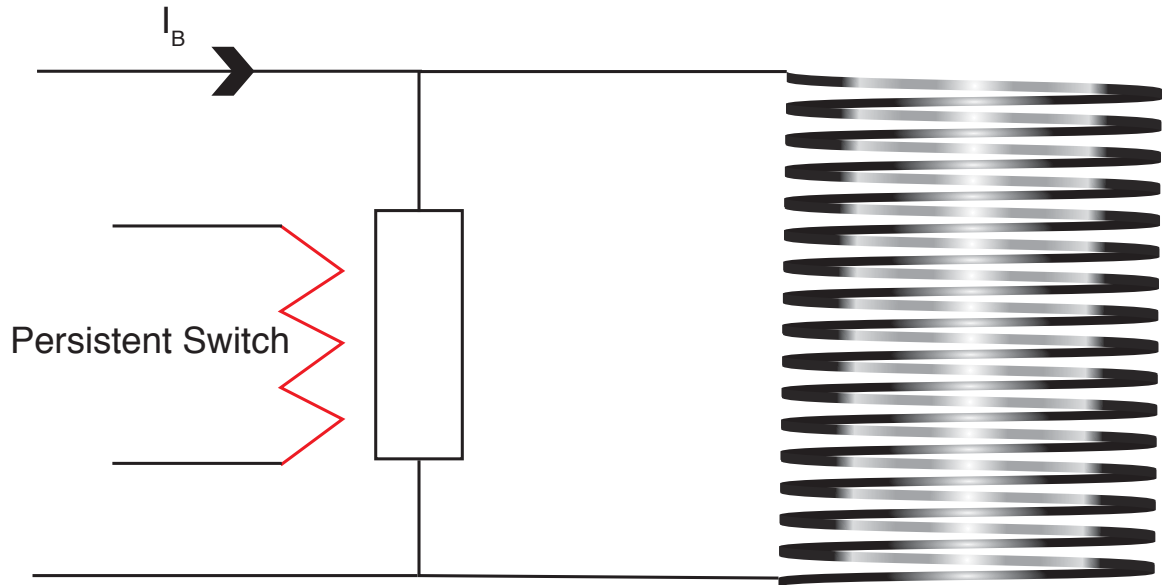


Figure 4.2.5: Persistent current switch. All the components are in LHe bath. The switch determines whether the current goes through the solenoid or not.

the universe [6]. If we can inject the current to the magnet and then isolate it from the power supply, we are able to reduce that noise. Using the persistent current switch in the magnet turns on/off the connection with the power supply. As shown in Fig. 4.2.5, the persistent current switch is basically a heater. When the heater is turned off, the resistor becomes a superconductor which shorts the solenoid. The magnet enters persistent mode. Turning off the external power supply will not affect the current inside the solenoid. When turning on the heater, the local temperature increases and the resistor becomes normal. The magnet is back in the external power supply circuit. One thing that needs care is that whenever turning on the persistent switch, the external current must match the internal current of the solenoid.

The output current of the power supply is controlled by the power supply programmer. With the P-switch on, to reach a specific field (current), the maximum ramping rate is 0.1 A. Setting the ramping rate too high will generate a lot of heat and burn LHe quickly. In field sweeping measurement, we need to maintain constant temperature. The ramping rate should be further reduced to 0.01 A or below.

4.2.3.3 Cooling Components

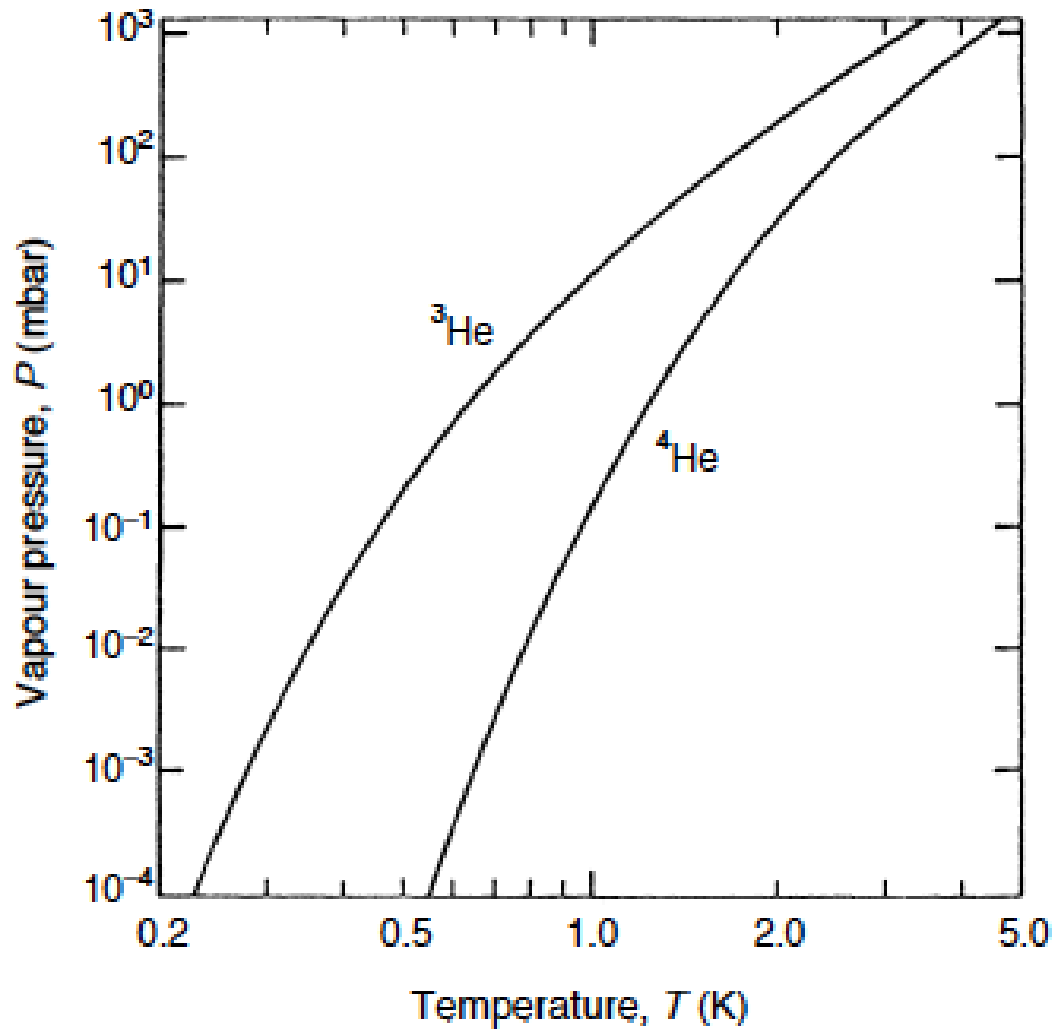


Figure 4.2.6: Vapor pressure of liquid He3 and He4 at various temperatures.[4]

As we will see later, the key coolant of the dilution refrigerator is the He3/He4 mixture. The circulation pump does the work to remove heat from low temperature part to high temperature reservoir. When the system is running, the whole fridge is below the boiling point of He3 and He4. However, He3 has much higher vapor pressure than He4 (see Fig. 4.2.6). For example, at 0.7 K, $P(\text{He4})=0.003$ mbar, $P(\text{He3})=1.800$ mbar. Thus, when the circulation pump is running, almost only He3 is circulating while He4 is in liquid state staying in the still and mixing chamber. Let

us follow the flow of the He3 gas to see the function of each component.

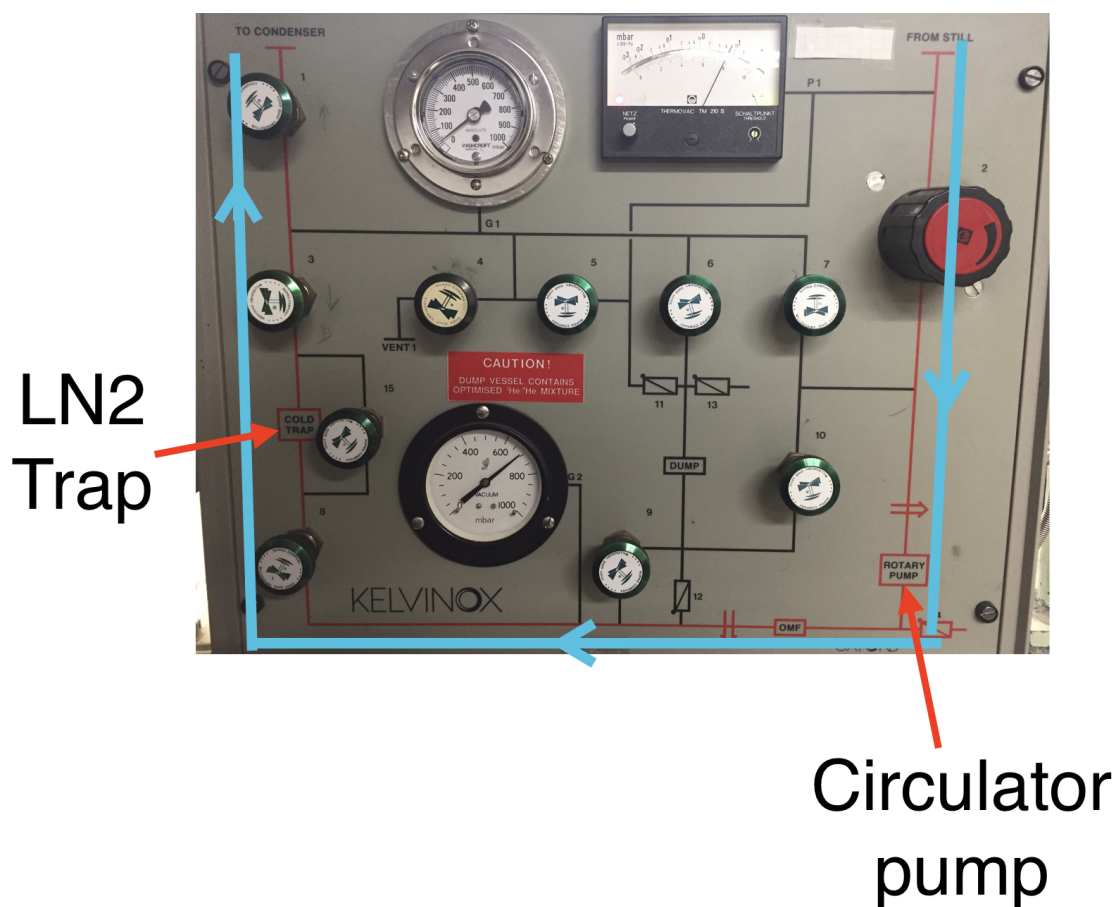


Figure 4.2.7: Gas handling system. The cyan line is the primary circulation path. There is a circulator pump along the path to provide the power for the flow. A LN2 cold trap captures impurities before the gas returns to the fridge.

The gas handling system provides the pressure difference for He3 to flow. As shown in Fig. 4.2.7, a circulator pumps the He3 atoms from the still. It is then pushed through a LN2 cold trap. The activated charcoal effectively removes the any impurity in the gas flow. This is an important process since the lines inside the fridge are very tiny (viscous flow is required to make the fridge work), any impurity in the mixture will freeze and plug the lines. The whole experiment is likely to fail if that happens. Because of the volume of cold trap, we usually refill it every 7 hours when the system is running. There are two gauges to monitor if the flow is impeded or not. Other components in the gas handling systems include a 11.5L

dump, which is used to store He3/He4 gas mixture at room temperature, and some other lines used to clean the mix or cryopump the fridge.

The He3 gas enters the fridge after leaving the gas handling system. The first cooling stage is '1K Pot'. As the name suggests, it maintains temperature around 1 K. This is achieved by continuous pumping liquid He4 by a mechanical pump. The evaporation of He4 gas takes away heat. Note that this is outside the He3/He4 mixture line. As the Helium level decreases, new Helium liquid from Helium bath flows in through a siphon tube automatically. A needle valve controls the flow rate, thus we are able to adjust the cooling power through the needle valve. A resistance thermometer is installed at this stage to monitor the temperature. $R = 670\Omega$ when the 1K pot is working properly.

The next stage is the 'Still'. The temperature is further cooled down to $700 \sim 800$ mK. It is more interesting on the return line side at this stage. Because of the vapor pressure difference we mentioned above, the still works like a distillation chamber where He3 atoms are separated from He4 liquid. Similar to a 'He3 pump', the evaporation of He3 at this stage will also take away heat. There is a heater installed. If the temperature at the still is too low, the vapor pressure will decrease. There will be little amount of He3 in circulation, resulting in low cooling power of the mixing chamber. The gauge 'P1' in Fig. 4.2.7 is used to monitor still pressure. If it drops below 0.4 mbar, we need to warm up the still a little bit using a still heater. Below the still, there is a heat exchanger. The incoming He3 in the condensing line is further cooled by the He3 returning from the mixing chamber. Thus, the heat exchange benefits the He3 on both sides.

The last stage is the mixing chamber. This is the core component of the fridge. The cooling is achieved by the unique phase separation of He3/He4 mixture at low temperature (see Fig.4.2.8). Pure He4 becomes superfluid below the lambda point. $T_c = 2.18$ K for this transition to happen at saturated vapor pressure. When

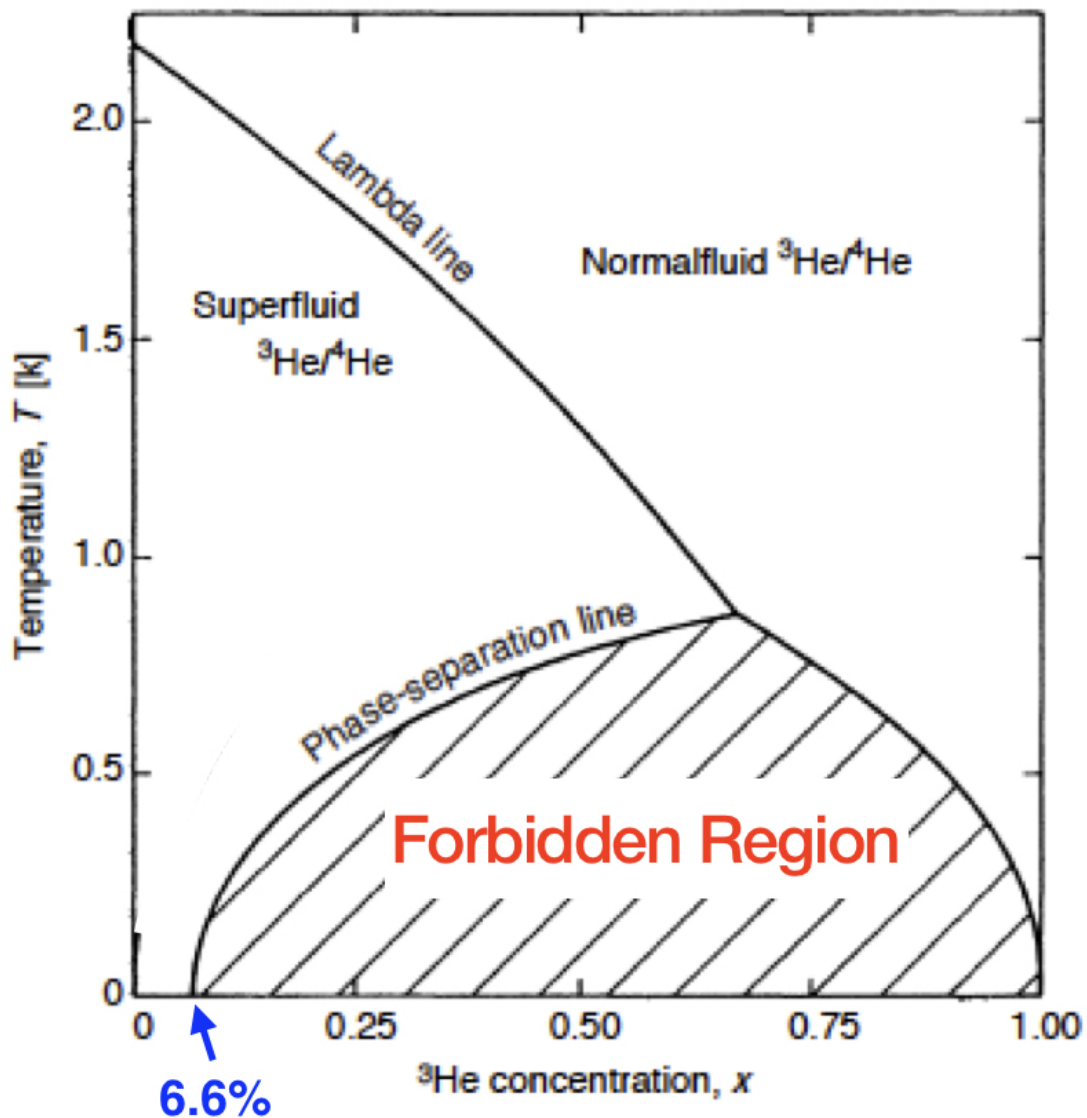


Figure 4.2.8: Phase diagram of He_3 and He_4 mixture at saturated vapor pressure [4]. At low temperature, the mixture are separated into He_3 rich and He_4 rich phases. The transition between two phases involves heat transfer that provides cooling power.

He_4 is mixed with Fermi liquid He_3 , the transition temperature is depressed (see the lambda line). At concentration above 67.5%, the superfluidity disappears no matter how low the temperature is. The lambda line meets the phase separation line at that concentration. The corresponding temperature is 0.87 K. That is the reason why we usually observe that the fridge starts cooling fast once it gets down

to ~ 0.8 K. Because of the existence of phase separation, if we start with some He3/He4 mixture, by continuous cooling, the phase boundary will automatically appear, and He3-rich liquid will float on the top of He4-rich liquid since it has lower density. To get the lowest possible temperature for the sample, we need to make sure the phase boundary appears within the mixing chamber. That requires us to have optimum amount of He3/He4. For the fridge in our lab, the mixture has a volume around 9.5 L under atmosphere pressure. 1.5 L of it is He3. So the concentration is around 15.7%.

Another interesting thing about that phase diagram is that on the He4-rich side, the accessible He3 concentration at the low temperature limit is 6.6% instead of reaching zero. This finite solubility of He3 in liquid He4 is crucial to make the dilution refrigerator work since we want to pull He3 atoms from He3-rich phase to He4-rich phase. It is impossible if He3 atoms cannot exist in He4 liquid. This process is again like a 'He3 pump' except that the environment is He4 liquid instead of vacuum. After He3 enters He4-rich liquid, it will flow back to the still and pumped out to the gas handling system. Then the whole process starts over again.

4.2.4 Helium Recovery System

Helium is recycled in our lab for both the flexibility of doing experiments as well as economic aspect. Fig.4.2.9 shows the helium recovery system. There are three outlets of Helium gas. One is the regular boil-off from the Helium bath in the dewar. Another one is from the magnet. When the magnet is on, the heat boils off some LHe, creating local high pressure gas inside the dewar. Those venting lines help rebalance the pressure. In normal operation, V1 and V2 are open with V3 closed. The boil-offs are monitored by three small flowmeters. When we are doing He gas or liquid transfers, V1 and V2 are closed while V3 is open. A large volume of cold gas will go through a fin tube and a large flowmeter. The fin tube effectively warms

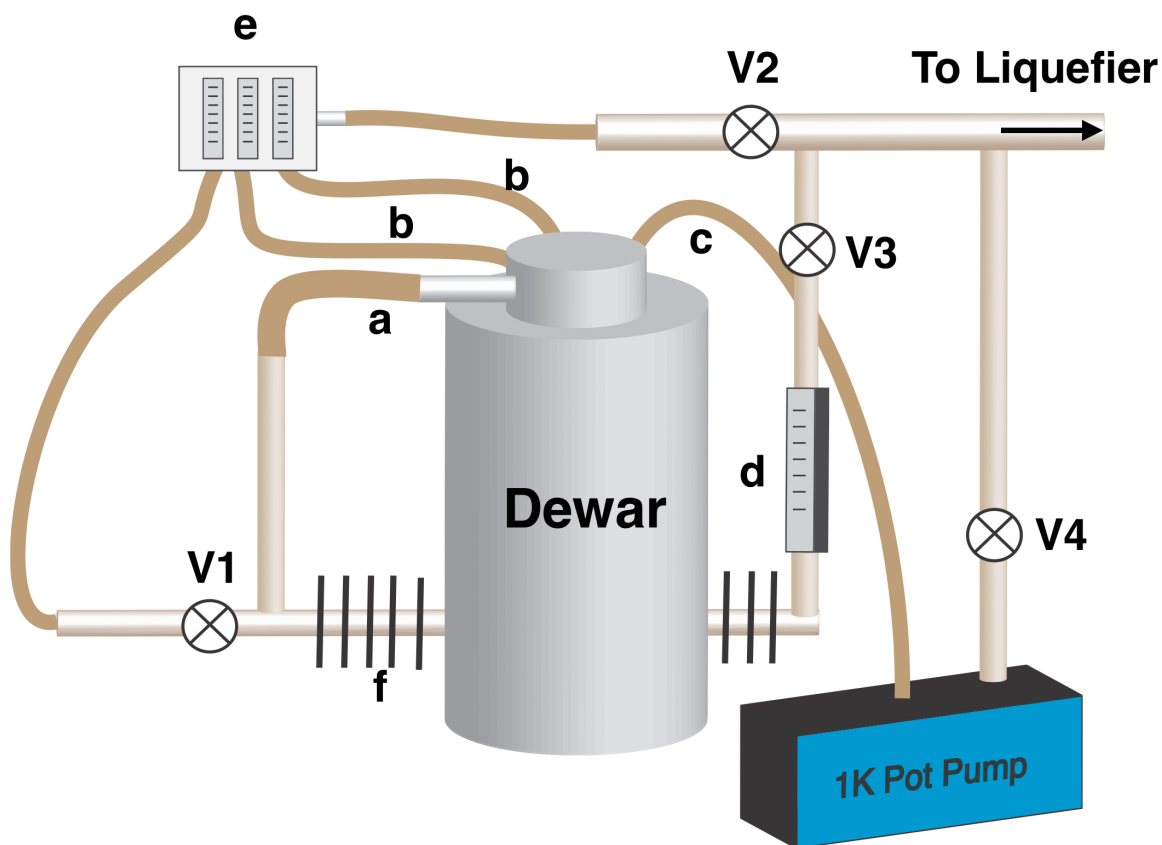


Figure 4.2.9: Helium recovery lines. (a) Dewar boil-off, (b) Magnet boil-off, (c) 1K pot pumping line, (d) A large flowmeter, (e) three small flowmeters, (f) Fin tube, (v) valves.

up the gas, preventing icing on the following parts in the line. The last Helium gas outlet is from the 1K pot pump. The vent line of the pump is joined with the boil-off line and the He gas is sent to the storage bag in a separate Helium liquefier room where the Helium is liquefied and stored in a big dewar.

4.2.5 Transport Measurement Equipments

There are various pieces of equipment to do electrical measurement. A home-made adjustable battery box, along with two pre-amplifiers and digital multimeters are used for DC current measurement. There are two digital and an analog lock-in amplifiers that are used for AC current measurement. The temperature is mon-

itored by the voltage output from the bridge circuits, which is proportional to the resistance of the thermometer. Those instruments communicate with Labview programs through a GPIB interface.

4.3 Experimental Techniques

I will show some experimental methods that are unique or tricky in our lab.

4.3.1 Source Calibration

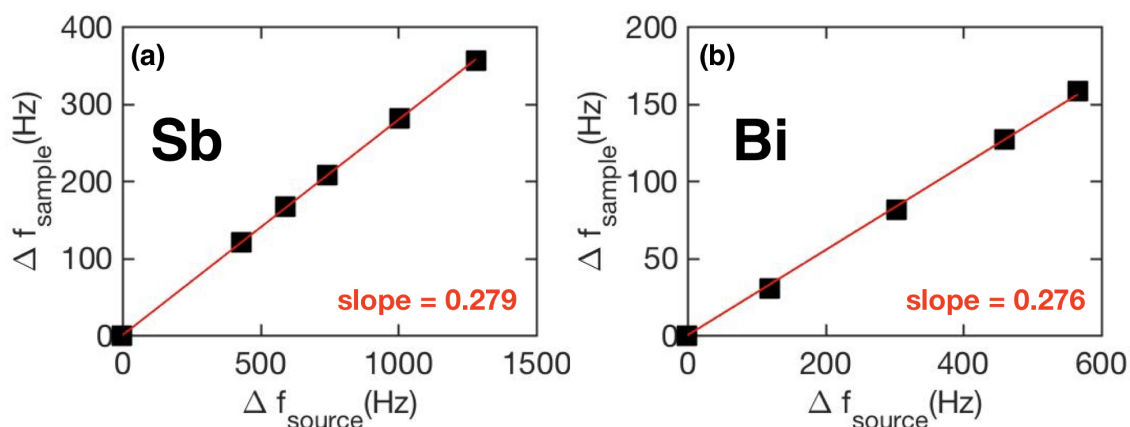


Figure 4.3.1: Source calibration for (a) Sb and (b) Bi.

As mentioned above, the QCM is not placed at the same height as the sample in the fridge. We need to do source calibration in advance to convert the frequency changes at that height to thickness of the sample. Two crystals are placed in the evaporator. One is closer to the source. That is the same crystal we will use in the fridge. The other one is placed farther away at the height same as the sample in the fridge. Fig.4.3.1 is a typical result from one of my experiments. The slope is less than 1 since the QCM closer to the source has higher frequency change. $\delta f/d(\text{Sb}) = 5.0 \text{ Hz/\AA}$ for the QCM at the sample. Therefore, the ratio is $17.9 \text{ Hz/\AA}$ for the QCM in the fridge. Similarly, it is $26.4 \text{ Hz/\AA}$ for Bi evaporated in the fridge.

Although those values do not vary much in different experimental runs, it is always recommended to do source calibration to get better estimates of the thickness.

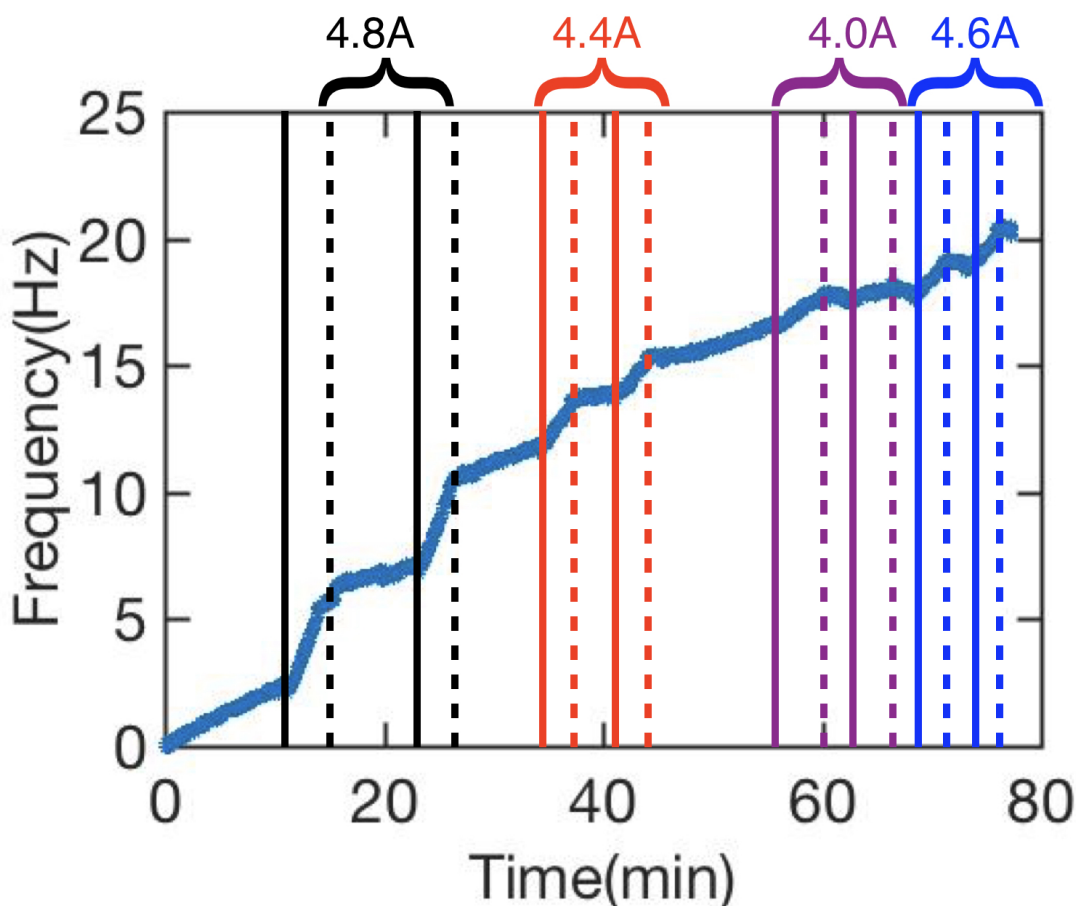


Figure 4.3.2: Source calibration for Gd. The y-axis is the frequency change of the QCM. Several attempts have been made with different evaporation currents. The solid lines represent the start of evaporation, and the dashed lines indicate the end of each run.

Source calibration for Gd is different from Sb and Bi. Since the frequency change is very small, we calculate the evaporation rate at specific current and use the same current for evaporation in the fridge. Fig.4.3.2 shows the several evaporations with different currents. Note that there is a frequency drift even without turning on the current. We need to remove that from the calculation. The average evaporation rate is 0.965 Hz/min for 4.8 A, 0.507 Hz/min for 4.6 A, 0.418 Hz/min for 4.4 A, and 0.117 Hz/min for 4.0 A. I chose 4.4 A for evaporation in the fridge.

Based on Table.4.1, that is 0.07 Å/min. The rate at specific current depends on the resistance of the tantalum. It is necessary to do calibration every time before cooling down.

4.3.2 Gd Evaporation In the Fridge

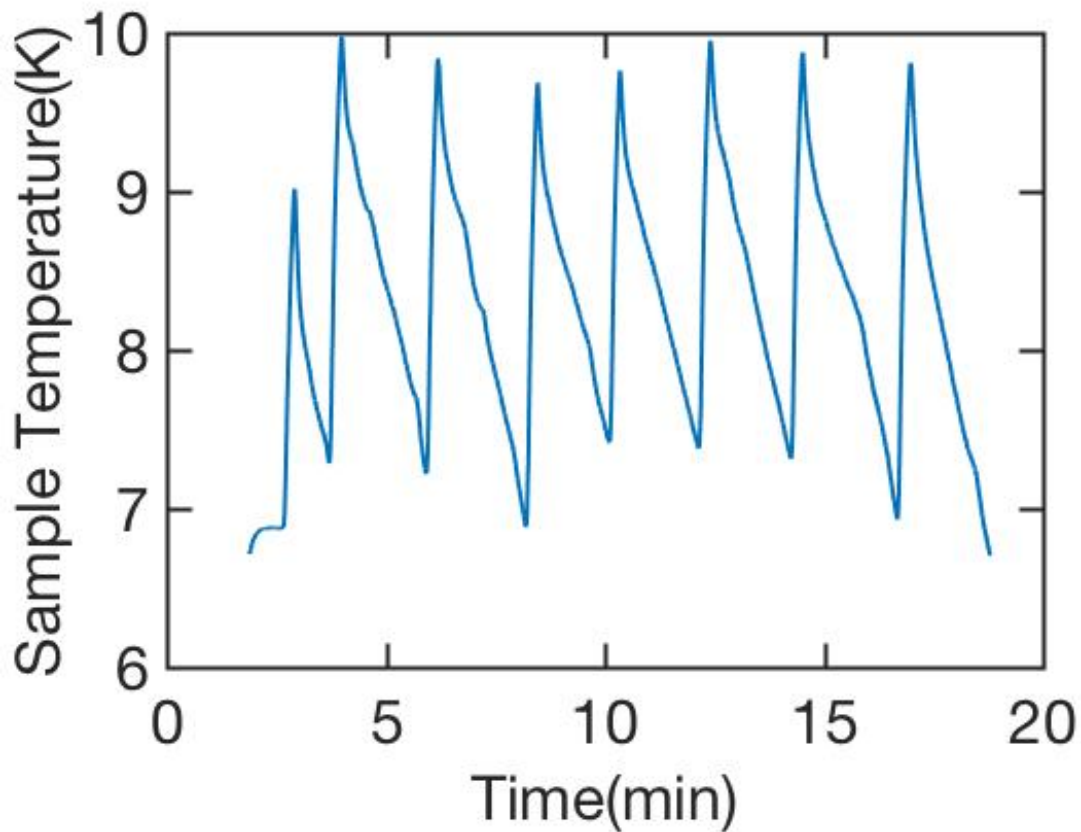


Figure 4.3.3: A series of Gd evaporations in the fridge.

With high melting point, Gd needs a relatively high temperature for evaporation. That radiation from the source will also increase the temperature at the sample. Unlike the calibration in the evaporator, we need to avoid the temperature getting too high that will anneal the Bi film. In experiments, we control the temperature of the film below 10 K using pulse evaporations method. Each pulse lasts ~ 15 seconds, and we record the accumulative evaporation time. Fig.4.3.3 shows a

total of 8 evaporations. The temperature increases up to 10 K quickly as we turn on the current. Then it drops when we take the current out. To make sure the film is not annealed, high temperature (8 K) resistance is measured and it stays constant in our experiments.

4.3.3 Resistance Measurement

The resistance depends on the geometry of the sample,

$$R = \rho \frac{L}{Wd} \quad (4.3.1)$$

where L, W, d are the length, width and thickness respectively. The characteristic resistance of 2D film should only depend on its resistivity and thickness. We can get rid of length and width by setting them equal. i.e. $R_{\square} = \rho/d$. So the resistance measurement should be conducted on a square or converted to square resistance afterwards.

The methods we used to measure resistance include 2-point DC, 4-point DC and 4-point AC measurements. 2-point DC cannot eliminate the contact resistances, so it is usually used to check whether the contacts are good or not. Sometimes, we also use it to qualitatively check the homogeneity of the film by pairwise measuring of the resistance between different contacts.

Typically, there are six contacts in total. Four of them are voltage contacts, and the other two are current contacts (see Fig.4.3.4). The voltage contacts correspond to two squares on the film. The extra square is measured to check the homogeneity of the film. Sometimes it also serves as the back-up choice if the other contacts fail. For the current contacts at the two ends, since there are no substitutes for them, each one is connected to two gold wires.

For high resistance(>1MΩ), DC measurement is preferred. It avoids the ca-

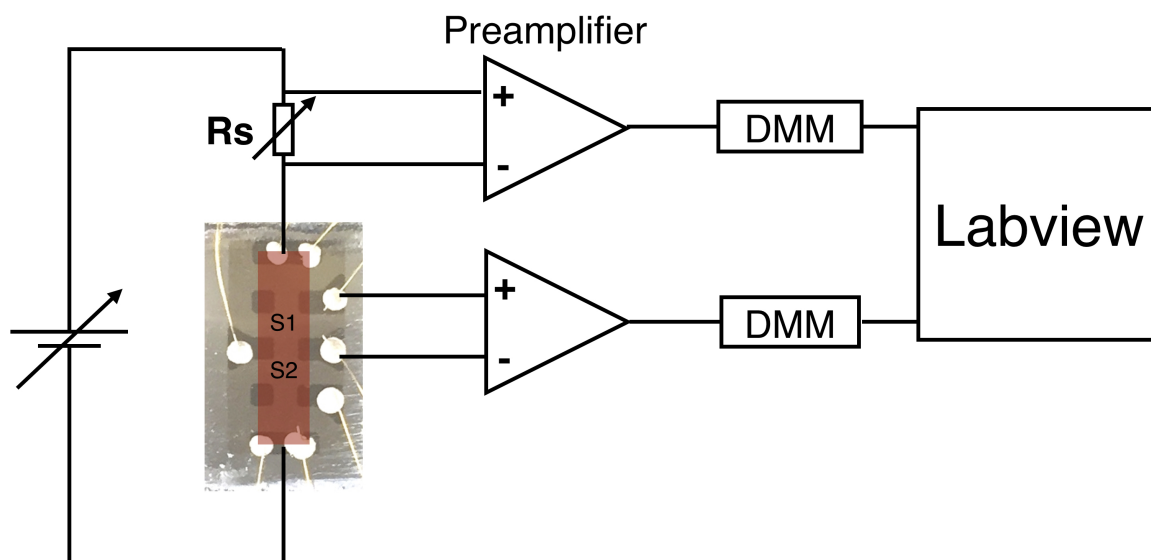


Figure 4.3.4: 4-point DC current measurement. The red region is the Bi film evaporated at low temperature. There are two squares, S1 and S2. The diagram shows the measurement on S1.

capacitance effect from the sample, which will cause large phase shift for AC current measurement. Also it enable us to check the IV curve to ensure the resistance is in the linear region. Fig.4.3.4 shows the the 4-point DC measurement on one of the sample squares. Both the voltage source and the series resistance are adjustable. The current is calculated by the voltage across the series resistor. Usually, the current range is around $0.1 - 1$ nA, while the measured voltage across the square is in mV range. Both signals are first amplified by the preamplifier and then sent to digital multimeter, which will be recorded by the labview program.

For lower resistance, AC method is preferred without worrying about the capacitance of the film. The biggest advantage over DC measurement is that AC method can continuously measure the resistance. It is more useful when we want to see the resistance change in temperature or magnetic field. As shown in Fig. 4.3.5, a big resistor is put in series with the film. The current signal comes from the signal output from one of the lock-in amplifier. I usually choose 200 mV output and $1G\Omega$ series resistor. The current is always 0.2 nA assuming the film resistance is below

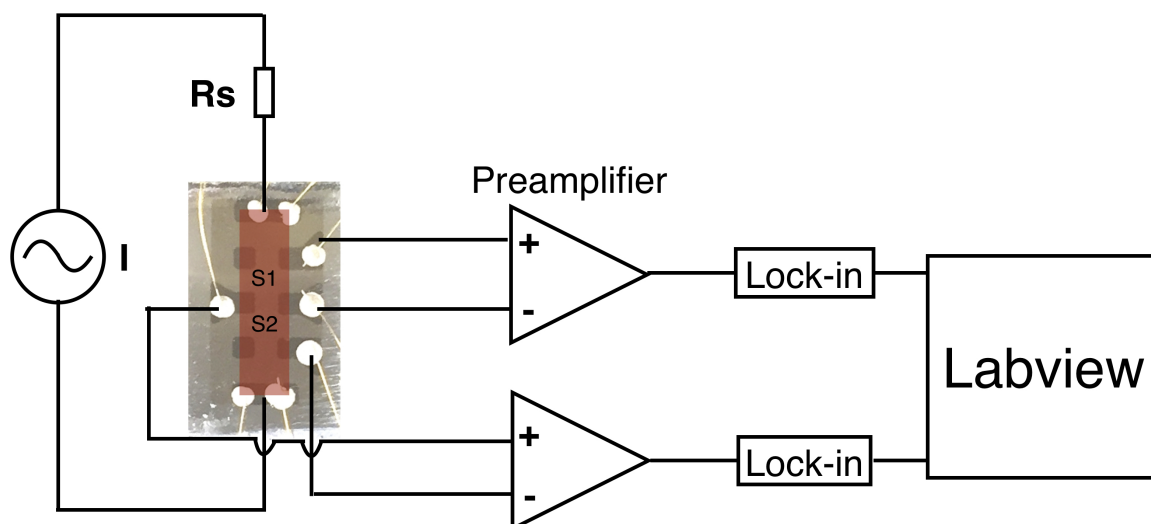


Figure 4.3.5: 4-point AC current measurement. The resistance of the series resistor R_s is much larger than the resistance of the film. The current remains constant even if the film resistance changes. The two squares are measured at the same time in the diagram.

$1M\Omega$. The voltage across two squares are measured at the same time by two lock-ins, and the output signals are sent to labview program, together with temperature and/or magnetic field for $R(T)$ and $R(H)$ measurements.

The overlap region of DC and AC methods needs close attention. As the AC measurement suffers from phase shift when the resistance is high, the measured resistance began to be flat or even drop when the actual resistance keeps increasing (see Fig.4.3.6). I usually start DC measurement from $R = 100K\Omega$. The AC measurement is not reliable when the deviation from DC method is more than 20% or so.

4.3.4 Isodissipative Measurement

Isodissipative measurement is in contrast to isothermal measurement. It is performed by fixing the resistance of the sample and find the corresponding temperature by controlling the heater. One practical use of that is to measure the superconducting critical temperature change in field, where T_c is defined as the

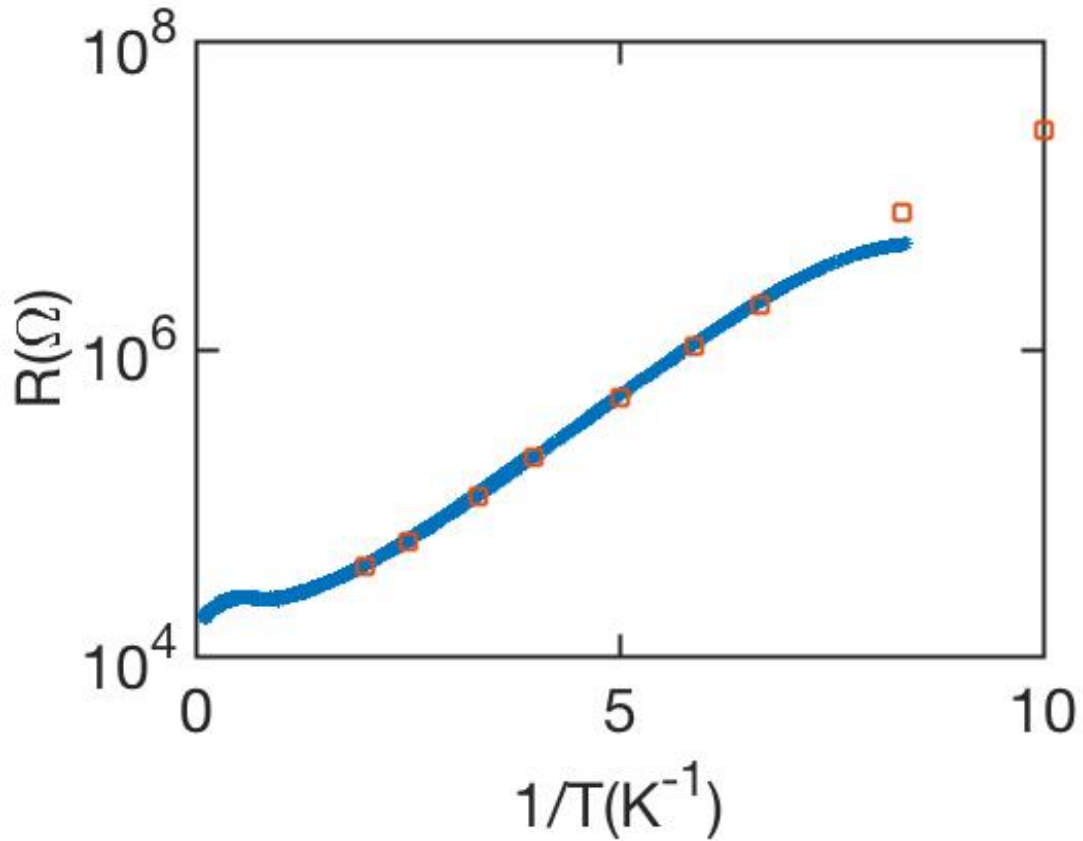


Figure 4.3.6: Flattening of AC measurement due to phase shift at high resistance region. The continuous curve is the AC measurements while the square markers are DC measurements. The data points are from Dec2017 experiment.

temperature the resistance decreases by half. Several isodissipative curves are shown in Fig.4.3.7.

To measure the isodissipative curve, the resistance bridge and temperature controller are used. The bridge is connected to the sample rather than the thermometer, while the AC 4-point measurement circuit is connected to the thermometer. So basically, we switch the position of the sample and thermometer and the temperature controller is acting as resistance controller. Another thing needs to change is switching the polarity of the feedback loop in the temperature controller, since the resistance of the superconducting sample has positive temperature coefficient while the thermometer is negative.

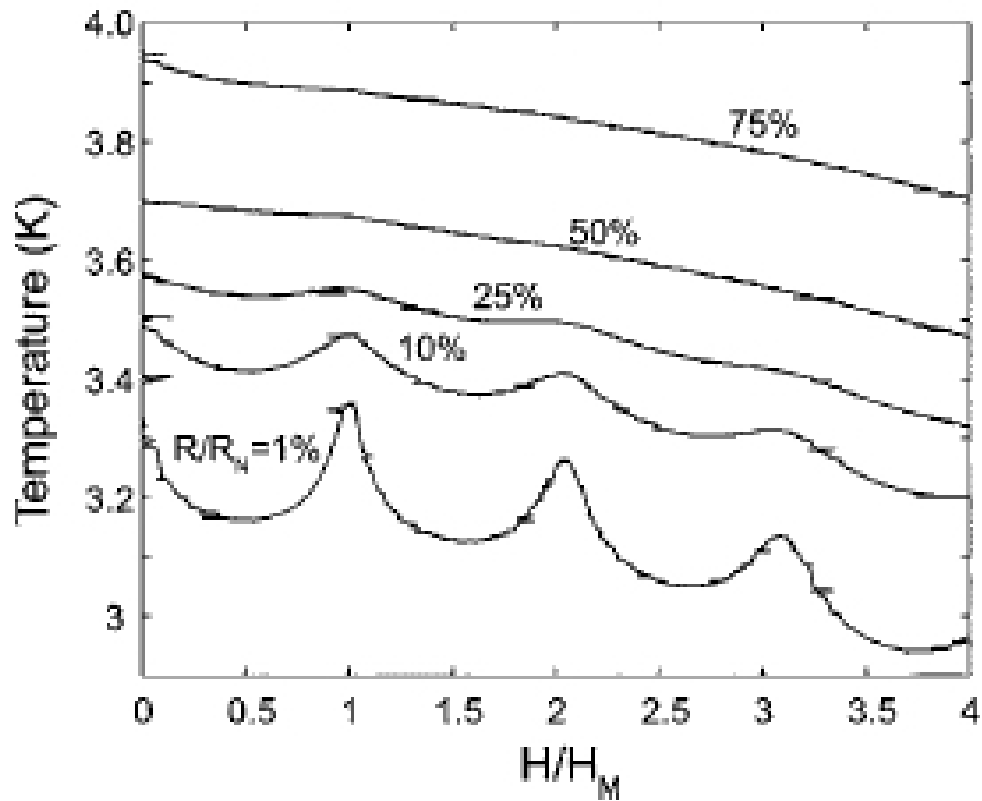


Figure 4.3.7: Isodissipative measurement of temperature versus magnetic field with fixed resistance [7]. The numbers represent the ratio of fixed resistance to the normal state resistance.

4.4 Experiment Procedure

Fig. 4.4.1 is the typical workflow in our lab. Some repetitive procedures are not shown. For example, the electrical check should be done multiple times. If it fails, the whole process needs to start over. Typically, it takes around one week to do preparation, two days to cool down to base temperature and another two weeks to do the transport measurements. The warming up procedure is fairly quick and takes ~ 1 hour or so.

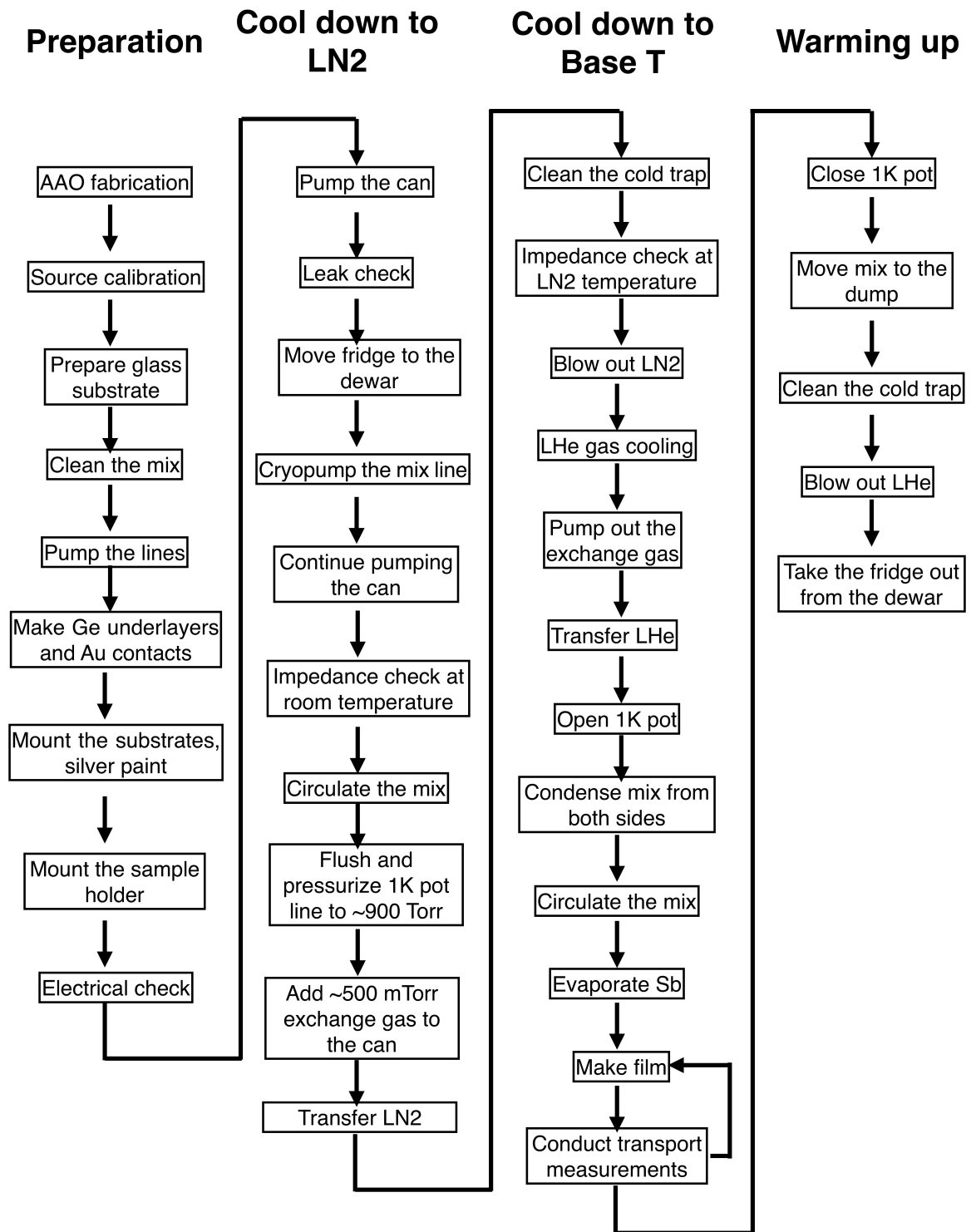


Figure 4.4.1: A typical workflow in our lab.

4.4.1 Prepare to Cool Down

Before starting the experiment, we need to make sure there is at least one cylinder of compressed Nitrogen gas, one cylinder of compressed Helium gas, two dewars of LN2 and two dewars (120L) of LHe. LHe is more accessible with the addition of the new recovery system. AAO fabrication and source calibration take around two days each. The rest part of preparation is done on the same day of LN2 cooling. The glass substrate is fire polished to make it perfectly flat. It is mounted on the sample holder using vacuum grease that has low vapor pressure. We always deposit 10nm Ge underlayers on both AAO and glass substrate. That enables us to attribute the transport difference to the morphology of the substrates instead of the sticking coefficient. The electrical contacts are made of 10 nm high purity Au with special mask and connected to the circuits using 0.002 inch gold wires and silver paint. Finally, after everything is installed, we need to do electrical check. It needs to be done multiple times later to make sure everything goes well. The electrical check includes checking measurement circuits, evaporation source connection and crystal connection. To prepare the fridge, we need to clean He3/He4 mixture in advance. The mixture is circulated through the cold trap for several hours. That can be done anytime before we start circulating through the fridge. Also, as we will see later, pumping the can is the most time consuming part of the day, it is preferred to pump on the lines first while we are doing other preparations. A diffusion pump is used to pump all the lines. I usually do this part as early as possible.

4.4.2 Cool Down to LN2

This is the first step of cooling. It cools the whole fridge to 77K with relatively cheap LN2 compared with LHe. First we need to pump out the can with the diffusion pump. I usually wait for the pressure to drop to 5E-6 Torr, and then start leak check.

The leak check is done by spraying Helium gas around the lines and the fridge. Since Helium atom is light and small, it will penetrate small leaks and detected by a mass spectrometry connected to a pump. After the leak check, we stop pumping the can and move the fridge to the dewar where we will fill LN2 and LHe later. Then we can connect the mixture circulation lines. A small volume in the line is open to air after every cooling experiment. We need to clean that using cryopump from the LN2 cold trap. 'P1' in the gas handling system (see Fig.4.2.7) can be used to monitor the pressure. At the same time, we start pumping the can again. We can stop cryopumping and start circulating the mixture when the pressure 'P1' drops to $0.7 \sim 0.8$ mbar. That usually takes several hours. Once we start the circulation, we can check the impedance of the fridge. To do that, we pressurize the condenser side of the fridge, and measure how long it takes for the pressure on the still side ('P1' gauge) to increase from 0.1 mbar to 1 mbar. It was around 3'50" in my experiment runs. Then we keep waiting until the pressure of the can drops below 3×10^{-6} Torr. After that, we can stop pumping and add ~ 500 mTorr Helium exchange gas to the can. The exchange gas accelerates heat transfer between the dewar and the fridge inside the can. It makes LN2 and cold helium gas cooling much faster. Finally, liquid Nitrogen is transferred to the dewar and the whole fridge will be cooled down to 77K within several hours.

4.4.3 Cool Down to Base Temperature

After cooling down to LN2 temperature and circulating the mixture for a day or so, I usually stop circulation for a while and warm up the cold trap to clean the impurity. This is optional but it helps saving LN2. Then we need to do impedance check again using the same method but at LN2 temperature this time. Lowering down the temperature increases the viscous flow and it should take only 30". The next step is blowing out the remaining LN2 in the dewar using warm Nitrogen gas. This

process is monitored by a thermometer at the bottom of the dewar. The temperature increases when there is no LN₂ left. Now we start cold helium gas cooling. Because of low heat capacity of liquid helium, it is more efficient to use evaporated cold helium gas to cool the fridge at first. Helium recovery valves should be opened at this time. It takes around two hours and ~ 30 L LHe to cool it down to 20 K. Then, we stop gas cooling and the exchange gas in the can is pumped out. The ultra high vacuum chamber provides excellent thermal insulation between the fridge and the dewar. A small amount of LHe is transferred to the dewar. I usually transfer to 15% at first, which is around 5 L in the dewar. Now we can open the 1K pot and the system will be slowly cooled down by it. After the fridge is cooled down by 1K pot, we start condensing the He₃/He₄ mixture on condenser side as well as the still side. All the mixture in the dump should be condensed in a short time (~ 1 hour). At that time, we can start circulating the He₃, and the fridge can be cooled to base temperature in several hours. If everything goes well, we can transfer more LHe to the dewar. It takes ~ 50 L of liquid in total for the initial cooling down.

For film evaporations at this stage, we warm up the sample holder to 8 K (in some cases, it is warmed up to 10 K). 1 nm Sb is firstly evaporated as a wetting layer. Then we do the evaporations of Bi and monitor the film resistance at the same time. In our lab, we calculated the desired resistance and draw the IV curve on the XY recorder. We stop evaporation when the film resistance reaches that curve. At the same time, temperature is always monitored during the whole process to avoid annealing the film. For each film, we do the transport measurements individually and increase the thickness again. For the magnetic impurity doping experiments, after Bi thickness has reached our goal, we do Gd evaporation using pulse methods mentioned above.

4.4.4 Warming Up

This is the last stage for each experiment. We first stop circulation and close the 1K pot. A still heater and mixing chamber heater is applied to evaporate the residual liquid mixture in the fridge and pump them to the dump. When the pressure (G2 in Fig.4.2.7) reaches pre-experiment pressure in the dump, we can stop pumping. The cold trap is then warmed up and cleaned by a vacuum pump. The gauge G1 is used to monitor the amount of impurity. Ideally, there should not be much impurity captured in the cold trap on a timescale of two weeks. Leak check is required if the impurity pressure is above $\sim 200\text{mbar}$. Helium inside the dewar, no matter it is gas or liquid, should be blown out using Nitrogen gas. If not, the helium left will 'soften' the dewar and results in bad thermal insulation with the atmosphere. Helium recovery system should also be closed at the time. It will take several days for the fridge to naturally warm up to room temperature. After that, we can move the fridge out from the dewar and take the sample out for further analysis.

Bibliography

- [1] KL Ekinici and JM Valles Jr. Formation of polycrystalline structure in metallic films in the early stages of zone i growth. *Acta materialia*, 46(13):4549–4557, 1998.
- [2] Zhenyi Long and James M Valles. Early stage morphology of quench condensed ag, pb and pb/ag hybrid films. *Journal of low temperature physics*, 139(3-4):429–438, 2005.
- [3] Hung Q Nguyen. *Experiments on a Cooper pair insulator*. PhD thesis, Brown University, 2010.
- [4] Frank Pobell. *Matter and methods at low temperatures*, volume 2. Springer, 2007.
- [5] Shawna M Hollen and JM Valles Jr. Cooper pair islanding model of insulating nanohoneycomb films. In *Journal of Physics: Conference Series*, volume 376, page 012002. IOP Publishing, 2012.
- [6] John C Gallop. *SQUIDs, the Josephson effects and superconducting electronics*. Routledge, 2017.
- [7] MD Stewart Jr, Zhenyi Long, James M Valles Jr, Aijun Yin, and JM Xu. Magnetic-flux periodic response of nanoperforated ultrathin superconducting films. *Physical Review B*, 73(9):092509, 2006.

Chapter 5

Evidence of Dissipative Process with Cooper Pair Tunneling

Previous experiments have shown the existence of Cooper pairs on the insulating side of the SIT, i.e. Cooper pair insulator (CPI) state. The transport is dominated by Cooper pair motion and the conductance has an Arrhenius temperature dependence. In this chapter we will see how magnetic impurity doping changes that behavior in two separate experiments. We show that Gd doping can be either detrimental or favorable for the Cooper Pair Insulator phase. The activation energy in films farther from the SIT decreases monotonically with doping while it increases in films closer to the SIT critical point. Comparisons with theoretical models suggest that the tunneling dynamics of the Cooper pairs are dissipative. Parts of this chapter comes largely from a manuscript on the cond-mat arXiv [1] that has also been submitted for publication.

5.1 Introduction

Experiments on thin films have established that simply activated Cooper Pair transport dominates in the insulating phase that develops at boson fluctuation driven superconductor to insulator transitions. Establishing the origin of the activation energy, however, remains as a significant challenge. When met, it will reveal microscopic insight into this so-called Cooper Pair insulator state. To test models of the activation energy, we have investigated how the Cooper Pair insulator state responds to magnetic impurity doping and magnetic frustration. This approach was partially motivated by the fruitfulness of early investigations of the different responses of superconductors to non-magnetic and magnetic impurities. Those led to microscopic models of the detrimental effects of spin flip scattering on the Cooper pairing energy that reduce the superconducting transition temperature, T_c .

The activation energy characterizing a process in a condensed matter system provides a window into its quantum many body ground state. For example, integer quantum hall transitions broaden with temperature at a rate dictated by the cyclotron energy and the heat capacity of BCS superconductors similarly increases at a rate dictated by the binding energy of electrons in Cooper pairs. This chapter focuses on an activation energy, T_0 , that grows from zero at disorder tuned bosonic superconductor to insulator quantum phase transitions. It appears as a barrier to incoherent Cooper pair tunneling between localized states in the insulator phase. Although many models have been proposed, experiments have established little about its microscopic origins.

In the following sections, we show two magnetic impurity doping experiments. We present measurements of the dependence of R and T_0 on magnetic impurity doping and magnetic frustration. We describe how the results indicate that this barrier depends on the average Cooper pair binding energy. This dependence

implies that Cooper pair transport involves dissipative quantum dynamics in the Cooper pair insulator phase.

5.2 Activated Transport

It has been observed in many experiments that thin films on the insulating side show simply thermally activated resistance [2, 3, 4, 5, 6],

$$R = R_0 \exp(T_0/T) \quad (5.2.1)$$

There have been many explanations, both qualitatively and quantitatively, for the underlying nature of T_0 . Sambandamurthy et al [3] observed the biggest giant magnetoresistance peak. They measured T_0 in different magnetic fields and related T_0 at the MR peak to the superconductivity transition temperature T_c . Delsing[2] et al separated the transport into quasi-particle dominated regime and Cooper pair dominated regime. They showed quasi-particles dominate when $\Delta/E_C < 2$, where Δ is the amplitude of the superconducting order parameter and E_C is the charging energy. They observed $T_0 = \Delta + E_C/4$ as well as negative magnetoresistance when quasi-particles dominate; In the Cooper pair dominated regime, activation energies are consistent with $T_0 = E_C$ that oscillates with a period set by $h/2e$ per plaquette and an amplitude roughly equal to E_J in the micro-fabricated arrays. Yamaguchi et al [7] measured the activation energy in a system with artificial defects, and proposed that in the single electron dominated region, T_0 depends on long range Coulomb interactions. Fistul et al [6] adopted the idea of the charging energy. They investigated collective Cooper-pair transport and provided the explanation for scale dependent behavior of the activation energy[8]. In their model, $T_0 = \Delta_c[1 - \alpha E_J(B)/E_c]$, where $\Delta_c = E_c/2 \ln(L/d)$ depends on the size of the sample. A big problem with charging energy explanation is that it is based on the

geometry of the system, the charging energy is equal to $E_c = q^2/\epsilon d$, where $q = 2e$, d is the average distance between two adjacent superconducting islands and ϵ is the dielectric constant. The result is enormous (~ 1000 K for $\epsilon \approx 10$ as expected for an insulating substrate). This issue was avoided by setting a diverging ϵ and screening length [9, 10]. Beloborodov [11] proposed another way to get around it. They considered the renormalization of the charging energy by virtual quasi-particle tunneling. The coupling energy enters in a perturbative manner. Thus, $T_0 = E_C - zE_J/2$. Jumping out of Josephson junction model, Markus et al [12] viewed it in a different aspect that is related to Anderson localization. They considered T_0 as the thermal activation to mobility edge of the system. They calculated the energy and magnetic field dependent localization length $\epsilon^{-1}(\epsilon_0, B) = \ln(\frac{W}{t}) + \epsilon_g^{-1}(\epsilon_0, B)$, where the first part represents interference and the second part represents simple hopping. The mobility edge is defined as the minimum energy when the localization length diverges.

In this chapter, we adopt the generally accepted 2D+1 frustrated XY model [13],

$$H = E_C \sum_j n_j^2 - E_J \sum_{ij} \cos(\theta_i - \theta_j - A_{ij}) \quad (5.2.2)$$

where the first term presents the charging energy and the second term is the Josephson coupling energy. The second sum runs over the nearest superconducting sites. The activation energy is the characteristic energy scale of the system. Phenomenologically, it takes the form

$$T_0 = E_C - \beta E_J < \cos(2\pi f) > \quad (5.2.3)$$

where f is the frustration term depending on the field and β is a constant. We already know the Josephson coupling energy E_J is proportional to Δ . By varying Δ in a consistent way and measuring the corresponding T_0 , we are able to calcu-

late the dependence of E_C on Δ and have insights into the microscopic transport mechanism.

Magnetic impurity is an excellent choice for perturbing T_0 . It reduces Δ with very tiny amount of doping while other parameters, e.g. disorder and frustration, remain constant. Magnetic impurity doping is accomplished by depositing successive amounts of Gd atop the Cooper pair insulator film[14]. The impurities produce time reversal symmetry breaking spin flip scattering, which reduces the pair binding energy 2Δ . Their effect extends through the entire thickness of the films since the films are much thinner ($d \leq 1$ nm) than the superconducting coherence length ($\xi \geq 10$ nm). The film thicknesses investigated were much smaller than the superconducting coherence length, which ensures that these pair breaking effects are uniform throughout the film[15].

5.3 Increasing Bi Thickness

To reach the CPI regime, we gradually increase the Bi thickness until we reach the planned activation energy on AAO. The normal state conductance changes with thickness as shown in Fig.5.3.1. The film begins to conduct at 5~6 Å. The conductance curve bends up until it reaches linear region. The data from two substrates prepared under the same condition show small difference which may come from a source calibration error or tiny Sb thickness difference.

5.3.1 R(T) on AAO

Both AC and DC 4-point methods are used to measure the resistance. R(T) curves with increasing thickness in two experiments are shown in Fig.5.3.2. All the curves show diverging resistance at low temperature, indicating insulating state. At ~2 K, the last few films in both experiment show non-monotonic behavior; with decreas-

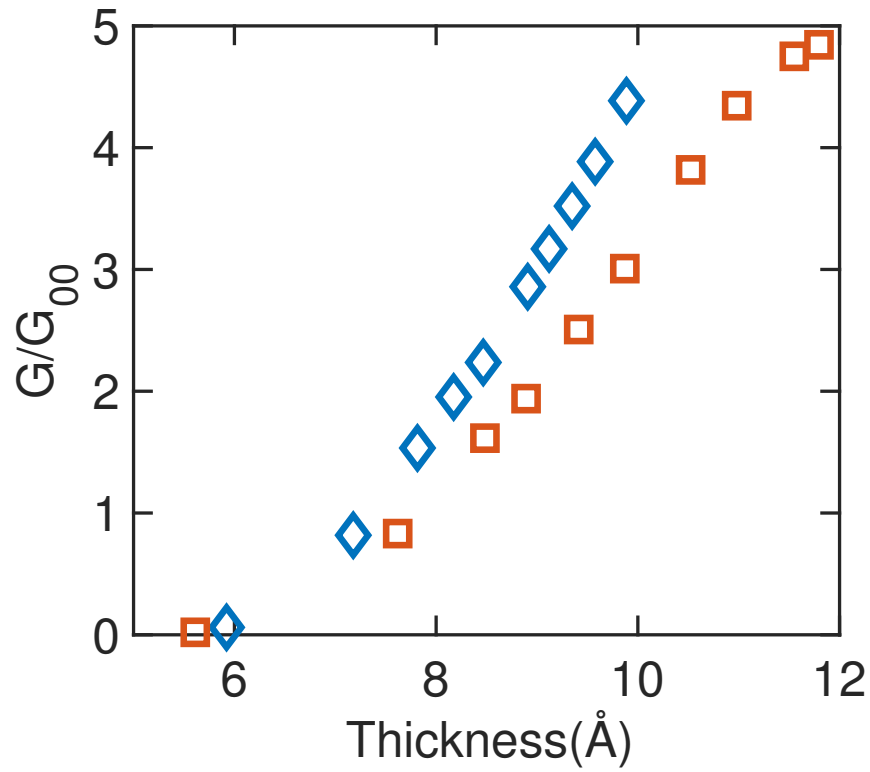


Figure 5.3.1: Normal state conductance increases with Bi thickness. The conductance is measured at 8 K and it is normalized by $G_{00} = 81 \text{ k}\Omega$. The blue diamonds are from Experiment I (Dec2017), and the orange squares present data points from Experiment II (March2017).

ing temperature, the resistance drops at some point and then starts increasing again. That is the sign of the onset of superconductivity. The drop is also consistent with the T_C on reference film. It can be qualitatively explained as follows. Cooper pairs tunnel with the help of single electron hopping that screens the charging energy. As the temperature keeps decreasing, the density of single electrons also decreases. Finally, the single electrons disappear and the transport barrier set by the charging energy is too high for coherent tunneling of Copper pairs, resulting in the insulating state again. One more thing to note is that the reentrance is more significant in the last film of Experiment II than Experiment I. That is one of the signs that we are closer to SIT critical point in Experiment II.

To present the lower temperature data, it is more useful to use semi-log plot

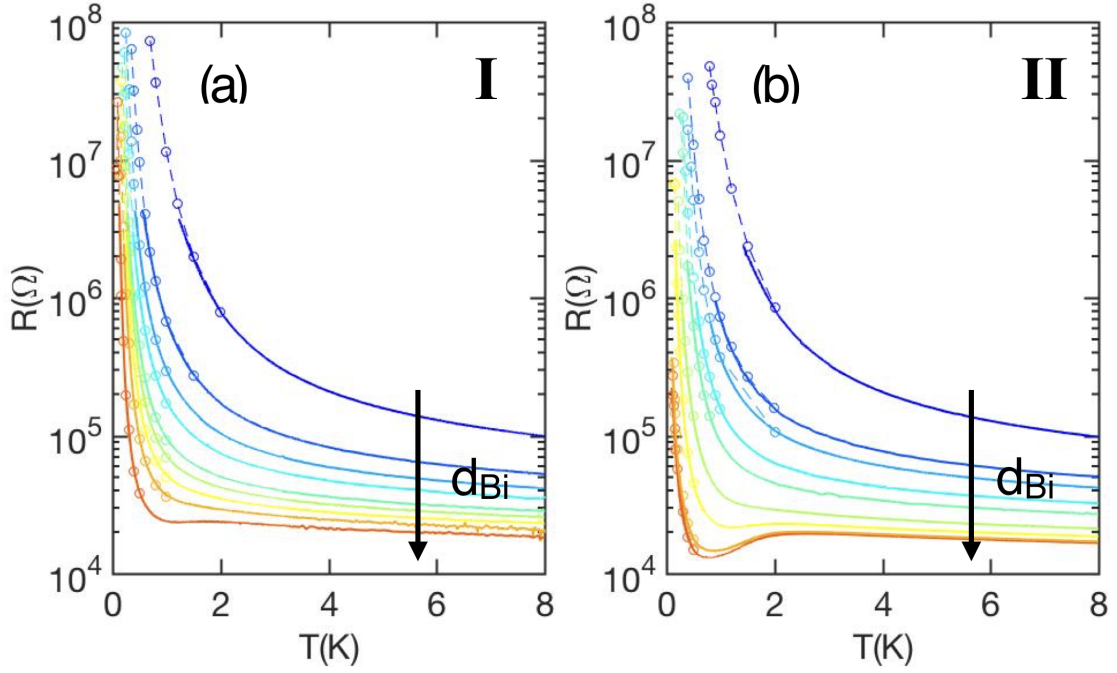


Figure 5.3.2: Sheet resistance at zero field versus temperature with increasing Bi thickness in Experiment I and Experiment II. The arrows indicate increasing Bi thickness. The solid curves represent AC measurement data and the dash lines are DC data.

as shown in Fig.5.3.3. In this scale, the lower temperature regions are located on the right side of the figures. Referring to Eq. 5.2.1, the linear relationship in low temperature regions indicate activated transport behavior and the activation energies are equal to the slopes from the linear fits. With increasing Bi thickness, T_0 gradually goes down to zero.

The graphs in Fig. 5.3.3 are the transport at $H=0$. We also measured the frustration effect at difference thicknesses. The matching field, $H_M = 0.215T$, is determined by the geometry of the substrate. Thus, $f = 1/2$ corresponds to $0.11T$ for both experiments. Fig.5.3.4 shows the difference of $f = 1/2$ and $f = 0$ becomes larger with increasing thickness. If we define,

$$\delta T_0 = T_0^{f=1/2} - T_0^{f=0} \quad (5.3.1)$$

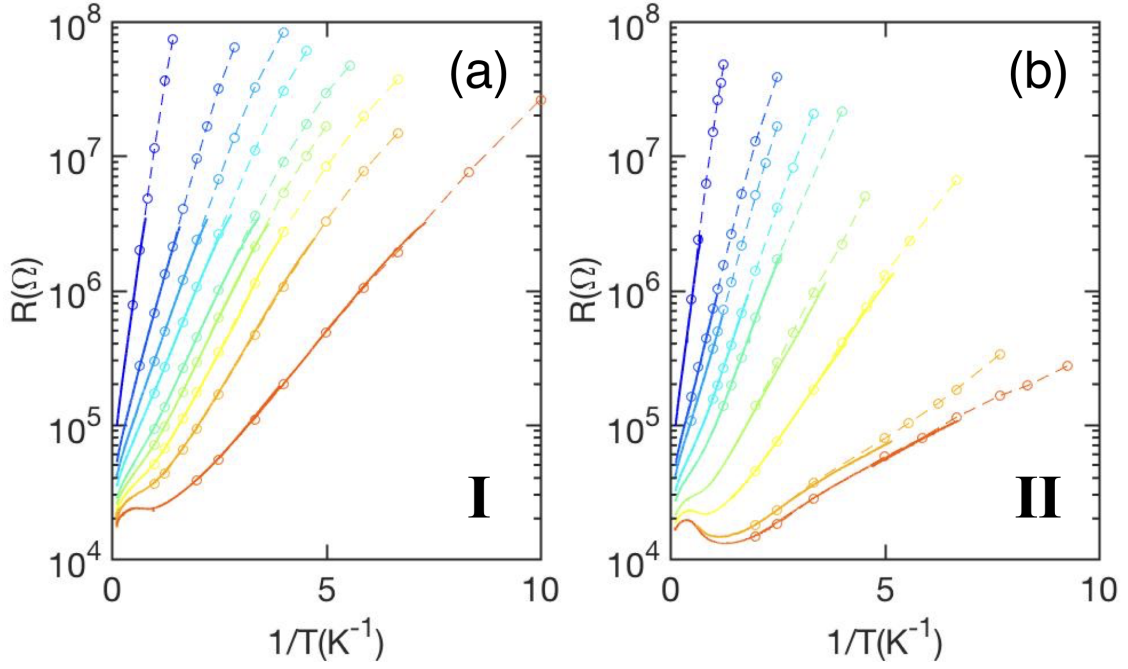


Figure 5.3.3: Resistance versus $1/T$ in two experiments. The solid curves are AC measurements and the dashed lines are DC points.

The data show δT_0 increases with Bi thickness.

Referring back to the Eq. 5.2.3, E_C is expected to be insensitive to frustration. Therefore, δT_0 is an indicator of the Josephson coupling energy, which is proportional to the normal state conductance and superconducting gap. Both of them increase with Bi thickness, so it is not surprising to see δT_0 is larger for thicker films.

5.3.2 R(T) on Reference

The reference films are deposited on flat glass substrates. It represents the maximum thickness on the AAO substrate, and thus the T_C on the reference indicates the maximum pairing amplitude on AAO. $R(T)$ curves of reference films are shown in Fig.5.3.5. One thing to note is that even the thinnest film is superconducting, whereas the film with the same thickness on AAO is deep in the insulating state. The universal critical resistance for SIT on a flat substrate is

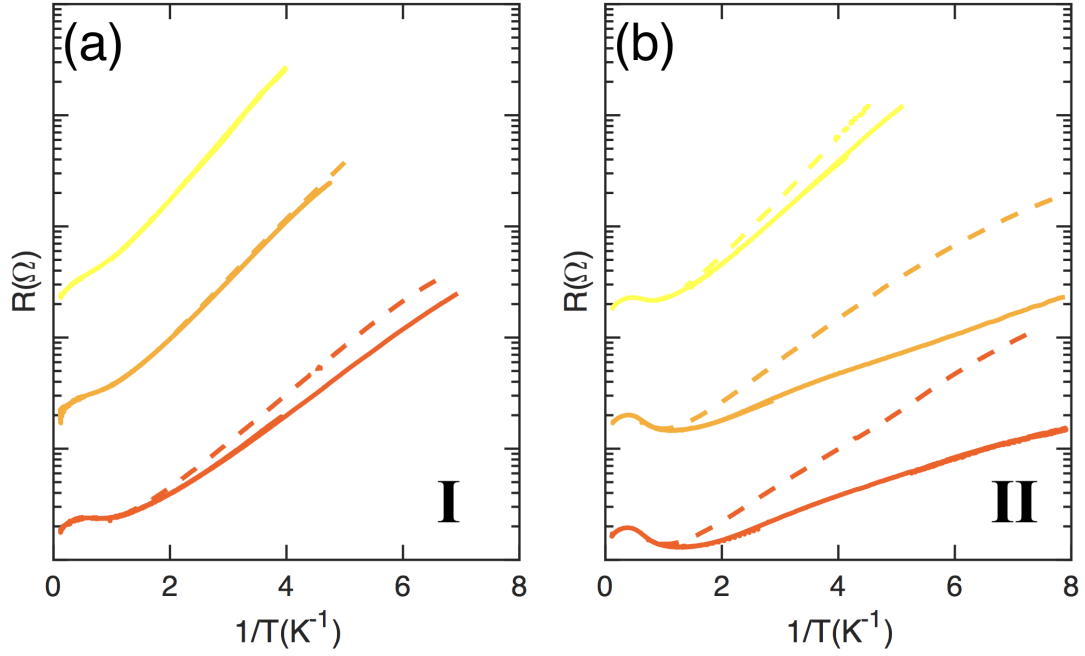


Figure 5.3.4: The development of δT_0 on the last three films in two experiments. The solid lines correspond to $f = 0$, and dashed lines represent $f = 1/2$. Bi thickness increases from top to bottom. The resistances of the last two films are shifted by a factor of 10 and 100 to separate the curves.

$R_C \sim R_Q = h/4e^2 = 6.45 \text{ k}\Omega$ [16]. The normal resistances in our experiments are below $3 \text{ k}\Omega$, so it is not surprising that the reference films are on the superconducting side. With increasing thickness, the normal resistance drops, so does the superconducting critical temperature T_C . Here we define T_C as the temperature where the resistance drops to 10%. As we will see later, this definition makes it easier to calculate T_C with the introduction of Gd.

5.3.3 Fermion Insulator to Boson Insulator Crossover

With the information mentioned above, we can calculate T_C and T_0 at specific thickness. The major results are listed in Table.5.1. There are ten films in total in each experiment. The first film barely conducts so we did not calculate T_0 . Those are all measured on Square 1. Square 2 has very similar results. For example, for f10 in

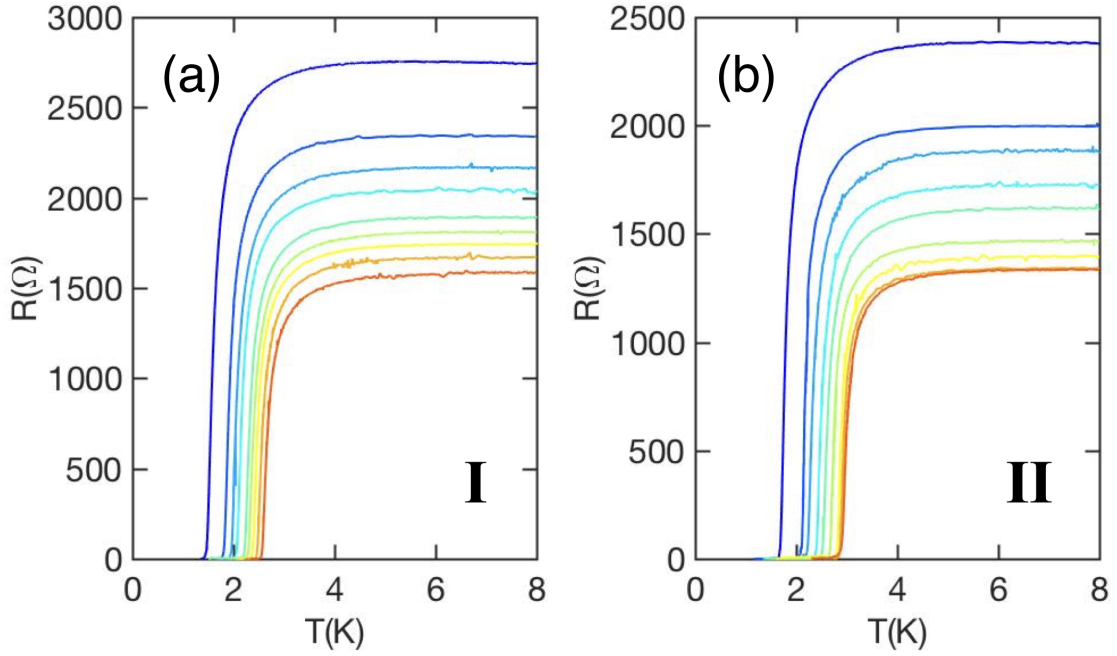


Figure 5.3.5: Resistance versus temperature for reference films in two experiments. The color maps for different Bi thicknesses are the same as in Fig. 5.3.2 and 5.3.3.

Experiment I, $T_C(S1) = 2.59$ K, $T_C(S2) = 2.61$ K, $T_0(S1) = 0.86$ K, $T_0(S1) = 0.66$ K. That indicates our films are quite uniform.

For very thin films, with small gap and large charging energy, $\Delta/E_C < 2$, it is more energetically favorable for Cooper pairs to break and tunnel through quasi-particle channel. On the contrary, with large Δ , it is unfavorable to break the binding energy. Therefore, Cooper pairs dominate the transport. There is a kink in T_0 as shown in Fig.5.3.6. It is observed in different experiments in our lab[17]. The corresponding thickness coincides with the beginning of $h/2e$ oscillation and positive magnetoresistance. It is reasonable to believe this kink represents the crossover from Fermion insulator(FI) to Boson insulator(BI). On the BI side, T_0 decreases linearly with thickness. We can apply linear fit and use the intercept with x axis as the critical thickness of SIT. In our case, $d^{SIT} = 1.22$ nm. That agrees with the previous experiments[18]. Applying the linear relationship between conductance and thick-

Table 5.1: List of major parameters with increasing Bi thickness in two experiments. Sb underlayers are ~ 1 nm in both experiments.

Experiment I					
		Reference		AAO	
Films	Thickness($\text{\AA}$)	$R_N(k\Omega)$	$T_C(K)$	$R_N(k\Omega)$	$T_0(K)$
f01	5.92	NA	NA	1355	NA
f02	7.18	2.74	1.50	99.78	4.56
f03	7.82	2.34	1.84	52.76	2.52
f04	8.17	2.16	1.99	41.44	2.03
f05	8.47	2.04	2.09	36.20	1.74
f06	8.90	1.90	2.25	28..34	1.50
f07	9.12	1.81	2.32	25.56	1.36
f08	9.35	1.75	2.41	23.02	1.23
f09	9.58	1.67	2.49	20.88	1.1
f10	9.88	1.59	2.59	18.50	0.86
Experiment II					
		Reference		AAO	
Films	Thickness($\text{\AA}$)	$R_N(k\Omega)$	$T_C(K)$	$R_N(k\Omega)$	$T_0(K)$
f01	5.61	4.31	0.53	5787	NA
f02	7.62	2.37	1.75	97.65	5.46
f03	8.48	1.99	2.13	50.28	2.94
f04	8.89	1.88	2.25	41.82	2.56
f05	9.42	1.73	2.43	32.23	2.16
f06	9.87	1.62	2.55	26.99	2.1
f07	10.53	1.47	2.70	21.21	1.39
f08	10.98	1.39	2.83	18.62	1.06
f09	11.55	1.34	2.88	17.06	0.56
f10	11.80	1.33	2.92	16.70	0.39

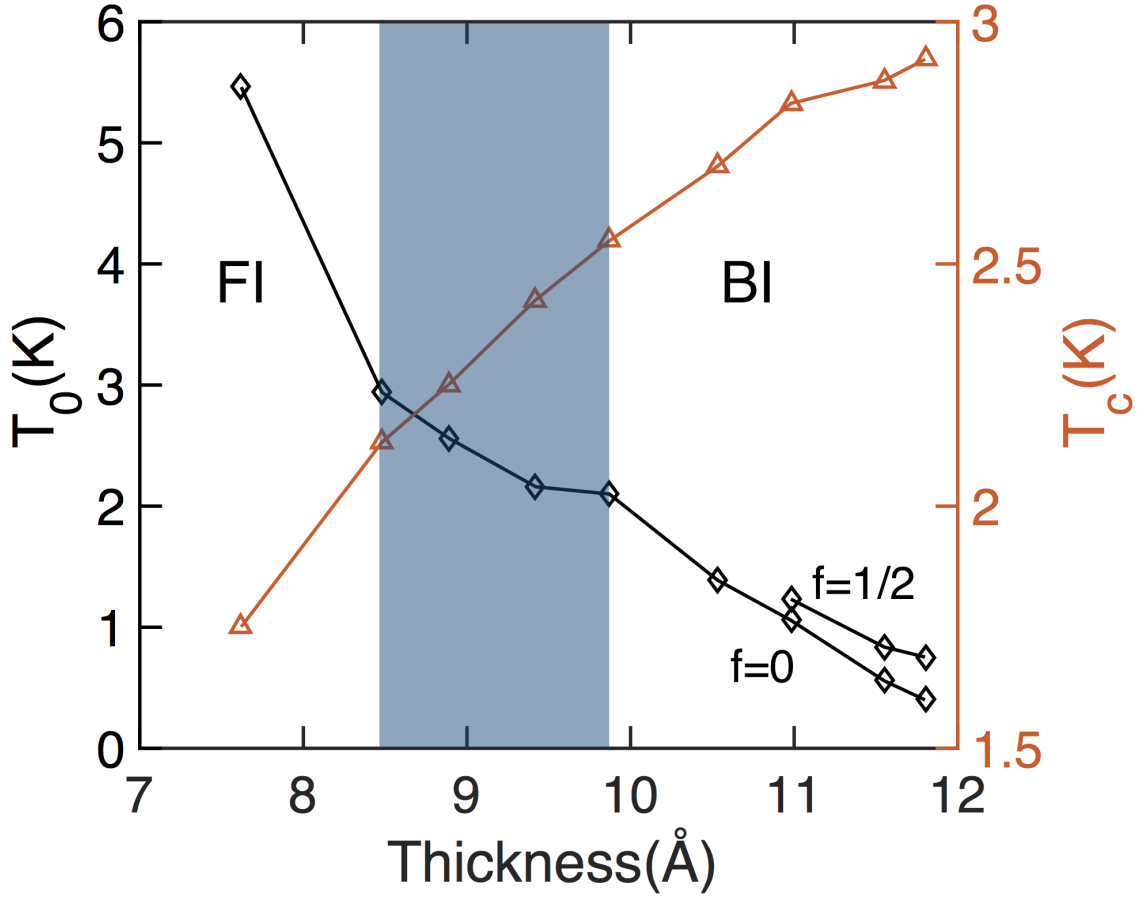


Figure 5.3.6: The crossover from Fermion insulator to Boson insulator. The data points are from Experiment II since it has a larger range of T_0 . The black line is T_0 on AAO and the solid line is T_c on reference. The shaded area is the crossover region. Notice the kink on the T_0 curve.

ness in Fig.5.3.1, we get the critical conductance at SIT. $G_C^{SIT} = 6.78 \times 10^{-5} \Omega^{-1}$. The corresponding resistance is simply inverse of that. $R_C = 14.7 \text{ k}\Omega$. Our system can be modeled as hexagonal arrays of superconducting islands [19, 20]. The critical resistance should be one third of that. Therefore, $R_C^{SIT} = 4.9 \text{ k}\Omega$. This value agrees well with the universal quantum resistance $R_Q = 6.45 \text{ k}\Omega$.

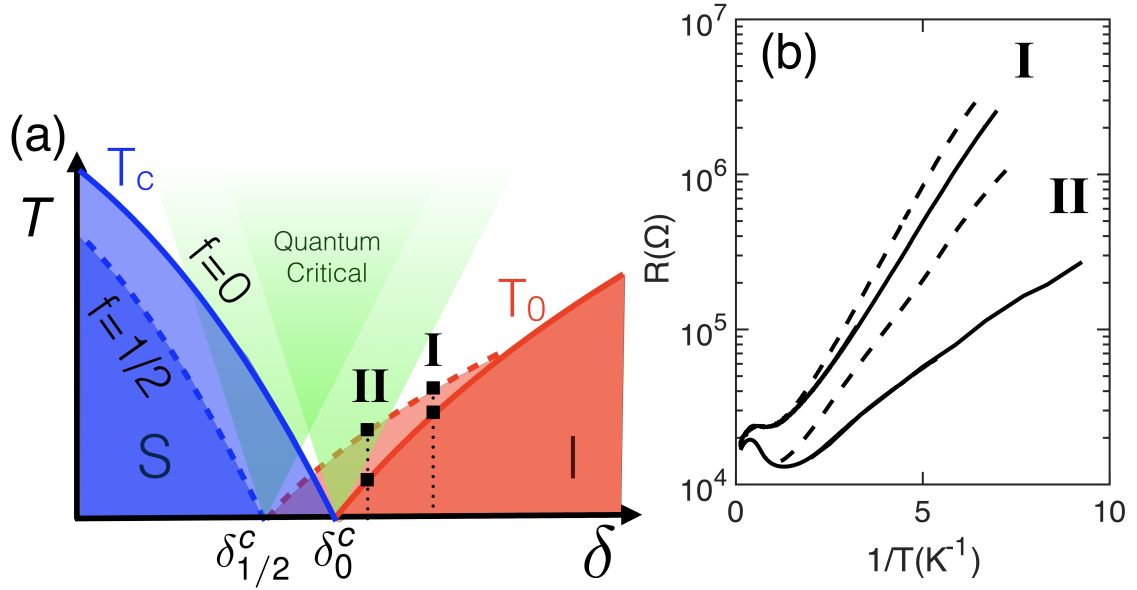


Figure 5.3.7: (a) Phase diagram. With fine tuning of disorder (thickness), the system undergoes superconductor (blue region) to insulator (red region) transition. The solid and dashed lines represent phase boundaries for $f = 0$ and $f = 1/2$, respectively. Experiment I and II have different distances to the quantum critical point (see the black squares). (b) Resistance versus temperature in semi-log plot for the different starting points before deposition of Gd. The solid and dashed lines correspond to $f = 0$ and $f = 1/2$.

5.3.4 Phase Diagram

In a quantum rotor model[21], the transition is tuned by varying a control parameter $\delta = \sqrt{E_C/E_J}$. E_C represents the average Coulomb energy cost of transferring a Cooper pair from one island to another. E_J represents the average coupling between neighboring regions of localized Cooper pairs. δ is varied by film thickness in our experiments. The critical values δ^c are different at varying commensurate f values[22]. Previous work[23] indicated that the critical values of the tuning parameters for the SIT followed $\delta_0^c > \delta_{1/2}^c$. Therefore, $f = 1/2$ undergoes superconductor insulator phase transition at higher thickness. Fig. 5.3.7 shows the typical phase diagrams for SIT. The energy scale of the system on the insulating side is T_0 , while it is T_C on the superconducting side. They both vanish at the transition. The last Bi film before Gd doping in Experiment II is closer to the quantum critical point than

Experiment I for the following reasons (see Table. 5.1 for part of the data).

- $Thickness(I) < Thickness(II)$. The transition is tuned by increasing Bi thickness.
- $T_0(I) > T_0(II)$ for both $f = 0$ and $f = 1/2$.
- $\delta T_0(I) < \delta T_0(II)$. $\delta T_0(I) = 0.12$ K. $\delta T_0(II) = 0.36$ K. That is a direct evidence that $E_J(I)$ is lower than $E_J(II)$.
- $R_N(I) > R_N(II)$, indicating higher coupling in Experiment II.
- $T_C(I) < T_C(II)$, indicating more robust Cooper pair binding in Experiment II.
- Larger reentrance in Experiment II.
- Higher magnetoresistance in Experiment II. We will discuss the magnetoresistance in the next chapter. Positive MR is a signature of CPI phase. Higher MR indicates film closer to the QCP.

Fig. 5.3.7(b) directly shows the relationship between four states in our study. In the next section, we will see how does the magnetic impurity doping changes those curves.

5.4 Magnetic Impurity Doping

5.4.1 T_C Shifts on Reference Films

We made eight successive dopings in total for both experiments. With increasing Gd concentrations, pair breaking effect becomes more significant. Fig. 5.4.1 shows the $R(T)$ curves shift with successive Gd doping. In general they move to the left as expected. However, in all the experiments we performed there is a kink on the curves. The kink also shows up in 2-point measurements. For each measuring

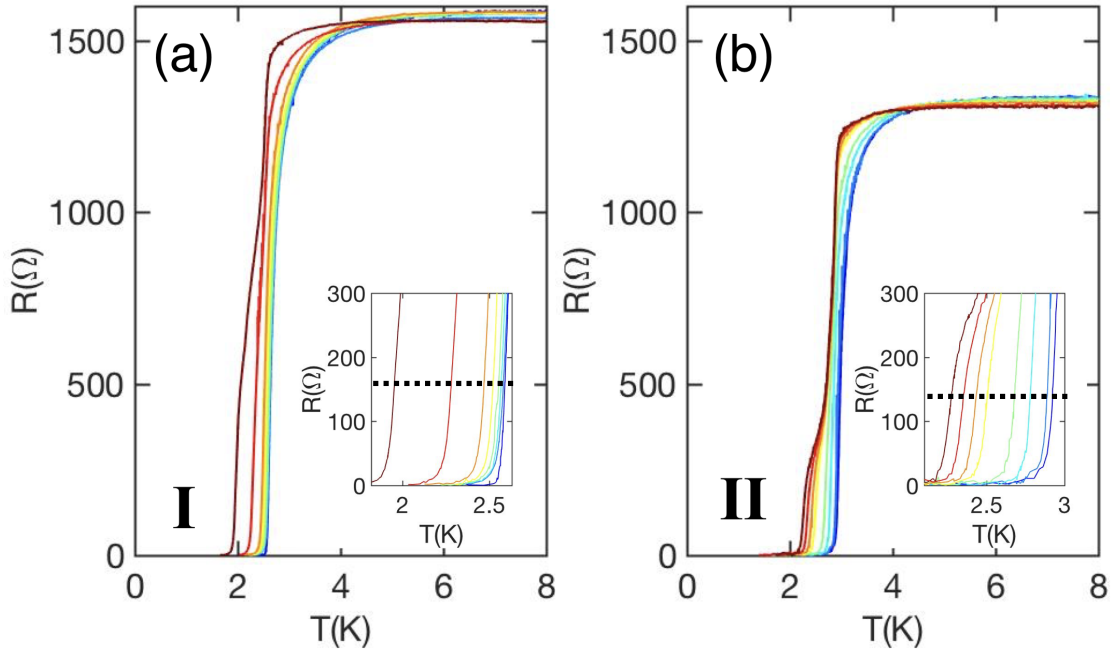


Figure 5.4.1: The effect of successive magnetic impurity doping on reference films. The blueish curves represent lower doping while the reddish curves represent high doping concentrations. Notice the kinks on both of the experiments. Inset: Enlarged view of the lower part of the curves. The dashed lines represent 10% resistance criterion that is used to calculate T_C .

configuration, the relative size of the upper and lower portions are different. If we look closer at each curve, it shifts to the left as expected for the first 2~3 dopings while kink appears at higher doping concentrations. The origin of the kinks are still not fully understood. We proposed that it might be because of shadowing effect. Unlike the mask on AAO, there is a ~ 0.5 mm gap between the glass substrate and the mask. Also, the Gd source is positioned directly below AAO, resulting in a small angle with respect to the glass substrate. Therefore, there are some shadowing areas that are not directly faced by Gd source. Those areas are not affected by the doping and thus contribute to the first drop of resistance. This idea is supported in another experiment where the doping concentration is high enough to drive the film to normal state while the kink still exists (see Fig.5.4.2). However, it does not explain why the kink does not show up at the first 2~3 dopings. More experiments

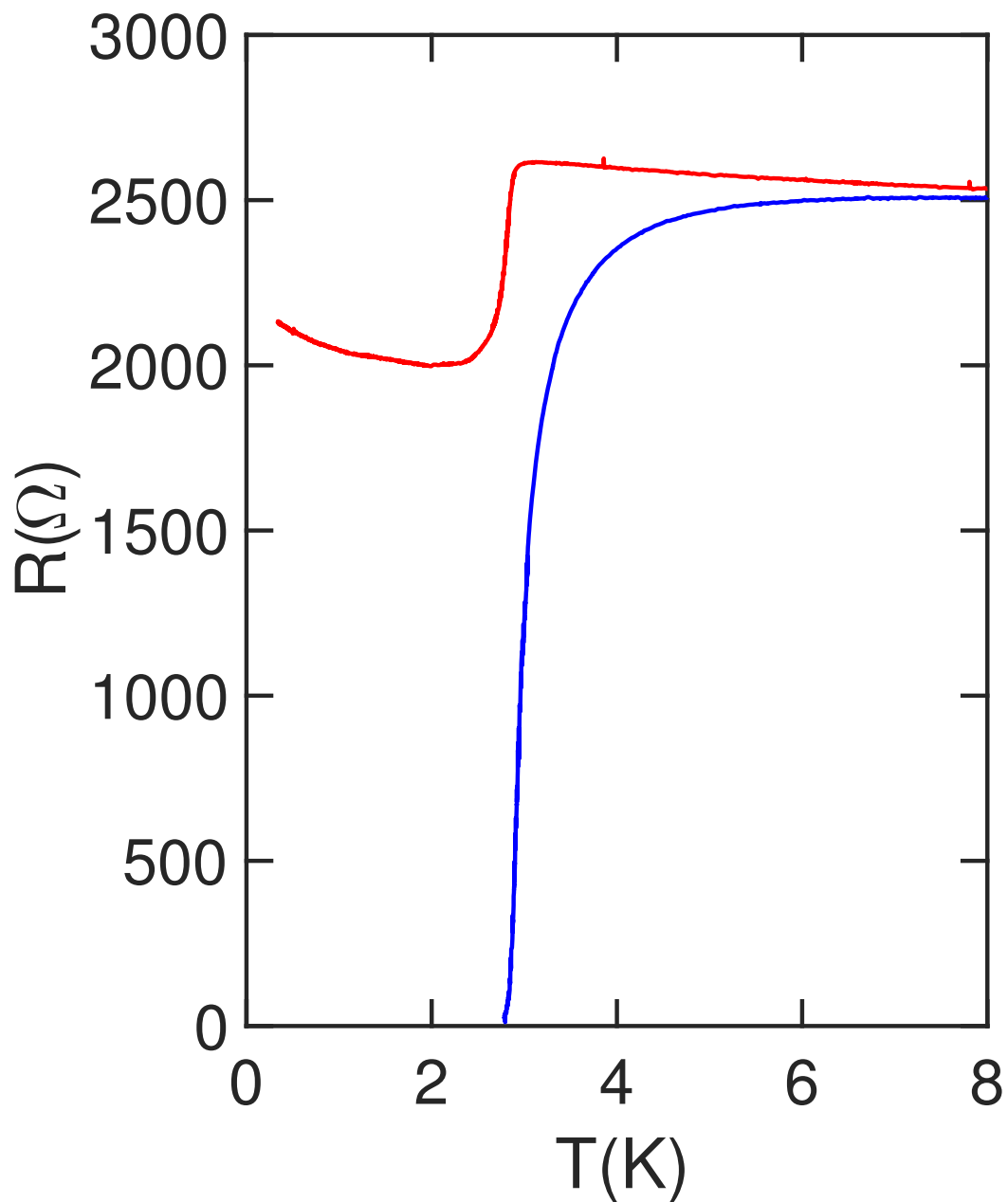


Figure 5.4.2: The kink appears in another experiment (Dec2016) where the doping concentration is so high that the film becomes normal. The blue curve is the original $R(T)$ for the Bi film on glass substrate. The red curve represents $R(T)$ after doping.

with a separate mask held directly on the glass substrate are needed to verify that scenario.

To avoid the confusion caused by the kink, we used 10% resistance criterion

that is well below the kink to find the T_C (see Fig. 5.4.1 inset). For low pair breaking strength, T_C should drop linearly with magnetic impurity concentration [24, 14]. Fig. 5.4.3 shows the relationship between T_C and Gd concentration in Experiment II. The Gd amount is estimated using the calibrated evaporation rate and the accumulated evaporation time. T_C on the reference film drops $\sim 25\%$ in total. The doping in Experiment I is more complicated since we applied different amount of current for evaporation. However, since it is linearly related to T_C , in the following, we use the relative T_c shift

$$\alpha_{Gd} = 1 - T_c(x_{Gd})/T_c(0) \quad (5.4.1)$$

to represent doping amount.

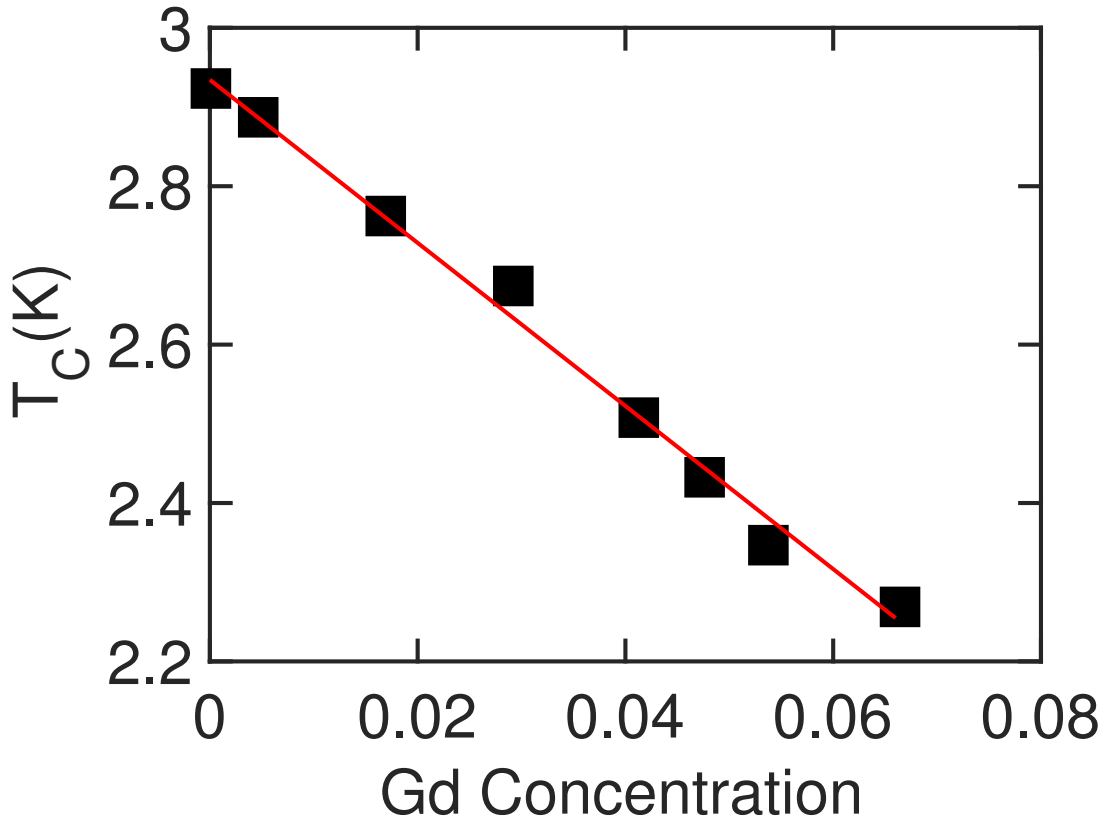


Figure 5.4.3: T_C drops with increasing Gd concentration in Experiment II. The red line is the linear fit $y = -10.3x + 2.9$.

5.4.2 R(T) on AAO with Doping

5.4.2.1 Effects on Reentrance Behavior

As mentioned above, reentrance results from the onset of superconductivity. The first direct effect of Gd doping on AAO is the quenching of reentrance behavior. Fig.5.4.4(a) shows the $R(T)$ curves with increasing doping. We can see the size of the reentrance decreases with increasing doping concentration. To see it more explicitly, we need to get rid of the quantum corrections to the conductance.

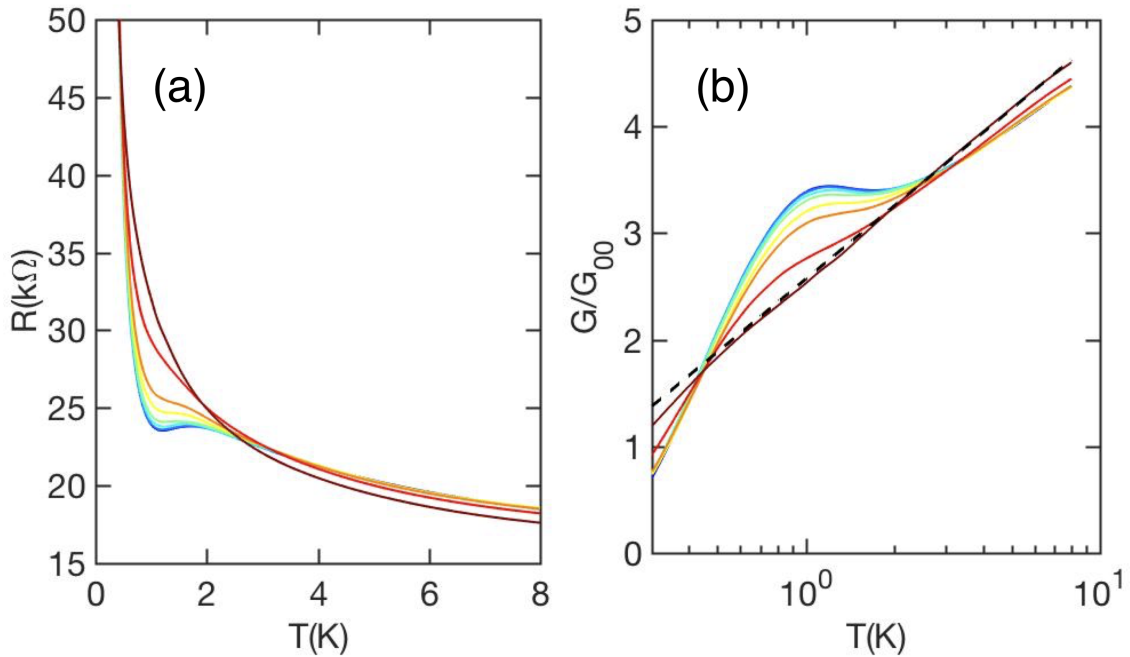


Figure 5.4.4: Weak localization correction for Experiment I. (a) $R(T)$ at high temperatures. Reddish curves represent higher magnetic impurity doping. (b) G versus $\ln(T)$. The conductance is normalized by the quantum conductance $G_{00} = 1/81k\Omega$. The black dashed line, $G/G_{00} = 0.99 \ln(13.4 \times T)$, is a representative fit to the last film.

In the regime above the pairing temperature ($T > 3$ K), the electron waves are in extended state and weak localization is prominent to determine the temperature dependence of the transport. It is caused by quantum interference from different trajectories and they interfere constructively along the loop. Therefore, the proba-

bility of finding an electron staying at the origin is larger than the classical result. The electrons are weakly localized at the original position. Quantitatively, it depends logarithmically on the temperature[25, 26],

$$\Delta G = \alpha G_{00} \ln(T) \quad (5.4.2)$$

where $\alpha \sim 1$. With lower temperature, the constructive interference becomes stronger, resulting in lower conductance. The correction from the weak localization effect is shown in Fig. 5.4.4(b). The high temperature part fits well with Eq. 5.4.2 with the slope approximately equal to 1. The deviation at low temperature comes from the pairing of electrons as well as strong localization effect which depends exponentially on the temperature.

We can separate the pairing effect from weak localization as shown in Fig. 5.4.5. The measured resistance is divided by R_N from the weak localization fit. It remains constant until the onset of superconductivity. The size of the reentrance decreases with Gd doping. For the last film, the strong localization effect exceeds the pairing effect and we only see a kink rather than a dip on the curve. The critical pairing temperature is usually defined as a constant fractional reduction of the resistance. It is hard to define here, especially for the last film. The second derivative of the curve is also too noisy to find the transition point. However, we can observe qualitatively that the onset of superconductivity is moving to lower temperature with successive deposition of Gd. It agrees with our expectation that magnetic impurity reduces the pairing temperature.

Following the same procedure, we can calculate the normalized $R(T)$ curves for Experiment II (see Fig. 5.4.6). In contrast to Experiment I, the size of reentrance is very large and we can see the dip even at the highest doping concentration. In this case, we are able to draw a line, for example 95% of the normal resistance, and estimate the pairing temperature on AAO based on that. As shown in Fig. 5.4.7,

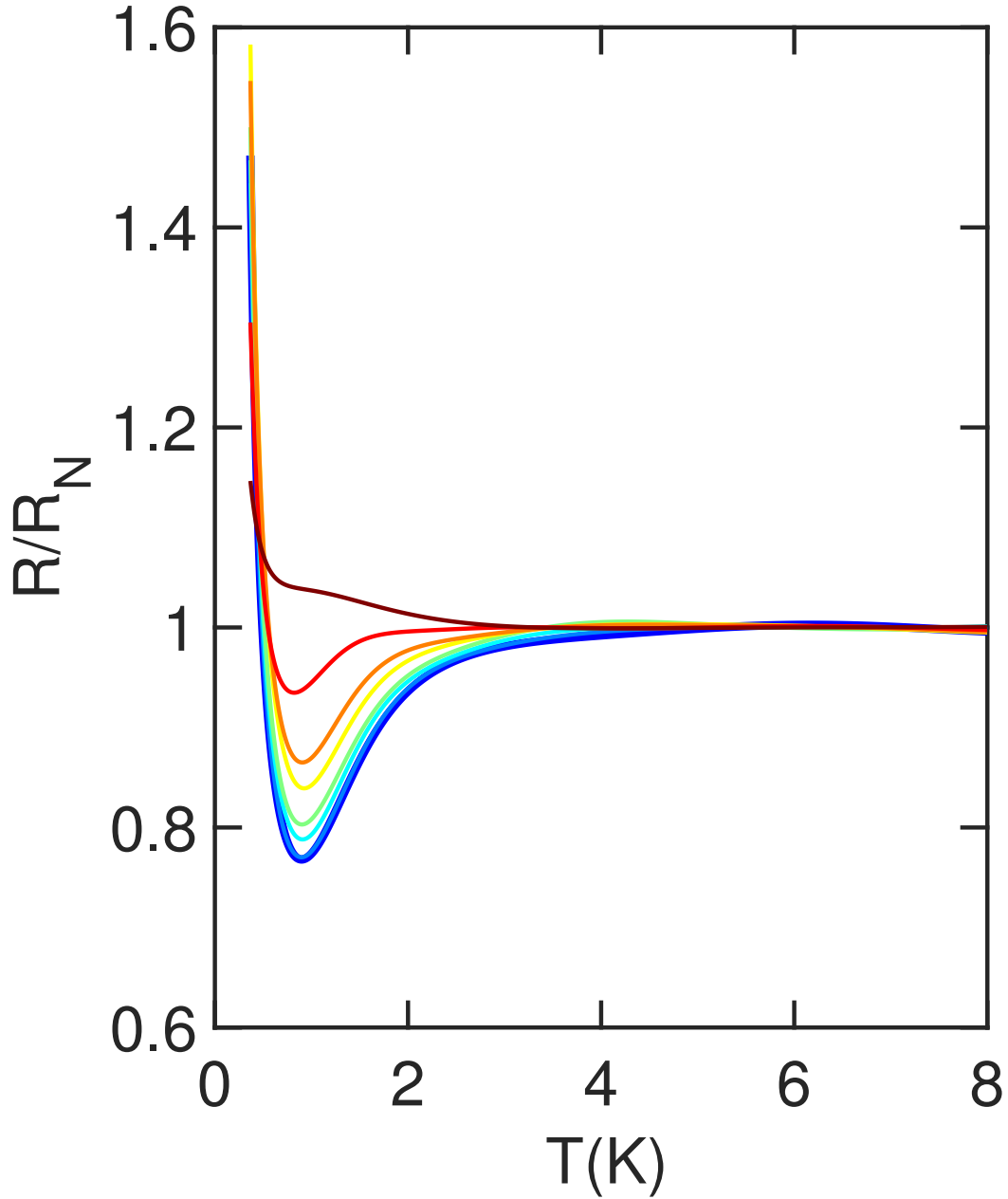


Figure 5.4.5: Normalized resistance at high temperature. R_N is the normal state resistance following weak localization temperature dependence.

it still shows linear relationship with Gd concentration. However, it drops much faster than T_C on reference films. As a result, the deviation between AAO and the Reference gets larger at lower T_C . There is also some other evidence that T_C on the reference does not represent the actual pairing temperature on AAO when

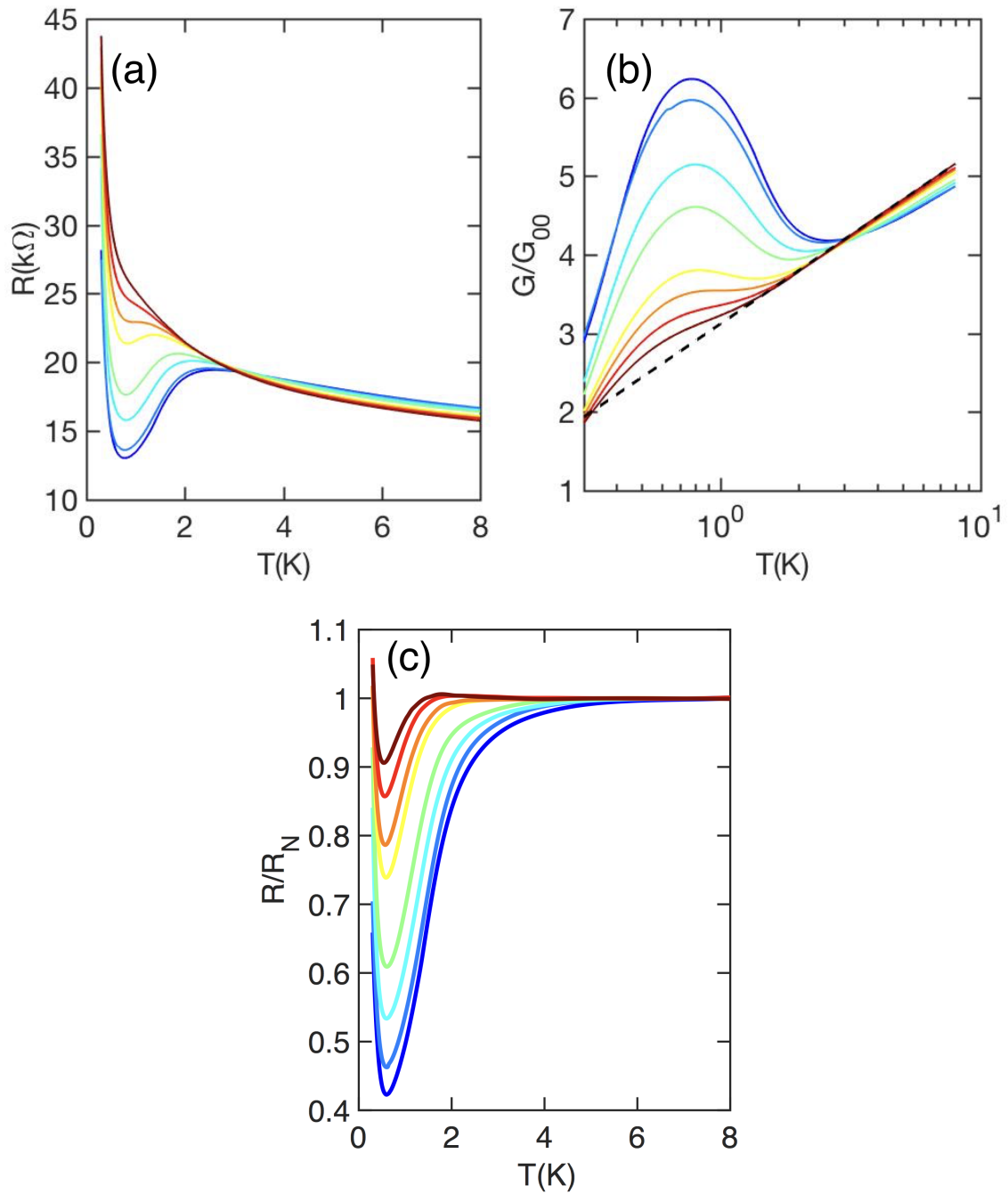


Figure 5.4.6: Weak localization correction for Experiment II following the same procedure. (a) $R(T)$ curves at high temperature with increasing Gd doping. (b) G versus $\ln(T)$. The black dashed line is a linear fit for the last film. $G/G_{00} = 0.99 \ln(22.7 \times T)$. (c) Normalized $R(T)$ curves. Resistance is renormalized by weak localization fit.

T_C is small. In the previous discussion, we mentioned that $\delta T_0 \propto E_J \propto G\Delta$. In BCS limit, $\Delta \propto T_C$. Thus, $T_C \propto \delta T_0/G$. For the last films in Experiment I and II, using the data from Table. 5.1, $T_C^{AAO}(\text{I})/T_C^{AAO}(\text{II}) = 0.37$, while the measured T_C on Reference is $T_C^{Ref}(\text{I})/T_C^{Ref}(\text{II}) = 0.88$.

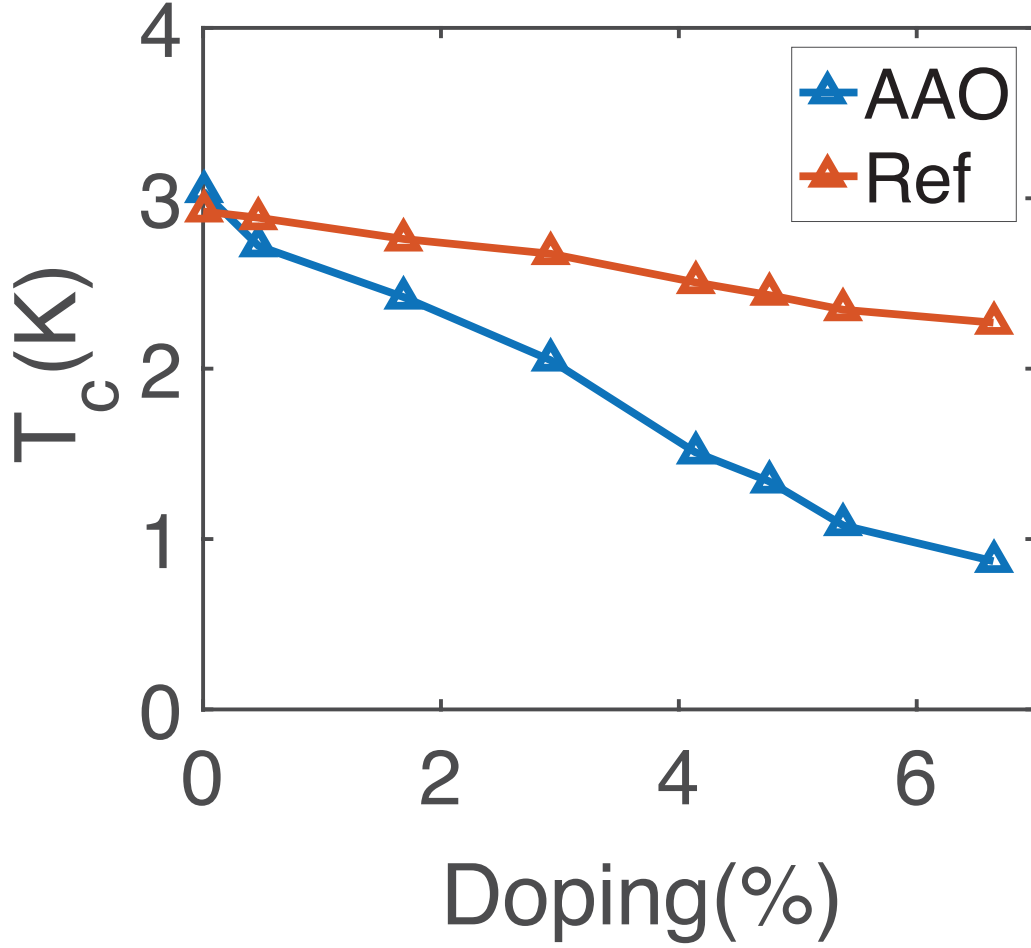


Figure 5.4.7: T_C calculated from AAO and Reference for Experiment II. The critical temperature on AAO is chosen at 5% drop of resistance compared with the normal state value. This choice enables us to match T_C on AAO with Reference for the first film.

We attribute the enhanced suppression of superconductivity to finite size effect of the superconducting nano-sized island as well as weak coupling proximity effect at the superconductor and normal metal interference. To estimate the size of the islands, we can consider the structure as twelve closely packed dots around each

pore. The diameter of each dot is $\sim \frac{\pi D_{int}}{12} = 26$ nm, which is comparable with the superconductivity coherent length $\xi \sim 10$ nm. For the proximity effect, the nearest superconducting islands are connected by normal metal or weak superconductors. Superconductivity is induced at the expense of reducing the average T_C . Both of them are equally important in determining the pairing temperature on AAO [27].

5.4.2.2 Resistance at Low Temperature Limit

The effects of Gd doping on the activated transport in Experiments I and II are displayed in Fig. 5.4.8. The Arrhenius plots of the $R(T)$ show that the activated form persists through the doping range. For Experiment I, which is farther from the transition, the resistance in the low temperature region monotonically goes down with doping for both $f = 0$ and $f = 1/2$. By contrast, for the film closer to the transition, the change is non-monotonic. At $f = 0$, the resistance first increases, and then it drops. For $f = 1/2$, it seems flat at the beginning, then it also drops with increasing doping. Fig. 5.4.9 provides a clearer view of the resistance changes at specific temperature $T = 150$ mK. In both experiments, $R(f = 1/2)$ decreases faster than $R(f = 0)$, and it drops below $R(f = 0)$ in the last few films. Since T_0 is the dominating factor to determine the resistance in the low temperature region, as we will see later, this plot is very similar to T_0 changes with doping.

Fig.5.4.10 shows the isothermal field sweep measurements for both experiments. The temperature is fixed at 300 mK while ramping the field. In Experiment I, both $R(f = 0)$ and $R(f = 1/2)$ decrease with doping while in Experiment II, $R(f = 0)$ increases at the beginning. It is consistent with the observation at lower temperature (Fig. 5.4.9). Also, the isothermal curves directly show the disappearance of Little-Parks oscillations, indicating the superconductivity is quenched by magnetic impurity. One thing to note is that in Experiment I, the last three curves drop a lot even though the oscillation is weak. That indicates the quasi-particle tun-

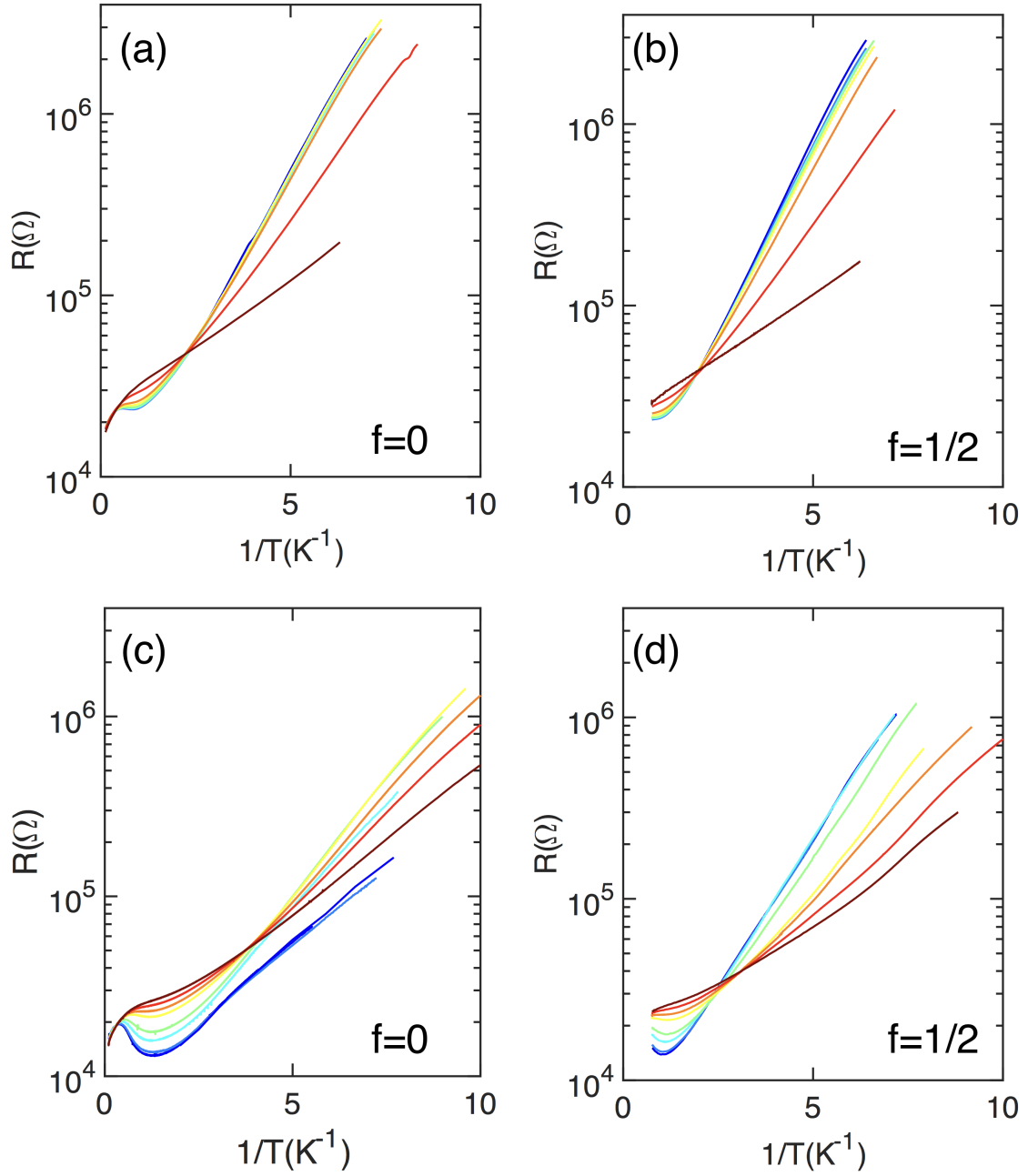


Figure 5.4.8: Resistance versus $1/T$ for (a),(b) Experiment I and (c),(d) Experiment II. The left figures are measured at $f=0$, and the right figures are measured at $f=1/2$.

neling still depends on the superconductivity ordering parameter. It is reasonable since the electrons need to overcome the superconducting gap to be broken into single ones and thus the energy barrier for quasi-particle tunneling is $\Delta + E_C/4$ [2].

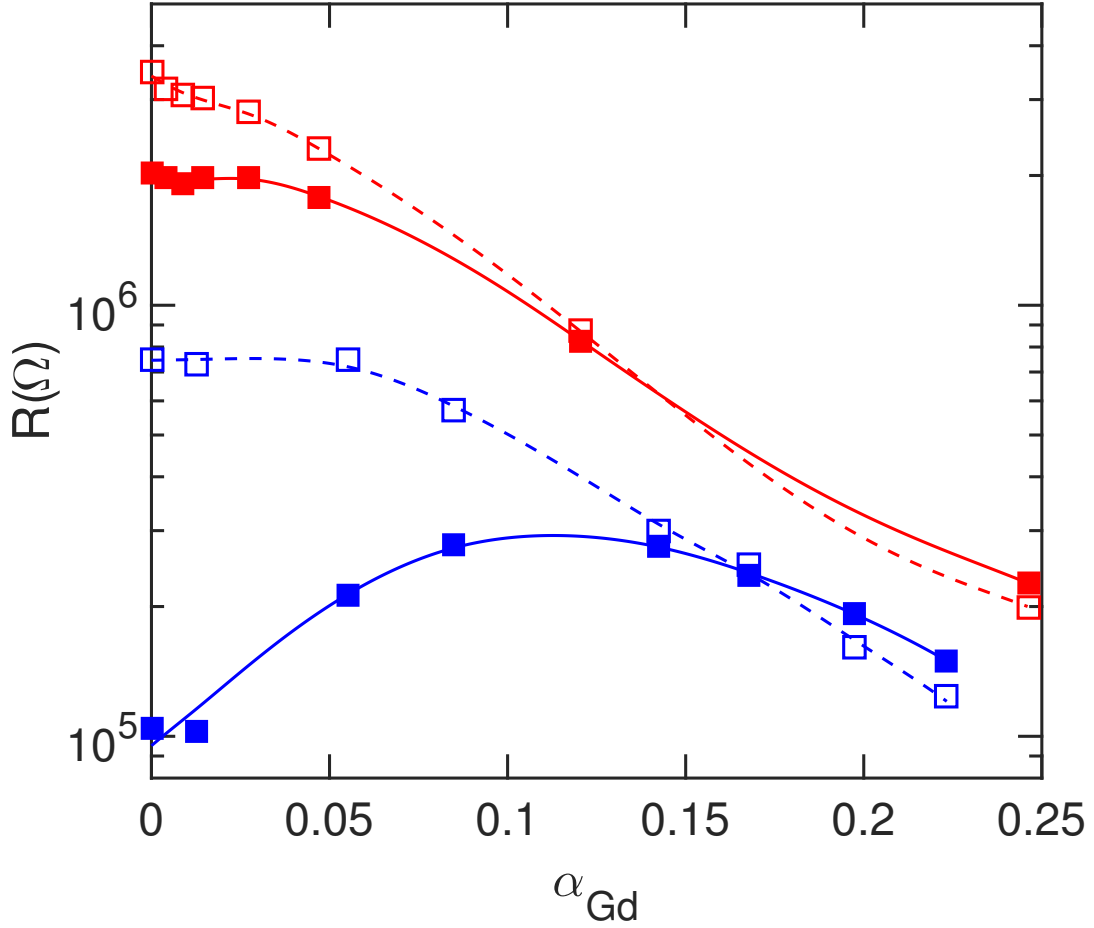


Figure 5.4.9: $R(T = 150mK)$ changes with Gd Doping. x-axis is the relative T_C shifts representing doping concentrations. The red points are from Experiment I, and blue points are from Experiment II. The filled squares represent $f = 0$ and open squares correspond to $f = 1/2$. The lines are guides to the eye.

5.4.3 T_0 Changes with Doping

We can calculate the activation energies from the linear fit to the low temperature regions in Fig. 5.4.8. We choose the data points below 300 mK that are far away from the pairing temperature. The results are shown in Fig. 5.4.11. Similar to the change of resistance, the evolution of T_0 at low doping depends on distance from the SIT. T_0 decreases or remains nearly constant and then decreases with Gd doping in the three films farthest from the SIT. By contrast, the film closest

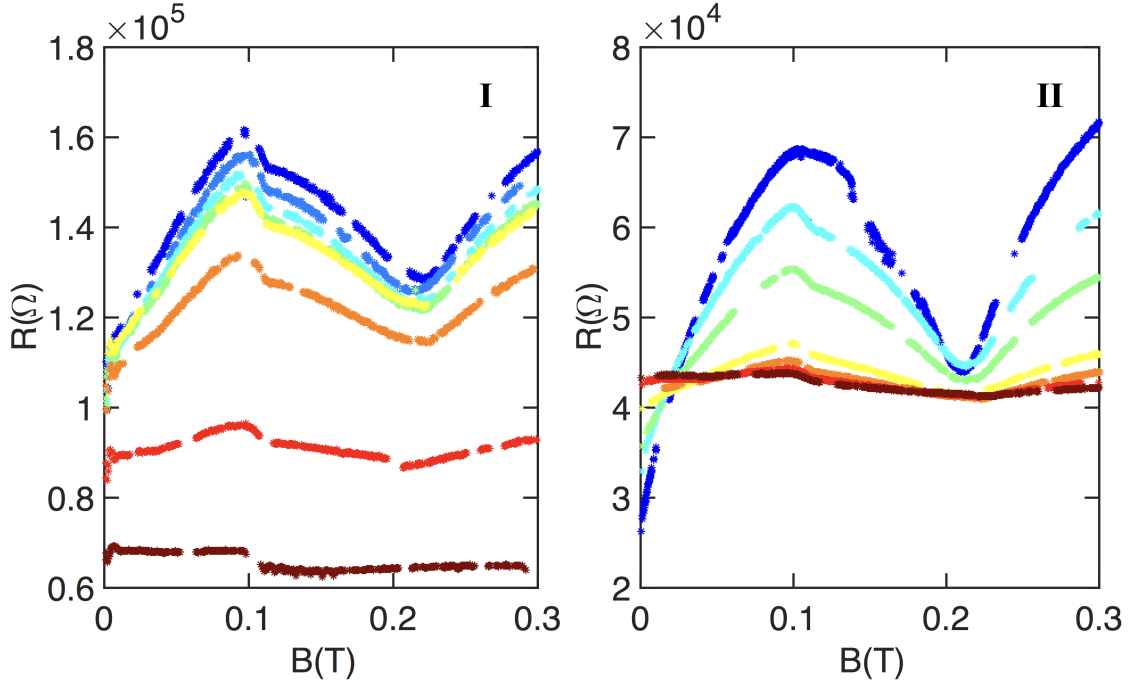


Figure 5.4.10: Disappearing of $h/2e$ oscillation at 300 mK. The matching field is $H_M = 0.215$ T.

to the SIT exhibits a maximum in T_0 . At the higher doping levels, T_0 becomes independent of frustration and decreases with doping. The difference between the activation energies at the two frustrations, $\delta T_0 = T_0^{f=1/2} - T_0^{f=0}$, is larger for the film closer to the SIT. For both films, δT_0 approaches zero at higher dopings.

Considering $T_0 = E_C - E_J$, where E_J decreases with pair breaking effect, our observation, especially in Exp I, shows the effective charging energy E_C decreases with shrinking Δ . This result is unexpected because in terms of the coulomb blockade, single junction bare charging energy can be estimated as $E_{C0} = q^2/\epsilon d$, where $q = 2e$ and d is the average distance between two adjacent superconducting islands. Magnetic impurity might shrink the islands, making E_{C0} increase or at least leave it unchanged. Our results show the simple model with pure Cooper pair hopping is not necessarily the case here. The effective charging energy has a nontrivial dependence on the superconducting gap.

The disappearance of T_0 's frustration dependence at higher doping levels sig-

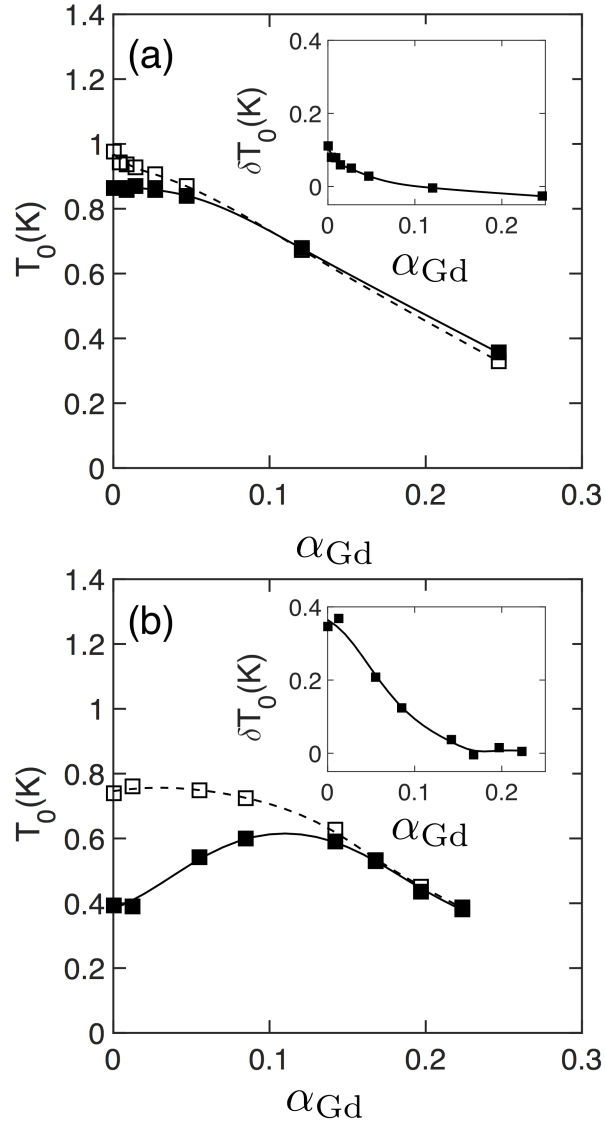


Figure 5.4.11: T_0 changes with Gd Doping. Inset: $\delta T_0 = T_0^{f=1/2} - T_0^{f=0}$ decreases with doping concentration.

nals a crossover from transport that involved Cooper pairs to quasiparticle dominated transport. The crossover is smooth: the $R(T)$ (Fig. 5.4.8) maintain an activated form and T_0 evolves without any clear discontinuities in its value or slope. The continued decrease of T_0 with Gd doping suggests that the quasi-particle transport depends directly on Δ . This dependence can arise if the transport is quasi-particle tunneling between superconducting dots as proposed to explain negative magneto-resistance in granular Pb [28] and Indium Oxide films [29]. Within this model, the inferred values of 2Δ at the crossover, presuming $T_0 = 2\Delta$, are 0.83 K and 0.6 K for films I and II, respectively. Both of these values fall below the transition temperatures of their associated reference films, which makes them reasonable.

For both experiments, the difference of T_0 at $f = 0$ and $f = 1/2$, which is proportional to Josephson coupling energy monotonically decreases with Gd concentration and drops to zero (see Fig. 5.4.11 inserts). This further assures us the superconducting gap is shrunk by Gd doping. δT_0 is larger in Experiment II, indicating higher initial Δ and E_J . Something interesting to note is, in Experiment II near the magnetic impurity induced peak, E_J remains finite, but it goes to zero shortly after that. This shows Cooper pairs still exist at the peak, while quasi-particles begin to dominate the transport beyond the peak where the pair breaking effect is too strong.

With low doping concentration, we have observed positive MR and MR oscillation in both experiments. This indicates Cooper pairs are the dominating charge carriers [17]. Combining the results from the two experiments, we found the E_J behaves as we expected, while E_C cannot be simply interpreted as a capacitance obstructing Cooper pair hopping. It depends on the superconducting gap and decreases when the gap is shrinking. The resulting behavior of T_0 depends on how far away the film is from the QCP, or microscopically, it depends on the relative size of E_C and E_J . As we are approaching the transition from the insulating side,

E_J increases relative to E_C and a magnetic impurity induced peak emerges. This behavior resembles the emergence of the giant MR peak from negative MR when getting closer to the transition, although the size here is smaller than the MR. The comparison of those two gives a lot of hints for the nature of widely debated MR peak.

5.5 Other Experiments

In addition to the two experiments discussed above, there are some other experimental runs we made to explore the effect of magnetic impurity doping. Initially, we tried to use Nichrome wire instead of Gd as Parker et al used for their a-Pb films [14]. It is easier to prepare and more controllable. Unfortunately, it does not seem to effectively reduce T_C on our quench condensed Bi films. Gd is chosen based on the work done by our previous lab members.

Fig. 5.5.1 shows one of the other experiments with Gd doping. We still observed a kink on $R(T)$ curves of reference films. Using the same 10% criterion, T_C drops linearly with Gd amount. However, the film on AAO is inhomogeneous. Part of the films superconducts while the resistance across the film is still finite. We suspected the sample is misaligned with the source, making part of the film thinner than the nominal deposited thickness. That is why we observed a very large dip before it reenters insulating regime in Fig. 5.5.1(c). The insulating behavior is contributed by the region with lower thickness as the thicker area is already superconducting. It still shows activated dependence on temperature. The activation energies in first two oscillations are shown in Fig. 5.5.1(e). Both T_0 and δT_0 decreases with increasing doping concentration.

The inhomogeneity makes this experiment data less reliable. The nominal d_c^{SIT} and R_C^{SIT} is far off the regular values. Nevertheless, the activated transport behav-

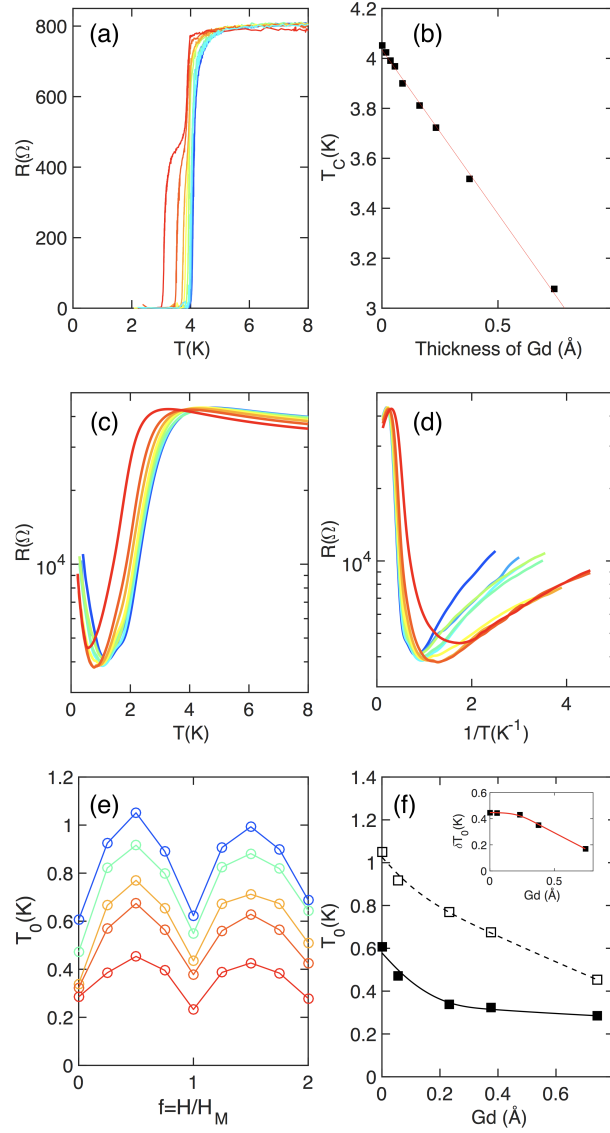


Figure 5.5.1: Data from Jan2017 experiment. (a) $R(T)$ with increasing doping on reference films. Reddish curves represent higher doping. (b) T_C decreases with Gd doping. (c) $R(T)$ for films deposited on AAO. (d) Arrhenius plot of $R(T)$. (e) T_0 oscillates in magnetic field. The x-axis is the frustration number. (f) T_0 changes with Gd doping. The solid line represents $f = 0$ and dashed line represents $f = 1/2$. Inset: δT_0 decreases with Gd amount.

ior at low temperature still stems from thin film region where the Δ is small and reduced by magnetic impurity doping. The activation energy is independent of the geometry at this scale. Therefore, the behavior of T_0 should still be reliable, at least qualitatively. The initial $T_0^{f=0}$ is ~ 0.6 K, which is closer to QCP than Experiment I, but not as close as Experiment II. It decreases with Gd doping. This is consistent with our previous discussions. $T_0^{f=1/2}$ is more complicated as the superconducting region can be turned insulating by frustration, where Δ is higher. As a result, the $h/2e$ oscillation persists even for the last film in this experiment.

5.6 Renormalization of Charging Energy

The salient features in our results can be explained by introducing a dissipative term in the Hamiltonian[11, 30, 31, 32]. The action for partition function is modified as $S[\Phi] = S_c[\Phi] + S_t[\Phi] + S_J[\Phi]$, where S_c describes the bare charging energy, S_t represents the tunneling from quasi-particles whose value depends on the superconducting gap and S_J is the Josephson coupling term. Note that if all relevant energy scales are small compared with the superconducting gap, no real quasi-particle tunneling occurs. The charging energy is renormalized by virtual tunneling instead. Following the renormalization approach in Ref. [11], those three terms can be calculated as,

$$\begin{aligned}
S_c &= \frac{1}{2e^2} \sum_{ij} \int_0^\beta d\tau C_{ij} \frac{d\varphi_i(\tau)}{d\tau} \frac{d\varphi_j(\tau)}{d\tau} \\
S_t &= \frac{3\pi g}{64\Delta} \sum_{\langle ij \rangle} \int_0^\beta \dot{\varphi}_{ij}^2(\tau) d\tau \\
S_J &= -\frac{1}{2} \sum_{\langle ij \rangle} \int_0^\beta J_{ij} \cos \{2[\varphi_i(\tau) - \varphi_j(\tau)]\} d\tau
\end{aligned} \tag{5.6.1}$$

where φ is the phase, C_{ij} is the nearest neighbor capacitance and J_{ij} is the nearest neighbor Josephson coupling. The effective charging energy in 2d system is given by the sum of the first two terms.

$$E_C = \frac{2\Delta}{3\pi^2 g} \ln(gE_{C0}/\Delta) \quad (5.6.2)$$

The bare charging energy E_{C0} is a constant on the order of ~ 100 K estimated from the geometry of our substrate. It is significantly reduced by the log function. The renormalization effect is more significant in a 3d system where the renormalized $E_C = \text{const} \times \Delta/g$ becomes independent of the bare charging energy. g is a dimensionless conductance measured in the units of quantum conductance $g = G/(2e^2/\hbar)$. Fazio et al [30] gives a qualitatively similar result of renormalization charging energy $E_C = E_{C0}/(1 + \alpha_t 3E_{C0}/(8\Delta))$, where $\alpha_t = \pi g$. The function reduces to a downward quadratic function of Δ when $E_{C0} \gg \Delta$. The peak position is at the order of E_{C0} that is much larger than the real Δ in experiments, thus E_C also decreases with shrinking gap. The exact form of E_C does not affect our conclusion here. We will use Eq. 5.6.2 for discussion in the following part.

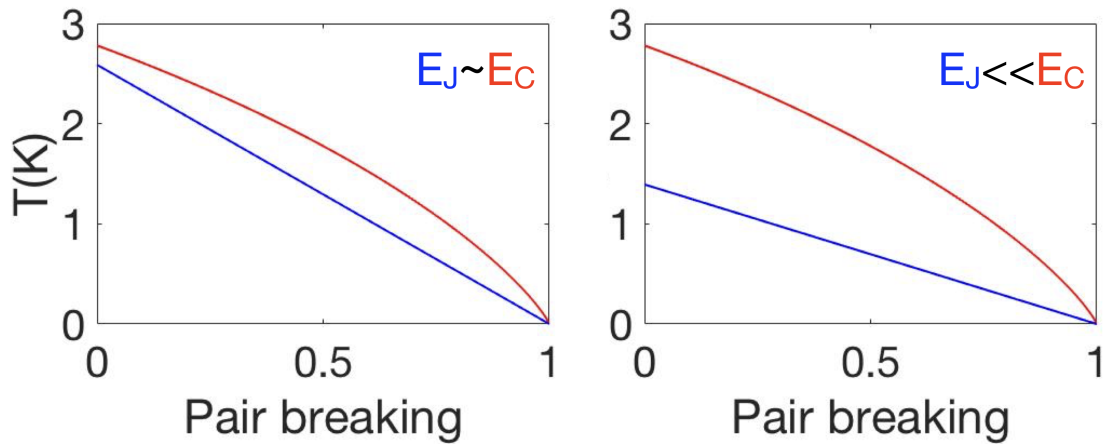


Figure 5.6.1: E_C and E_J change with the pair breaking effect. The blue curve represents E_J which decreases linearly with shrinking gap. When they are comparable(left figure), their difference first increases and then drops. If E_J is much lower, the difference monotonically decreases.

The Josephson part is approached by mean-field approximation, enabling us to take J_{ij} term out from the summation. The resulting effective coupling energy $E_J = E_{J0} < \sum_{\langle ij \rangle} \cos(\phi_i - \phi_j - A_{ij}) > = E_{J0} < \cos(2\pi f) >$, where $E_{J0} = \frac{\hbar}{8e^2} \frac{\Delta}{R_n} = \frac{\pi}{2} g \Delta$. Therefore, the effective Josephson coupling energy is still proportional to the superconducting gap. Closer to the SIT with $g < 1$ and $E_J \ll E_C$, the Josephson coupling energy reduces the activation energy in a perturbative manner, $T_0(g) = E_C(g) - \beta E_J/2$. Qualitatively, we presume the above expression holds when E_J and E_C are comparable. Same with E_J , E_C is a monotonically decreasing function with pair breaking effect. Fig. 5.6.1 shows E_C and E_J response to shrinking superconducting gap using some typical parameters in our experiments. If E_C dominates, T_0 will also decrease monotonically. Otherwise, a peak results because of the log function in E_C and the minus sign in front of E_J .

In summary, T_0 can be written as,

$$T_0 = \frac{2\Delta}{3\pi^2 g} \ln(gE_{C0}/\Delta) - \beta g \Delta < 2\pi f > \quad (5.6.3)$$

Fig. 5.6.2 shows how T_0 changes with decreasing gap. The contours were calculated using parameter values, $E_{C0} = 200$ K, $\beta = 1$, $\Delta_0 = 5$ K and $f = 0$ with g varying from 0.3 to 0.45, that fell in a plausible range for these AAO films. At lower g , farther from the SIT T_0 decreases monotonically with $\delta\Delta$. At higher g , closer to the SIT, $T_0(\delta\Delta)$ develops a maximum. These trends qualitatively resemble the observed trends in the T_0 data as a function of α_{Gd} and distance from the SIT critical point (see inset of Fig. 5.6.2).

The situation, however, becomes more complicated when the pair breaking is large. In the discussion above, we attribute the activation energy to the Cooper pair transport renormalized by quasi-particle tunneling. That is valid only if the relevant energy scales are all below Δ . When the gap is shrunk to a point that $\Delta/E_C < 2$ [2], quasi-particles dominate the transport and measured T_0 will not go to zero as

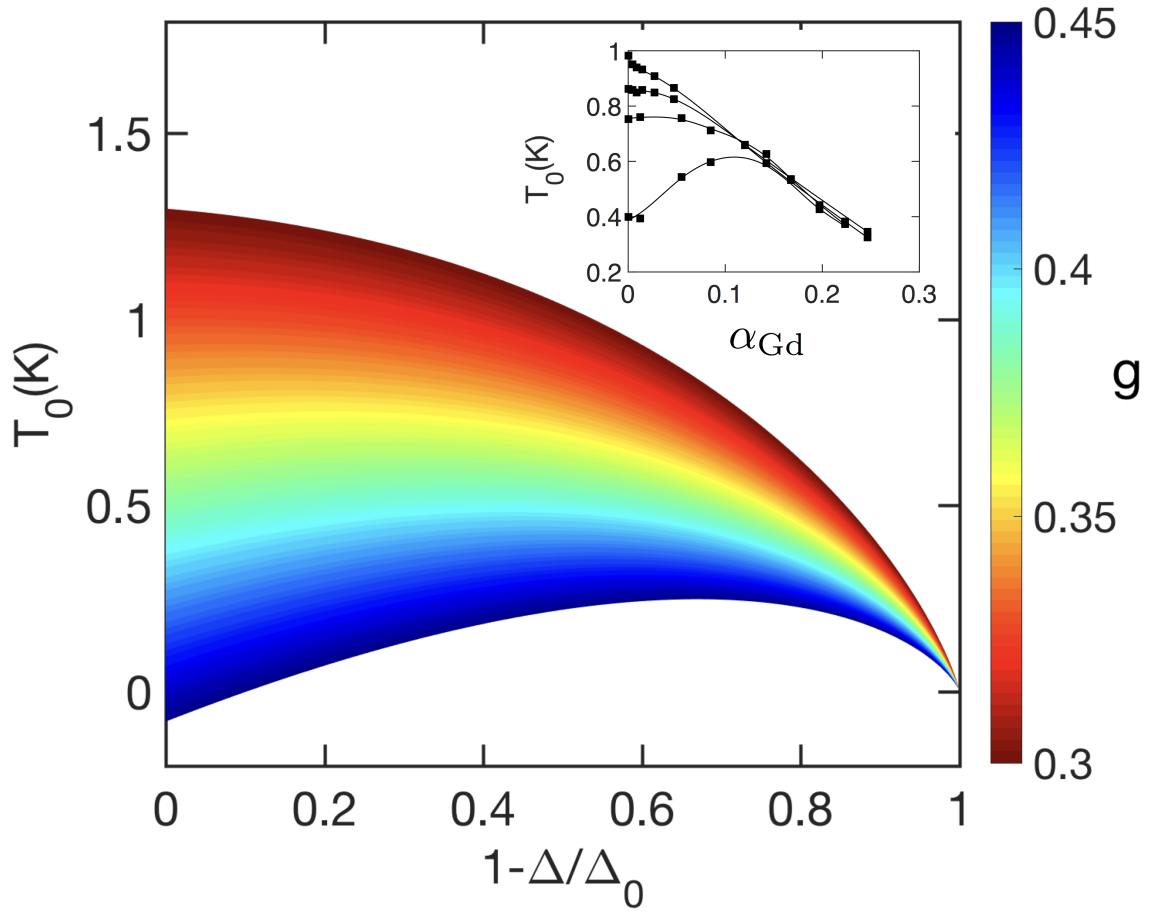


Figure 5.6.2: Comparison of the data with the Mott insulator with virtual quasiparticle screening model. The main figure gives contours of T_0 at constant g versus the normalized change in Δ as calculated from Eq.(5.6.3) for the case $f = 0$. The normalized change in Δ is proportional to α_{Gd} for low doping. The model parameters were set to $E_{C0} = 200$ K, $\beta = 1$, and $\Delta_0 = 5$ K with g varying from 0.3 to 0.45. Over this range of g the activation energy at zero doping changes sign indicating that it spans the SIT. Using $f = 1/2$ generates a qualitatively similar spectrum of curves that have a weaker maximum at the largest g . Inset: Experimental results for films I and II with lines that are guides to the eye.

Eq. 5.6.2 suggests.

5.7 Conclusion

Our system provides a useful tool to study the effect of magnetic impurity on low dimensional transport behavior. Gd has been successively deposited onto a quench condensed ultra-thin Bi film in the Cooper pair insulator state. The uniform spin flip scattering enable us to reduce the superconducting gap while keeping other parameters constant. Our data indicates both effective charging energy and Josephson coupling energy are suppressed by magnetic impurity doping, while T_0 can be enhanced at small doping amount when the film is close to QCP.

The model of $E_C - E_J$ with E_C independent of Δ is too simple. It cannot account for the monotonic decrease of T_0 with magnetic impurities exhibited by the 3 curves in Fig. 5.4.11. This behavior rules out Josephson junction array models that include large dielectric constants to reduce the Coulomb blockade energy[9, 10]. It also rules out scenarios of Anderson localization physics in which the activation energy involves the excitation of Cooper pairs across a mobility edge[12]. Since the Cooper pair mobility is proportional to the inter-island tunneling rate or Josephson coupling. It is supposed to decrease with shrinking Δ .

Cooper pair hopping combined with dissipative quasi-particle tunneling needs to be considered to explain those novel behaviors. Our data are in agreement with the computation results except in the strong pair breaking region. In that case, single electron transport needs to be integrated to fully explain the experiment. This is the first experimental evidence as we know to show the dissipative transport is nontrivial even in the regime Cooper pairs dominate the transport. The magnetic impurity induced resistance peak near the critical point definitely needs more attention to study the widely observed MR peak.

Bibliography

- [1] Xue Zhang, James C Joy, Chunshu Wu, Jin-Ho Kim, JM Xu, and James M Valles Jr. Quasiparticle screening near a bosonic superconductor-insulator transition revealed by magnetic impurity doping. *arXiv preprint arXiv:1806.10636*, 2018.
- [2] P Delsing, C D Chen, D B Haviland, Y Harada, and T Claeson. Charge solitons and quantum fluctuations in two-dimensional arrays of small Josephson junctions. *Physical Review B*, 50(6):3959, 1994.
- [3] G. Sambandamurthy, L. W. Engel, A. Johansson, and D. Shahar. Superconductivity-Related Insulating Behavior. *Physical Review Letters*, 92(10):107005–1, 2004.
- [4] T. I. Baturina, A. Yu. Mironov, V. M. Vinokur, M. R. Baklanov, and C. Strunk. Localized superconductivity in the quantum-critical region of the disorder-driven superconductor-insulator transition in TiN thin films. *Physical Review Letters*, 99(25):257003, dec 2007.
- [5] H. Q. Nguyen, S. M. Hollen, M. D. Stewart, J. Shainline, Aijun Yin, J. M. Xu, and J. M. Valles. Observation of Giant Positive Magnetoresistance in a Cooper Pair Insulator. *Physical Review Letters*, 103(15):1–4, oct 2009.
- [6] M. V. Fistul, V. M. Vinokur, and T. I. Baturina. Collective Cooper-Pair Transport in the Insulating State of Josephson-Junction Arrays. *Physical Review Letters*, 100(8):086805, feb 2008.

- [7] Takahide Yamaguchi, Ryuta Yagi, Shun-Ichi Kobayashi, and Youiti Ootuka. Two-Dimensional Arrays of Small Josephson Junctions with Regular and Random Defects. *Journal of the Physical Society of Japan*, 67(3):729–731, 1998.
- [8] D. Kowal and Z. Ovadyahu. Scale dependent superconductor-insulator transition. *Physica C: Superconductivity*, 468(4):322–325, feb 2008.
- [9] Tatyana I Baturina and Valerii M Vinokur. Superinsulator–superconductor duality in two dimensions. *Annals of Physics*, 331:236–257, 2013.
- [10] Alexey Yu Mironov, Daniel M Silevitch, Thomas Proslie, Svetlana V Postolova, Maria V Burdastyh, Anton K Gutakovskii, Thomas F Rosenbaum, Valerii V Vinokur, and Tatyana I Baturina. Charge berezinskii-kosterlitz-thouless transition in superconducting nbtin films. *Scientific reports*, 8(1):4082, 2018.
- [11] I. S. Beloborodov, A. V. Lopatin, V. M. Vinokur, and K. B. Efetov. Granular electronic systems. *Rev. Mod. Phys.*, 79:469–518, Apr 2007.
- [12] Thuong T Nguyen and Markus Müller. Magneto-oscillations of the mobility edge in coulomb frustrated bosons and fermions. *arXiv preprint arXiv:1606.07747*, 2016.
- [13] K Kim and D Stroud. Quantum Monte Carlo study of a magnetic-field-driven two-dimensional superconductor-insulator transition. *Physical Review B*, 78(17), 2008.
- [14] J S Parker, D E Read, A Kumar, and P Xiong. Superconducting quantum phase transitions tuned by magnetic impurity and magnetic field in ultrathin a-Pb films. *Europhysics Letters*, 75(6):950–956, 2006.
- [15] J A Chervenak and J M Valles. Pair-Breaking by Magnetic-Impurities in Ultrathin Superconducting Films - T-C Degradation Mechanisms in Disordered Superconductors. *Physical Review B*, 51(17):11977–11980, 1995.

- [16] D B Haviland Liu, Y., and Goldman, A. M. Onset of superconductivity in the two-dimensional limit. *Physical Review Letters*, 62:2180–2183, 1989.
- [17] S M Hollen, G E Fernandes, J M Xu, and J M Valles. Fate of the Bose insulator in the limit of strong localization and low Cooper-pair density in ultrathin films. *Physical Review B*, 90(14), 2014.
- [18] S. M. Hollen, H. Q. Nguyen, E. Rudisaile, M. D. Stewart, J. Shainline, J. M. Xu, and J. M. Valles. Cooper-pair insulator phase in superconducting amorphous Bi films induced by nanometer-scale thickness variations. *Physical Review B*, 84(6):064528, aug 2011.
- [19] Shawna M Hollen and JM Valles Jr. Cooper pair islanding model of insulating nanohoneycomb films. In *Journal of Physics: Conference Series*, volume 376, page 012002. IOP Publishing, 2012.
- [20] HQ Nguyen, SM Hollen, J Shainline, JM Xu, and JM Valles Jr. Driving a superconductor to insulator transition with random gauge fields. *Scientific reports*, 6:38166, 2016.
- [21] Subir Sachdev. *Quantum phase transitions*. Cambridge university press, 2011.
- [22] H S J van der Zant Elion, W.J., Geerligs, L.J., and Mooij, J.E. Quantum phase transitions in two dimensions: Experiments in Josephson-junction arrays. *Phys. Rev. B.*, 54(14):10 081–10 093.
- [23] M D Stewart, Aijun Yin, J M Xu, and James M Valles. Superconducting pair correlations in an amorphous insulating nanohoneycomb film. *Science*, 318(5854):1273–1275, nov 2007.
- [24] M Tinkham. Introduction to Superconductivity. *The McGraw-Hill Companies, Inc.*, 1996.

- [25] Shih-Ying Hsu and JM Valles Jr. Observation of a well defined transition from weak to strong localization in two dimensions. *Physical review letters*, 74(12):2331, 1995.
- [26] V. F. Gantmakher. *Electrons and Disorder in Solids*. Oxford University Press, aug 2007.
- [27] M D Stewart, H Q Nguyen, S M Hollen, A J Yin, J M Xu, and J M Valles. Enhanced suppression of superconductivity in amorphous films with nano-scale patterning. *Physica C-Superconductivity and Its Applications*, 469(13):774–777, 2009.
- [28] Richard P Barber Jr, Shih-Ying Hsu, James M Valles Jr, Robert C Dynes, and Rolfe Eldridge Glover III. Negative magnetoresistance, negative electroresistance, and metallic behavior on the insulating side of the two-dimensional superconductor-insulator transition in granular pb films. *Physical Review B*, 73(13):134516, 2006.
- [29] V F Gantmakher, M V Golubkov, V T Dolgoplov, G E Tsydynzhapov, and A A Shashkin. Destruction of localized electron pairs above the magnetic-field-driven superconductor-insulator transition in amorphous In-O films. *Jetp Letters*, 68(4):363–369, 1998.
- [30] Rosario Fazio and Gerd Schön. Charge and vortex dynamics in arrays of tunnel junctions. *Physical Review B*, 43(7):5307, 1991.
- [31] Sudip Chakravarty, Steven Kivelson, Gergely T Zimanyi, and Bertrand I Halperin. Effect of quasiparticle tunneling on quantum-phase fluctuations and the onset of superconductivity in granular films. *Physical Review B*, 35(13):7256, 1987.

- [32] Al Larkin and Yu N Ovchinnikov. Decay of the supercurrent in tunnel junctions.
Physical Review B, 28(11):6281, 1983.

Chapter 6

Shrinking Magnetoresistance Peak with Magnetic Impurity

One of the signature features in Cooper pair insulator phase is the giant magnetoresistance (MR) peak. Although the exact nature has not been revealed yet, it is widely believed that the peak is a consequence of the competing transport mechanism between Cooper pairs and quasi particles. Therefore, it is reasonable to expect that the peak will be directly affected by magnetic impurity doping. In this chapter, we present experimental data that shows the shrinking of the peak by Gd doping. We will see how the transport behaviors at high fields change with doping. The comparison between the MR peak and the magnetic impurity induced peak provides useful insights into the emergence of the MR peak.

6.1 Introduction

Nonmonotonic magnetoresistance has been observed in various systems in the vicinity of the SIT, including a-Bi [1, 2], InO_x [3, 4, 5, 6, 7], TiN [8], PbBi [9], a-MoSi [10] and High T_C superconductors [11]. The disorder plays a crucial role for the emergence of the peak. The pairing amplitude becomes spatially inhomogeneous with increasing disorder [12], resulting in superconducting islands separated in an insulating background. That is the prerequisite for the appearance of MR peak.

Disorder can be added as thickness fluctuations over mesoscopic length scales. Bi films deposited on flat nano-patterned Si substrates are smooth. They show no signs of Cooper pairs in the insulator and the MR peak is absent [13]. This behavior contrasts with behaviors of films deposited onto AAO substrates [1], which includes a giant MR peak. The underlayer on a flat substrate can also affect the thickness variation. Bi deposited on a thick a-Sb underlayer is rough and exhibits a MR peak near the SIT, while on a thin underlayer, the film is homogeneous and exhibits direct SI transition [2]. Another source of disorder is called "compositional disorder" that is added by different chemical compositions. Givan et al [14] did chemical analysis for InO_x films with different electron densities and showed the existence of disorder even if the thickness seems to be homogeneous.

For the MR peak, the size R^{peak} and position B^{peak} of the peak depends on temperature. The peak resistance is $\sim 70\%$ higher at 100 mK compared with $T = 120$ mK [1]. The location of the peak B^{peak} also moves to lower values with decreasing temperature. It is still unknown whether it will move to B_C , the critical field for the SIT, or remains larger than B_C in the zero temperature limit[16]. Besides the temperature, the angle of magnetic field also affects the peak. Both perpendicular and parallel fields can induce the resistance peak [15, 17]. Fig. 6.1.1 shows the perpendicular and parallel magnetic isotherms for the same sample. They show

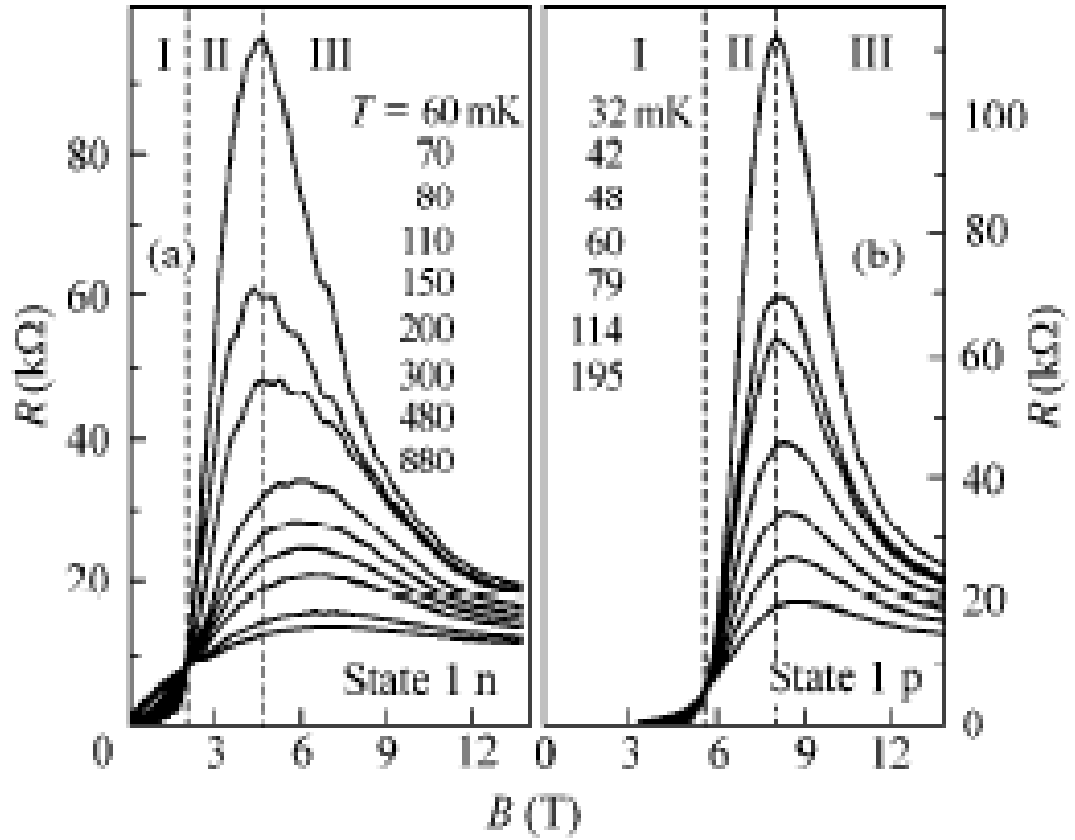


Figure 6.1.1: Isotherms $R(B)$ for (a) perpendicular and (b) parallel magnetic field. The upper curves represent lower temperatures. Note the resistances start to increase at higher field for the parallel field. Figure is excerpted from Ref. [15].

similar shape. The size of the peak, however, is much larger at the same temperature in the perpendicular case. In addition, B^{peak} moves to higher field when the field is applied parallel to the sample.

Despite the extensive of experimental studies, the theory behind the giant peaks is not well established. The experiments suggest that the nonmonotonic behavior is related to a pair breaking effect, either through dephasing or shrinking of the gap. Because of particle statistics, Bosons usually exhibit positive magnetoresistance since constructive interference from different paths of forward propagation is suppressed by magnetic field [18, 19]. By contrast, Fermions have occasional negative interferences and thus exhibit negative magnetoresistance [20, 21, 22].

Therefore, a peak appears at the cross-over region where CPs disintegrate into QPs. In experiment, the positive MR is usually regarded as a signature of Cooper pair transport while negative MR indicates single electrons. That is consistent with our observation that $h/2e$ oscillation appears only on the left side of the peak.

Quantitatively, Galitski et al [23] implemented two-fluid model. The resistance has a contribution from a field induced vortex channel and a quasi-particle channel. The vortex transport dominates the lower field region while quasi-particle tunneling is more preferred at high fields, resulting in a 'Vortex Metal' phase in-between. Dubi et al [24] used a more phenomenological model that assumes that the size of superconducting islands is reduced by magnetic field. The conduction is mainly from Cooper pair tunneling at low fields. As those islands shrink, the energy barrier for Cooper pair tunneling increases and the normal state area becomes larger. Finally, the normal electrons dominate the transport beyond the peak.

In our lab, we developed an experimental method to investigate the underlying mechanism of the MR peak. Since the peak is related to superconducting order parameter, magnetic impurity doping should affect the peak by reducing the gap. We expect the location of the peak to move toward zero as the pair breaking effects of magnetic impurity and magnetic field are additive. The size of the peak is also expected to decrease since Cooper pairs contribute to the resistance increase. With magnetic doping, there will be fewer Cooper pairs involved at lower fields.

Also, the magnetic field affects the order parameter by reducing the amplitude as well as introducing extra phase fluctuations. When the field is perpendicular to sample, the vector potential shifts the phase of the electrons as they traverse the system. The parallel field, however, does not couple as strongly to the phase because the electron motion perpendicular to the field is restricted by the thin film geometry. That simple model explains the difference between perpendicular and parallel fields shown in Fig. 6.1.1. The crossover point for two transport mecha-

nisms is thus at a higher field in the parallel case. By contrast, magnetic impurity has low magnetic moment. As a result, it can be regarded as pure amplitude reduction effect. Using the magnetic impurity doping helps us separate those two effects and gives us more insights on the origin of MR peak.

We will present data from the same two experimental runs described in the last chapter. Here, the focus is more concentrated on the transport in fields. As the films in two experiments behave similarly in high fields, Experiment II is primarily used for a detailed discussion while data from Experiment I is also plotted as supplementary information in the last section.

6.2 Magnetoresistance with Gd Doping

6.2.1 Peak and Oscillation

Fig. 6.2.1 shows a field sweep isotherm. The magnetic field is ramped up to 7 T while a temperature controller is used to maintain the sample temperature at 300 mK. The resistance peaks at 2.8 T, where $R(\text{peak}, 300 \text{ mK}) = 151 \text{ k}\Omega$ compared with zero field resistance $R(B = 0, 300 \text{ mK}) = 28 \text{ k}\Omega$. Reducing the sample temperature can push up the peak but it requires longer time to do the field sweep.

Both the resistance oscillations and the positive MR indicate that the charge carriers are Cooper pairs. We have not observed oscillations on the right side of the peak, which is consistent with our previous experiments. The absence of oscillations indicates the crossover from Cooper pair to quasi-particle transport. As we will show later, our doping experiments provide evidence that the superconducting gap remains finite in the high field region.

The oscillation itself shows some unexpected feature that we have not observed before. Fig. 6.2.2 shows the enlarged view in the low field region. The resistance reaches local minima at integer frustration. However, besides the regular H_M os-

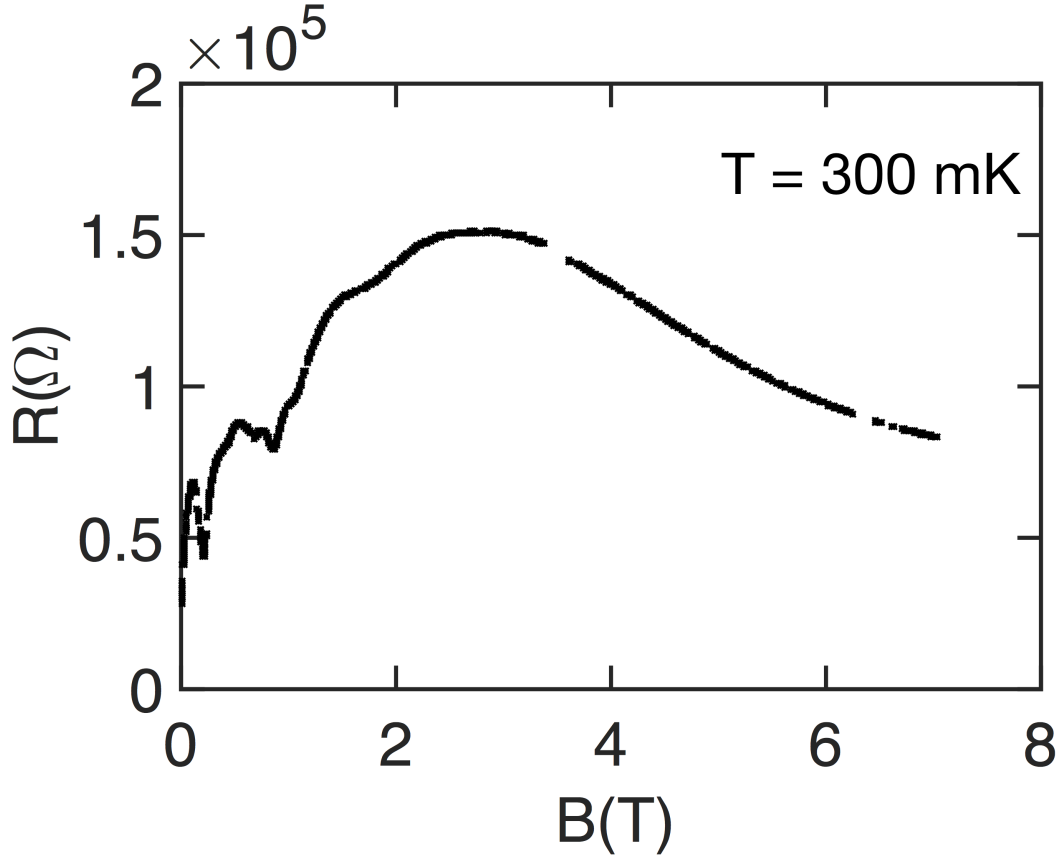


Figure 6.2.1: Field sweep at 300 mK for the last Bi film before deposition of Gd.

cillation, we have observed a superposition of another oscillation with period that exactly equals $4H_M$. Since $B \cdot S = n\Phi_0$ the larger oscillation requires characteristic area that is one quarter of the unit cell. In other words, one unit cell contains 4 flux quanta.

Fig. 6.2.3 shows a possible explanation for the double oscillations. Because of the condensation energy, an Abrikosov vortex finds it energetically favorable to reside in weak superconducting regions like the pores and the superconducting island links in our case. They still form a triangular array. It is a stable lattice structure and the vortices are unlikely to move. Therefore the resistance, which is caused by the movement of vortices, reaches a minimum. There are four vortices inside each cell. Thus the corresponding period is four times the original matching field. It is still unclear to us why we did not observe the bigger oscillation in previous

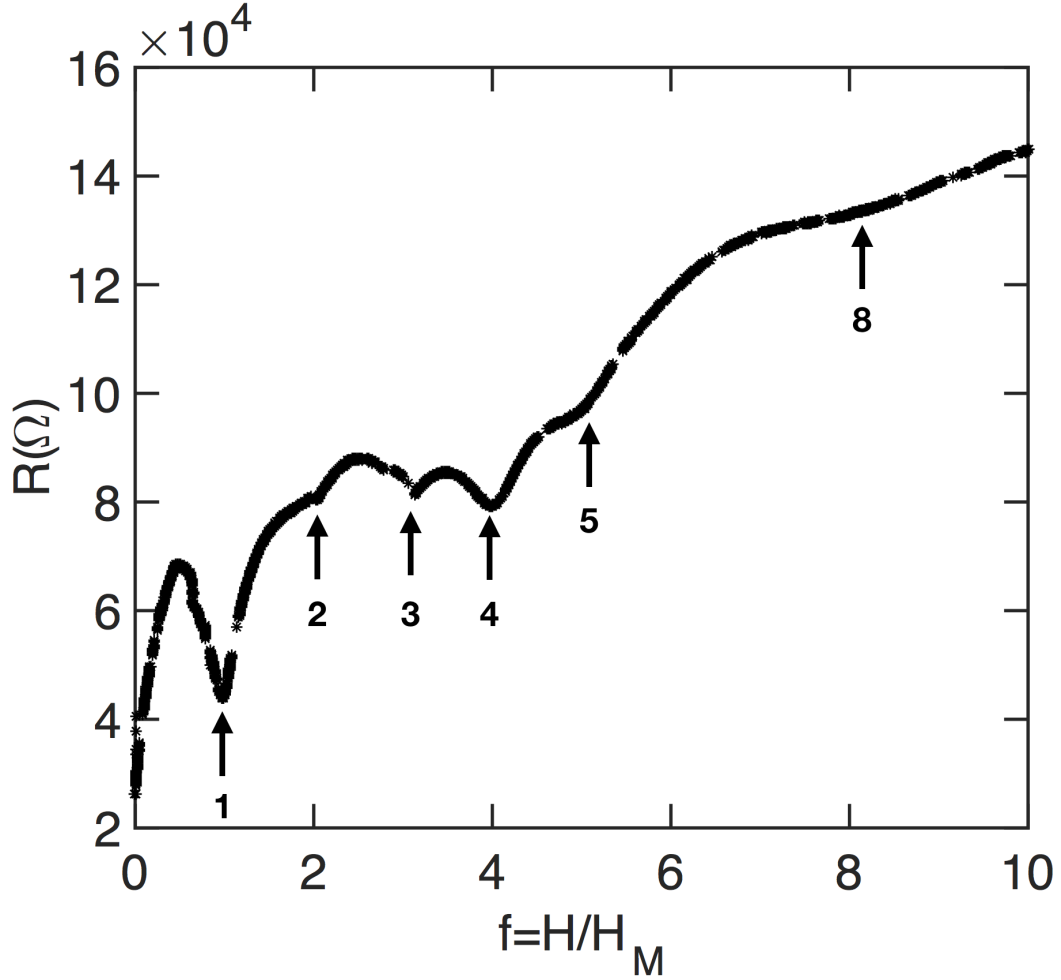


Figure 6.2.2: Resistance oscillations at low fields. The field is shown in unit of matching field $H_M = 0.215$ T. The resistance dips at integer frustration number.

experiments. It may be because the pore size is smaller this time, so that the links are sufficiently wide for the superconducting current to circulate that forms vortex cores. Future experiment with etched pores will be helpful to answer this question.

6.2.2 Adding Magnetic Impurity

For consistency with the previous chapter, We still use $\alpha_{Gd} = 1 - T_c(x_{Gd})/T_c(0)$ to represent the pair breaking strength. Fig. 6.2.4 shows the change of the magnetoresistance at $T = 150$ mK with the introduction of magnetic impurity. We retrieved the low temperature resistance data from $R(T)$ curves in field. Note that in the

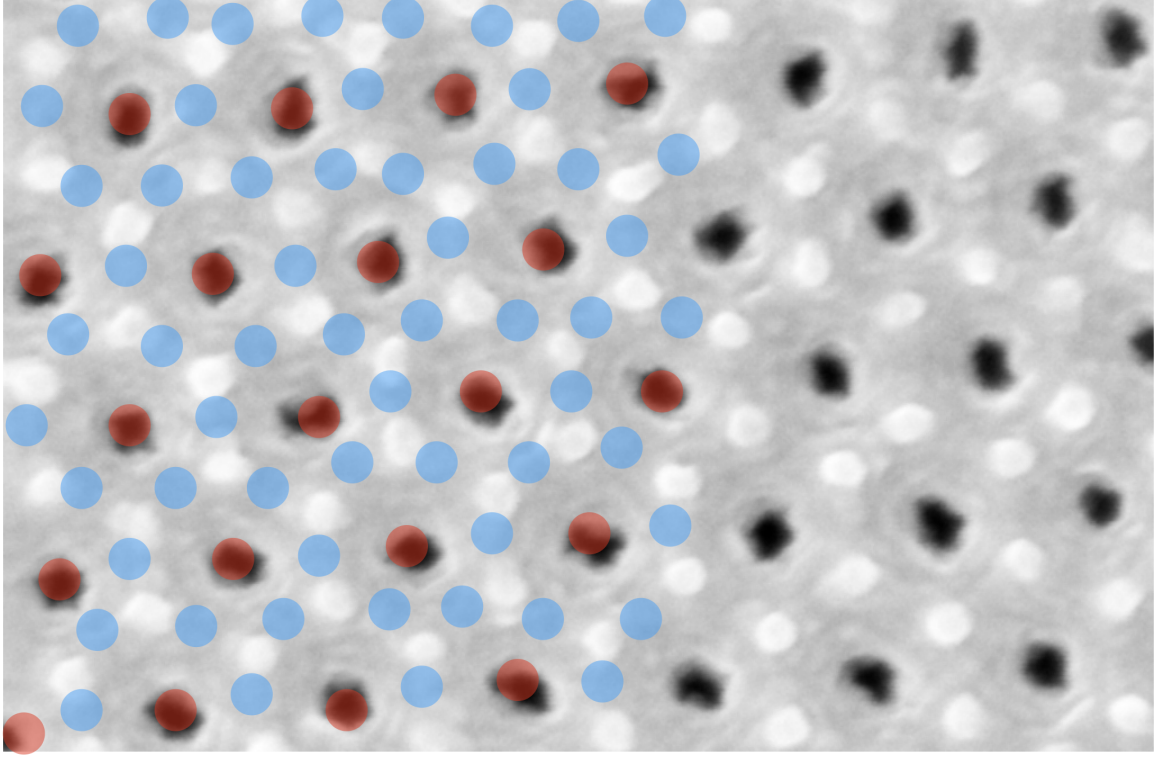


Figure 6.2.3: Possible vortex configuration. The red dots represent the pores which contribute to the regular H_M oscillation. The blue dots are located at the links where superconductivity is weak. There are six blue dots around each pore and each dot is shared by two pores. Thus, the total flux quantum in each unit cell is 3 blue ones plus the red one, which counts for the $4H_M$ oscillation.

low field region we only measured the first oscillation. Its presence indicates that Cooper pairs dominate the transport in the low magnetic field and low doping limit. Adding magnetic impurities produces a peak in the resistance (solid black curve) at zero magnetic field. Concomitantly, the giant magnetoresistance peak, located to the right of the shaded region, shrinks and moves to lower magnetic fields. The Little-Parks oscillation also shrinks and disappears near $\alpha_{Gd} = 0.15$. At the same time, the giant peak has shrunk by more than an order of magnitude.

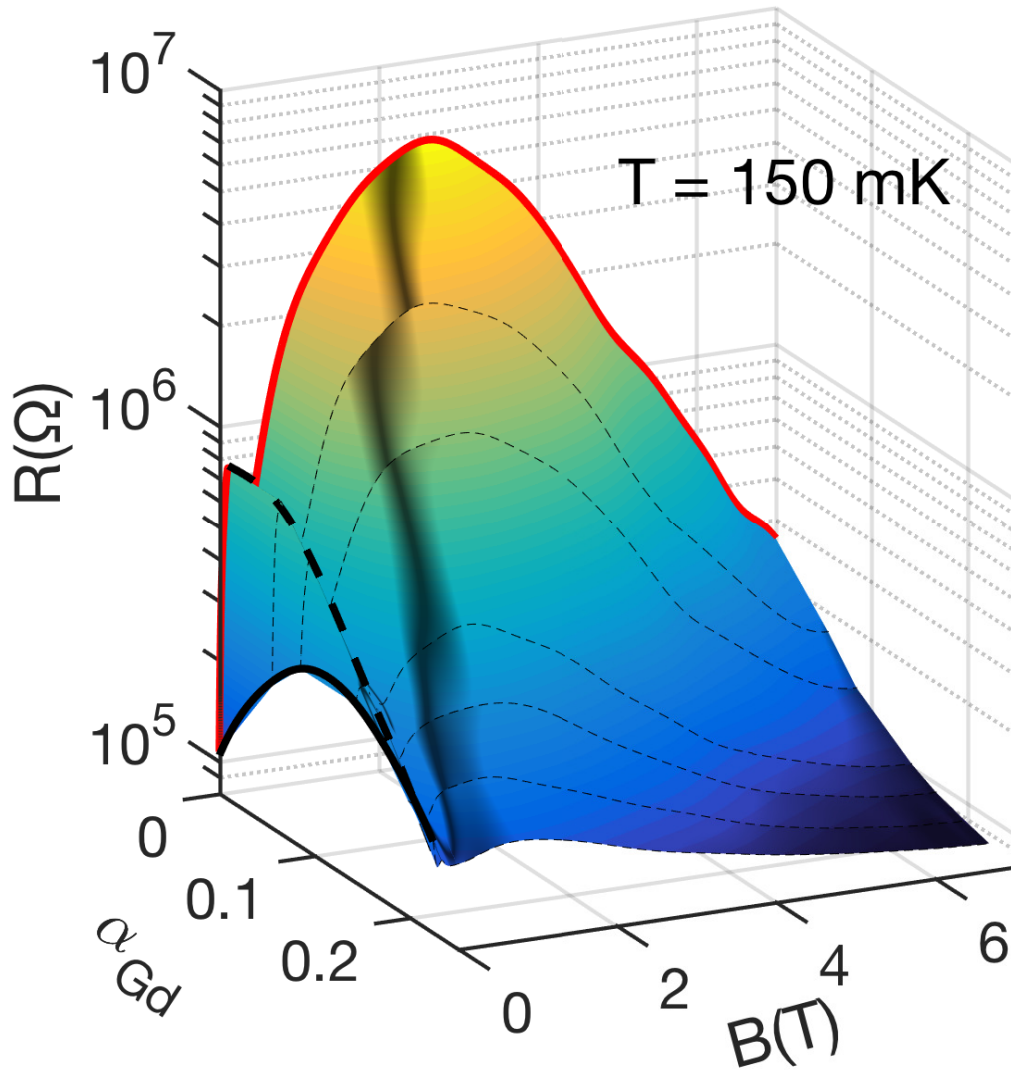


Figure 6.2.4: Surface plot $R(T = 150 \text{ mK}, \alpha_{Gd}, B)$. α_{Gd} is the pair breaking strength defined in the text. The light dashed lines are the isotherms that are used to construct the plot. The red curve is the field sweep with zero doping. The MR peak is indicated by the dark region in the middle. The bold solid and dashed lines are traced at fixed magnetic field values corresponding to zero and $1/2$ of a flux quantum per unit cell, which are explicitly discussed in the previous chapter.

6.3 Activation Energies in Fields

The transport still has an activated dependence on temperature in the high field regime, even though the charge carriers are quasiparticles rather than Cooper

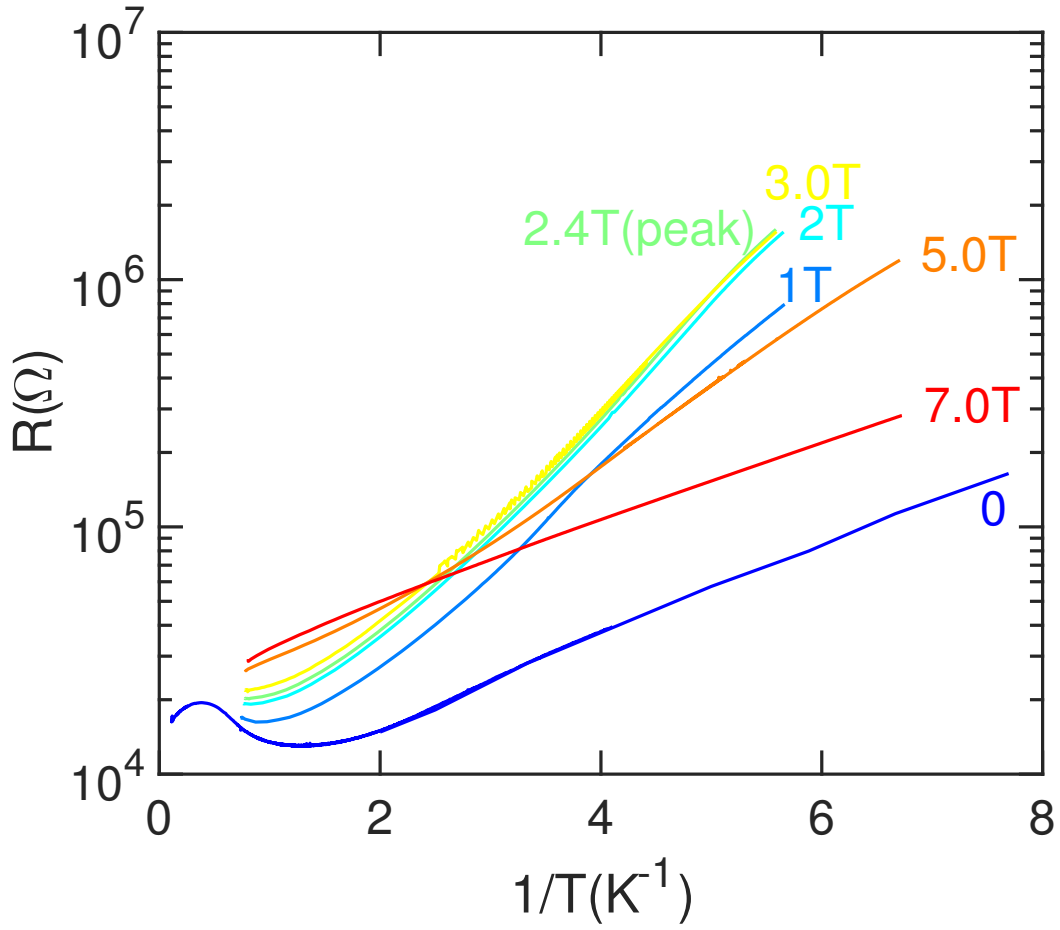


Figure 6.3.1: $R(T)$ in fields for the zero doping film. The curves are labeled by the corresponding magnetic fields. The MR peak appears at 2.4 T.

pairs. Fig. 6.3.1 shows some representative $R(T)$ curves in fields. The reentrance dip vanishes in the highest fields, indicating the quenching of pairing. The activation energies can be retrieved by fitting low temperature data to the Arrhenius equation $R = R_0 \exp(T_0/T)$. Although R_0 changes in fields [1], the resistance is mainly determined by T_0 at low temperatures because of the exponential function. We expect T_0 behaves similarly to the resistance shown in Fig. 6.2.4.

Fig. 6.3.2 shows the activation energies in magnetic field varying with Gd doping. T_0 peaks at the resistance maximum. The peak, while broad, clearly moves to the lower field with increasing doping. The magnitude of the activation energies at fixed magnetic field decreases monotonically with doping in high field region.

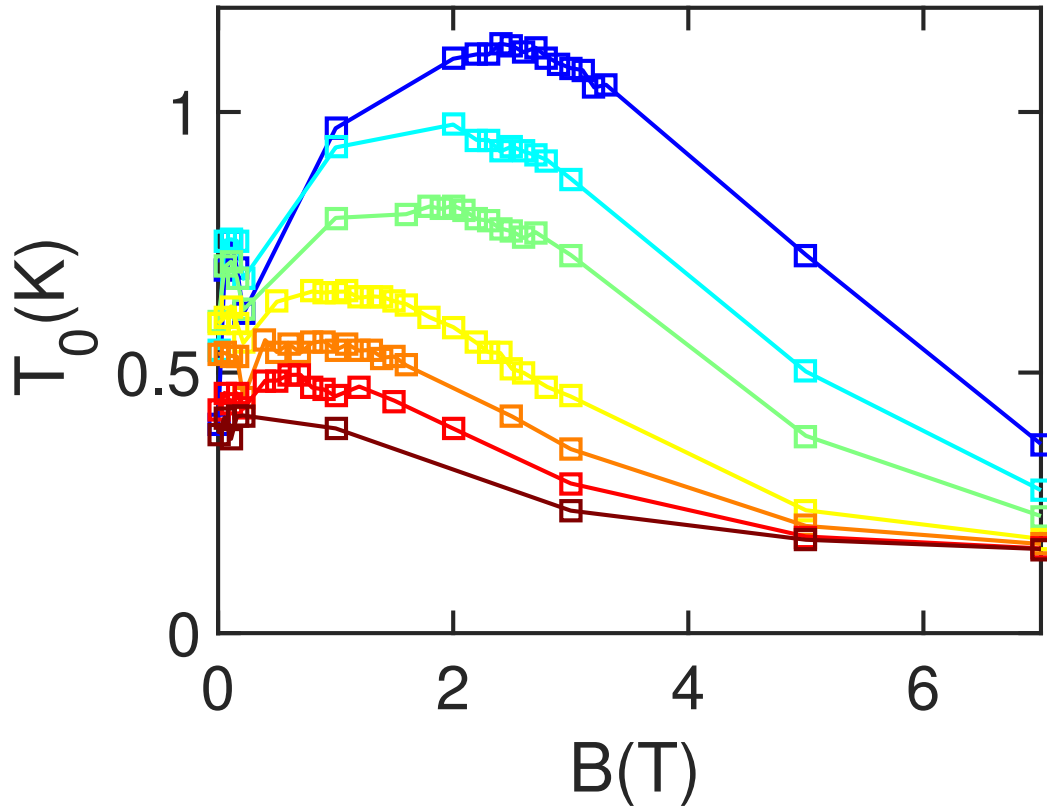


Figure 6.3.2: Response of activation energies to magnetic field and magnetic impurity. The blueish curves represent lower doping while the reddish curves represent high doping concentrations.

6.3.1 T_0^{peak} and B^{peak}

One feature of great interest is the change of the activation energy at the peak, T_0^{peak} . Fig. 6.3.3 shows that the T_0^{peak} drops almost linearly with increasing pair breaking, with a slope of 3.2 K per unit change of α_{Gd} . Initially, $T_0^{peak} = 1.1$ K, compared with $T_0^{f=0} = 0.4$ K. In the high doping limit, the oscillations disappear. $T_0^{f=0}$, $T_0^{f=1/2}$ and T_0^{peak} approach the same value.

The behavior of T_0^{peak} can be qualitatively explained using Dubi et al's model [24]. The peak is the breakeven point for the Cooper pair channel and the normal electron channel. The normal electrons are created by the magnetic field reducing the gap. The required magnetic field is lower the more magnetic impurity scatter-

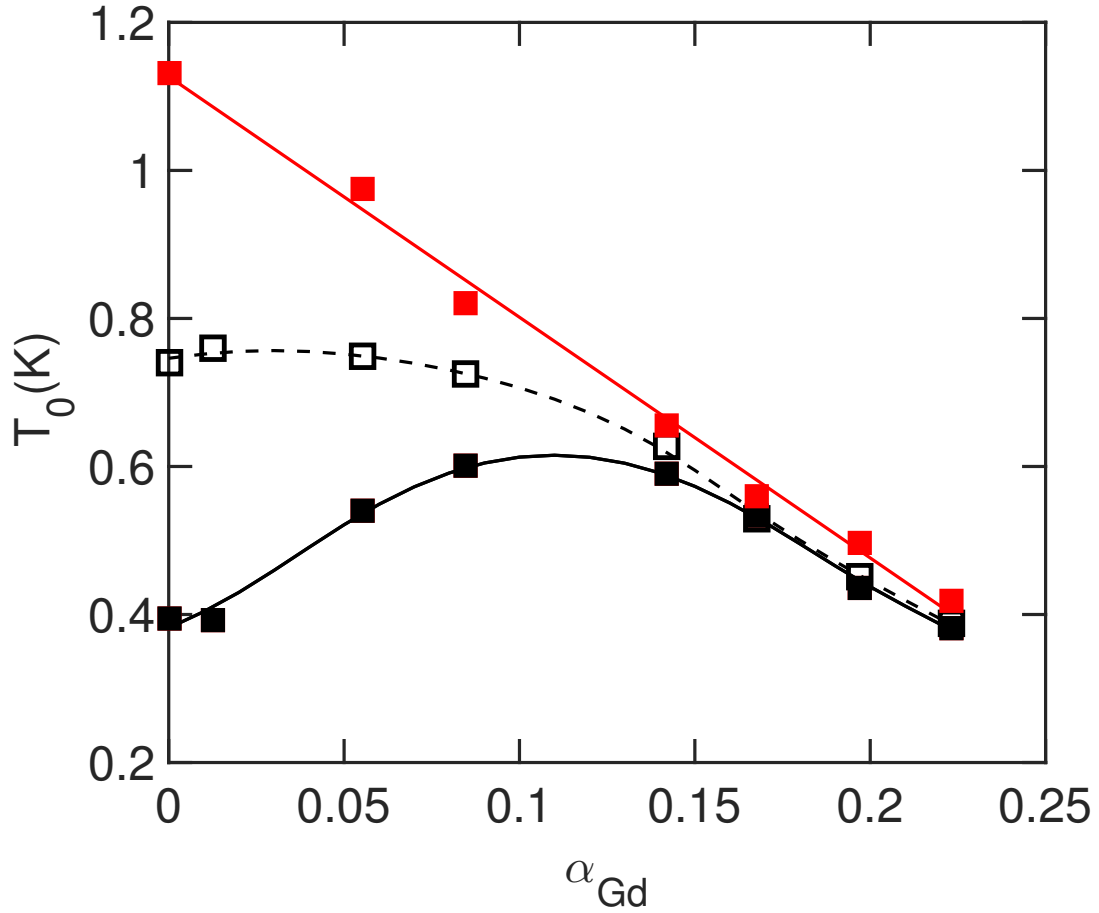


Figure 6.3.3: T_0^{peak} decreases linearly with increasing doping concentration. The red squares are the maximum activation energy retrieved from $R(T)$ curves in fields. The red line is linear fit to it. The filled squares are $T_0^{f=0}$ and the open squares are $T_0^{f=1/2}$.

ing contribute to pair breaking. Therefore, the energy barrier for normal electron transport decreases. In order to hold the breakeven condition, T_0^{peak} should also decrease. Ref. [3] also points out T_0^{peak} is close to T_C . As T_C is reduced by doping, it is natural that T_0^{peak} should also be reduced. Notice this is in contrast with T_C being reduced by thickness/disorder, which will lead to the increase of normal electron resistance, and thus, T_0^{peak} has inverse relation with T_C in that case.

The position of the peak, B^{peak} , bears large uncertainty as the peak in Fig. 6.3.2 is flat. But undoubtedly, the general trend is decreasing with increasing doping.

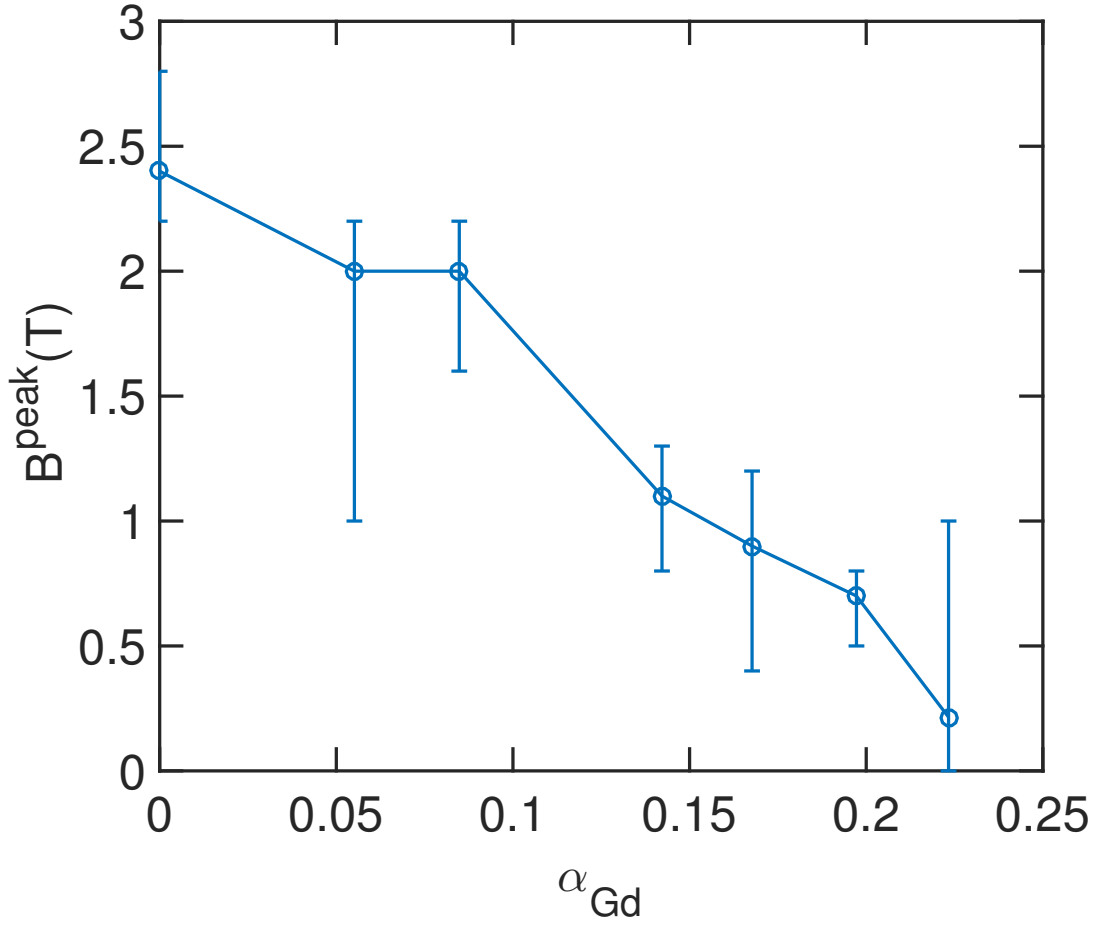


Figure 6.3.4: B^{peak} moves to zero with increasing doping concentration. The circles represent the corresponding field with the maximum T_0 . The error bar indicates 98% uncertainty range of T_0 .

Fig. 6.3.4 shows B^{peak} versus α_{Gd} . The initial B^{peak} is 2.5 T. It can be further increased if we move closer to the SIT with increasing thickness [1]. The error bar shows the uncertainty of the peak position. In the last doping, it decreases to ~ 0 , where quasi-particles begin to dominate at the whole range of magnetic field and the corresponding MR is negative.

Because of the lack of a complete theory, we do not know the explicit form of B^{peak} . Qualitatively, however, we know it is pair breaking effect and B^{peak} should be related to the upper critical field B_{c2} [1, 24]. In dirty superconductor limit, $B_{c2} \propto T_C$ [25]. Thus, it is reasonable to expect B^{peak} decreases with doping in the similar

trend as T_C^{AAO} . Note that T_C^{AAO} here is the pair temperature on AAO. Because of superconductivity size effect, it is lower than T_C^{REF} on the reference film when the superconducting island size is small [26]. Thus, we expect that $\alpha_{Gd} < 1$ when B^{peak} approaches zero. This is verified by the other experiment we will discuss later where the peak vanishes while α_{Gd} remains well below 1 (see Fig. 6.4.1). In fact, the Little-Parks oscillation is a better measure of T_C^{AAO} in this context. $B^{peak} \Rightarrow 0$ when the oscillation disappears.

6.3.2 High Field Region

In the two fluid model, the charge carriers are supposed to be normal electrons when the field is much higher than B^{peak} . In that regime, the transport is no longer activated [27]. Instead, it should be variable range hopping (VRH) with resistance [28],

$$R = R_0 \exp\left(\frac{2r_{ij}}{\xi_{loc}} + \frac{\epsilon}{T}\right) \quad (6.3.1)$$

where r_{ij} is the distance between two hopping sites, ξ_{loc} is the localization length and ϵ is the energy difference between the localized states at two sites. Assuming constant density of state near Fermi level, the resistance obeys Mott's law where $R = R_0 \exp(T_M/T)^{1/(d+1)}$ with d being the dimension of the system. However, in the presence of a Coulomb gap, like in our case, a gap opens near the Fermi level. The resistance follows Efros-Shklovskii(ES)'s law in the low temperature limit [29],

$$R = R_0 \exp\left(\frac{T_{ES}}{T}\right)^{1/2} \quad (6.3.2)$$

Fig. 6.3.5 shows the evolution of $R(T)$ with increasing doping in both activated plot and ES plot. Surprisingly, we find only a few films with highest doping in $B = 7$ T fits better to ES's law than Arrhenius plot. Most of the curves still show activated behavior. It suggests that the superconductivity on the zero doping film has not

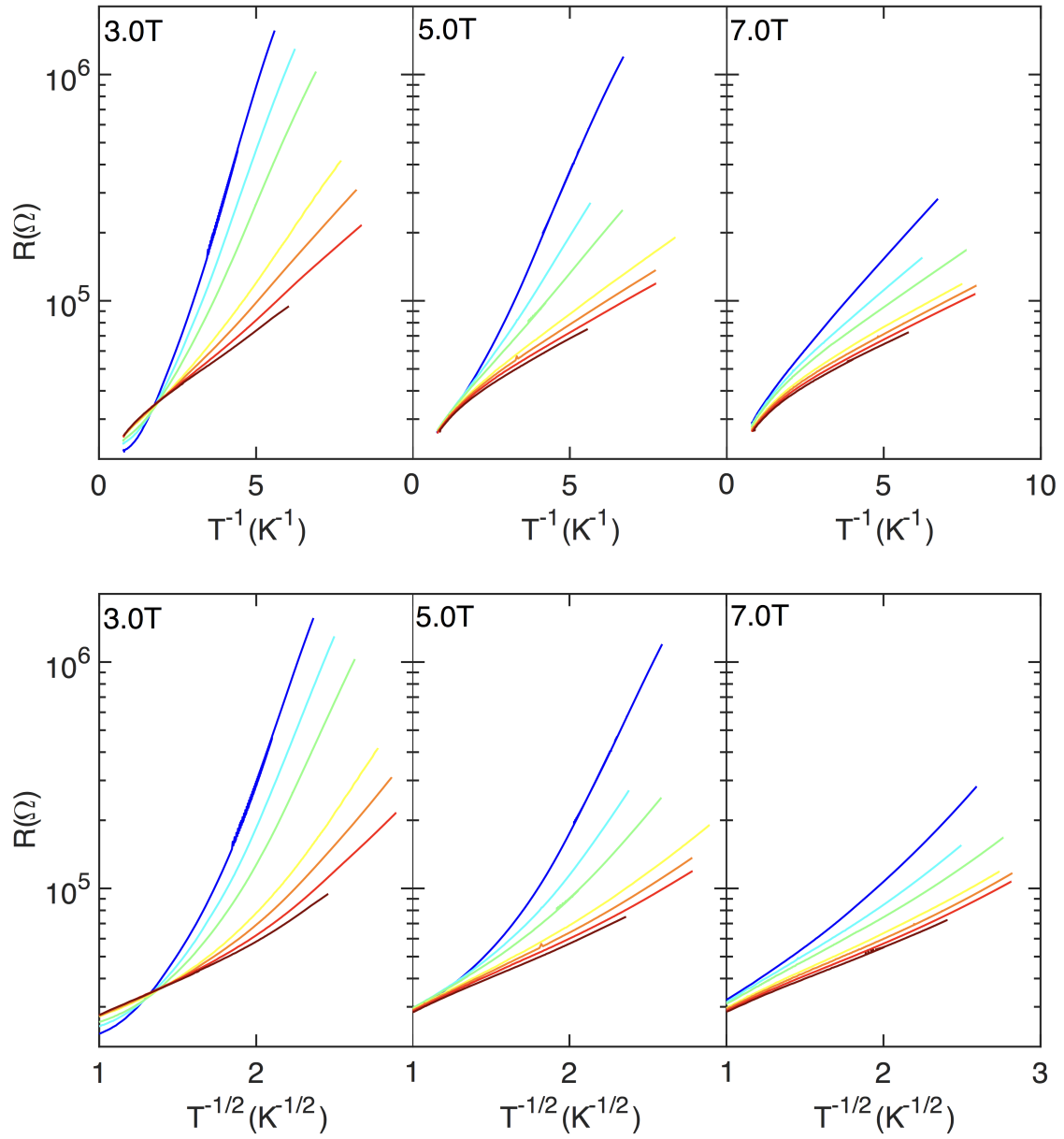


Figure 6.3.5: $R(T)$ curves at 3 T, 5 T and 7 T with increasing doping. The upper panels are Arrhenius plots and the lower panels are variable range hopping plots in the Efros-Shklovskii regime.

been fully suppressed even in the highest field achievable in our lab. The disappearance of the Little-Parks oscillation beyond the peak is due to the suppression of the phase coherence length that is less than the inter-island distance. The gap remains finite.

Magnetic impurity doping provides a way to test for the existence of the superconductivity gap. 6.3.6 shows the change of the activation energy with doping at high fields. All of them decrease with doping. It is direct evidence that the gap remains finite beyond the peak. The highest field data shows the weakest dependence on doping. It makes sense as the superconductivity becomes less and less important for the transport.

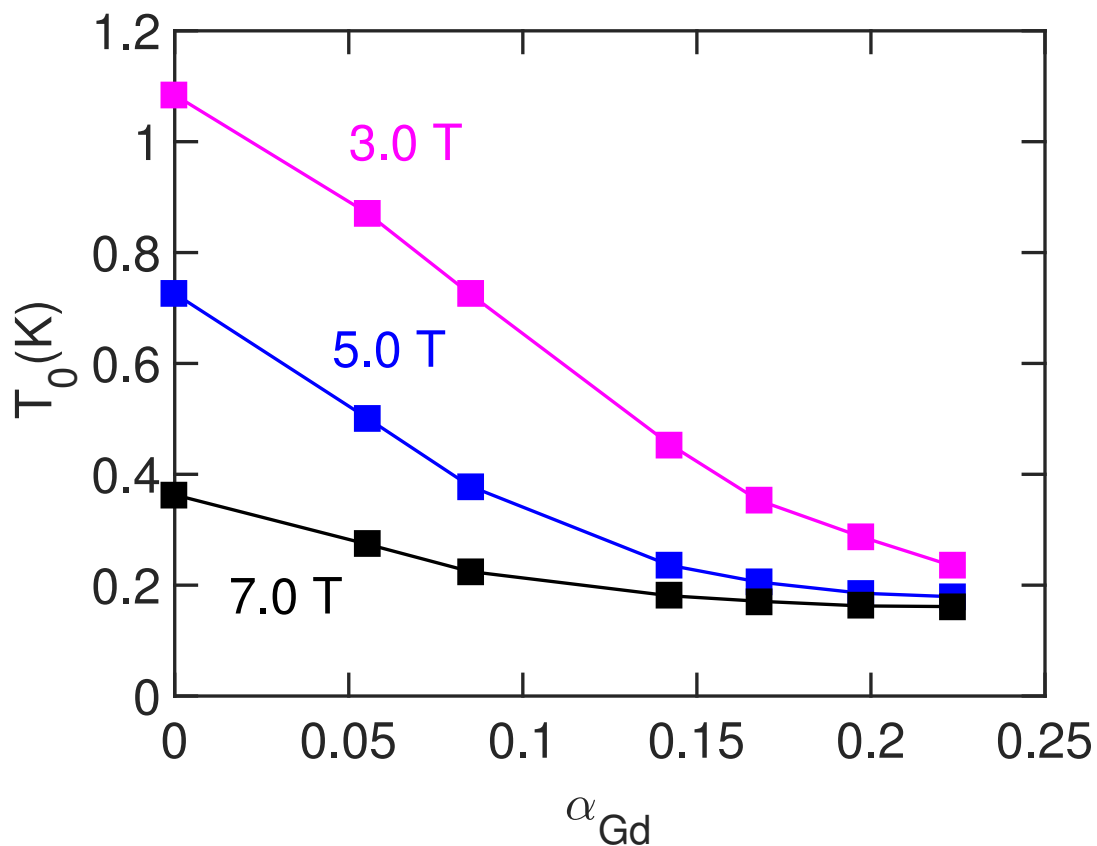


Figure 6.3.6: T_0 changes with doping under specific fields. The curves are guides to the eye. Each curve is labeled by their corresponding magnetic field. Note that T_0 is still retrieved from the activated form, although it fits better to ES hopping.

In the high field region, even though local superconductivity persists inside the islands, the negative MR indicates that Cooper pairs do not directly participate in the transport. The superconducting phase term does not affect the global transport. In other words, tunneling between islands is activated with an activation energy proportional to Δ . Therefore, magnetic field and magnetic impurity are expected to have additive pair breaking effects on the transport. If that is the case, the three curves in Fig. 6.3.6 should be able to scale to a single one by shifting the horizontal axis.

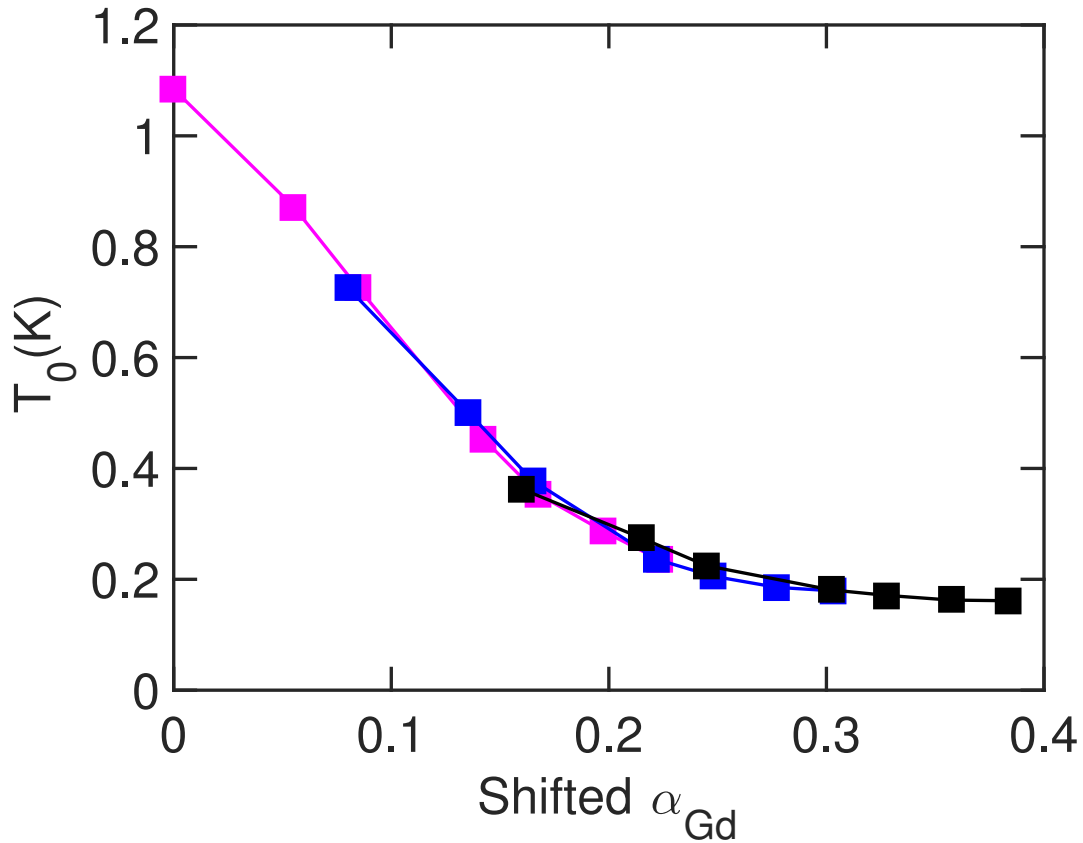


Figure 6.3.7: Scaling of T_0 versus α_{Gd} in fields. The magenta curve present 3 T without any shift. The blue curve is 5 T shifted to the right by 0.08. The black curve is 7 T shifted to the right by 0.16.

Fig. 6.3.7 shows the shifted data. It scales very well. Interestingly, the shifted value indicates 2 T field is equivalent to $\alpha_{Gd} = 0.08$ in this regime. This conclusion

needs more data point to verify. Also notice that in the high doping and high field limit, T_0 becomes almost independent of α_{Gd} . It is consistent with our previous $R(T)$ observation that they are no longer activated. It suggests that the superconductivity is completely destroyed in that regime. Thus, beyond the peak, we have a smooth crossover from quasiparticle transport, where T_0 is proportional to Δ and subjected to doping, to a normal state, where the gap is totally suppressed and T_0 becomes weakly dependent on the magnetic field and the magnetic impurity. Ref. [30] suggests a new quantum metallic phase in the high field limit where the zero temperature resistance is h/e^2 , independent of disorder. Another paper by Sacepe et al. [31] shows the measurement of the indium oxide films up to 30 T. They found the crossover coincides with B_{c2} . Beyond this high field, the system enters a new insulating state that obeys Mott hopping.

6.4 Results from Experiment I

Experiment I, which is farther from the transition, gives similar results in the high field regime. Fig. 6.4.1 shows the plots we discussed above for Experiment I.

For the zero doping film, $R(B = 0, 300 \text{ mK}) = 105 \text{ k}\Omega$, $R(\text{peak}, 300 \text{ mK}) = 235 \text{ k}\Omega$. Compared with Experiment II which is closer to the SIT critical point, the MR is smaller. Also, the peak field, $B^{\text{peak}} \sim 1.5 \text{ T}$, is lower than the value in Experiment II. It is reasonable as we think the peak location is proportional to the B_{c2} which is higher for a more robust superconductor. The AAO substrate is prepared under the same condition. Thus it is not surprising that we also observed the double oscillation again in this experiment.

With Gd doping, we observed the decreases in the resistance oscillation amplitude and the shrinking of the resistance peak. Something interesting to note is the comparison between magnetic impurity and magnetic field. Although both of

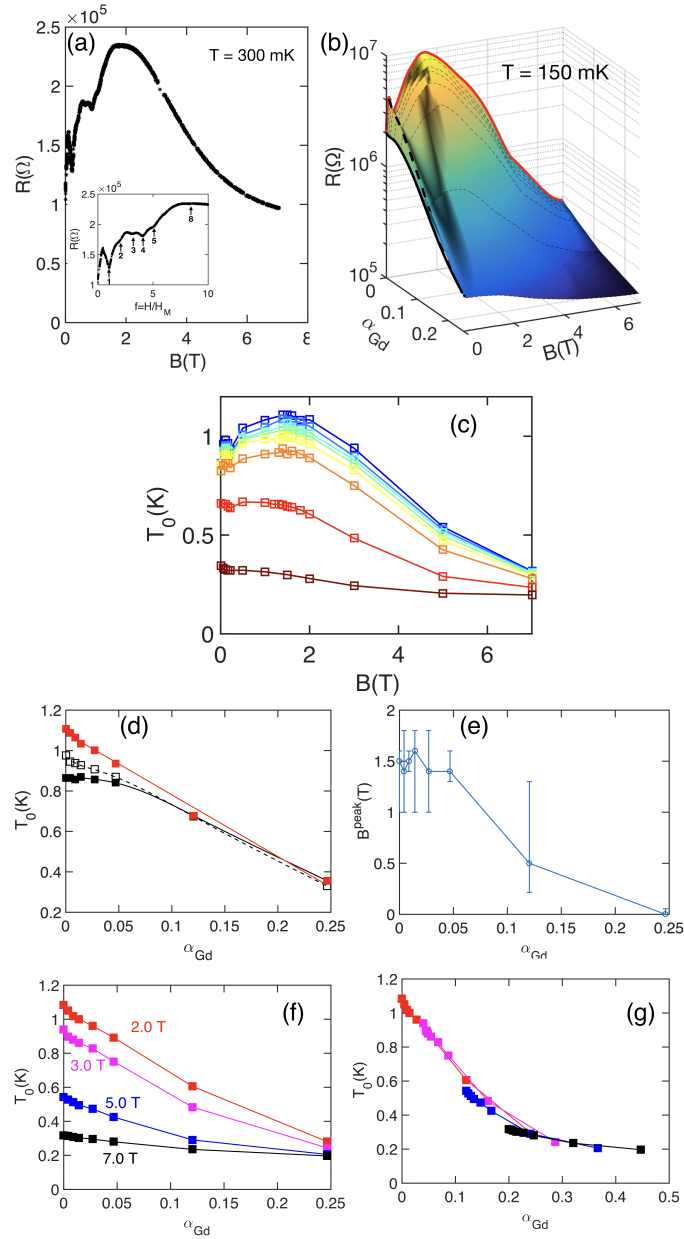


Figure 6.4.1: High field data from Experiment I. (a) Magnetoresistance for the zero doping film. (b) Surface plot $R(T = 150 \text{ mK}, \alpha_{Gd}, B)$. (c) T_0 with doping in field. (d) T^{peak} decreases with Gd. (e) Response of B^{peak} to doping. (f) T_0 beyond the peak. (g) Scaling of high field data. The horizontal axis is shifted by 0.04, 0.12, 0.2 for 3 T, 5 T and 7 T, respectively.

them induce pair breaking effects, the resistance monotonically decreases with Gd doping while in the low doping and low field limit, it shows $h/2e$ oscillations and positive magnetoresistance. This observation confirms that unlike magnetic impurity, the effect of magnetic field is more complicated and it does not simply reduce the superconducting gap. We will discuss this more in the discussion section.

Similar to Experiment II, both T_0^{peak} and B^{peak} decreases with doping. T_0^{peak} also shows linear relation with α_{Gd} . The slope is 3.0, which is very close to the value 3.2 from Experiment II. B^{peak} also has large uncertainties as the peak is flatter when the film is deeper in insulating state. But we can still see it decreases to zero with increasing doping amount. For the activation energies beyond the peak, we have an extra curve $B = 2$ T as the peak is below 2 T. Again, all of the values monotonically decrease with doping. We used the same shifting method, i.e. $B = 1$ T $\leftrightarrow \alpha_{Gd} = 0.04$. They scale quite well into a single curve.

6.5 Discussion

To understand the behaviors described above, we need to understand how the field influences the transport. It is very interesting to compare the peak induced by magnetic field at zero doping and the peak induced by magnetic impurity at zero field. It helps for understanding the exact roles the magnetic fields plays. First, they shows many similarities (see Fig. 6.5.1).

- T_0 has monotonically negative dependence on B (or α_{Gd}) when the system is deep in the insulating state.
- The peaks show up only when the system is closer to the SIT.
- The size of the peak increases and the position of the peak moves to a higher field (or magnetic impurity concentration) as the system gets closer to the

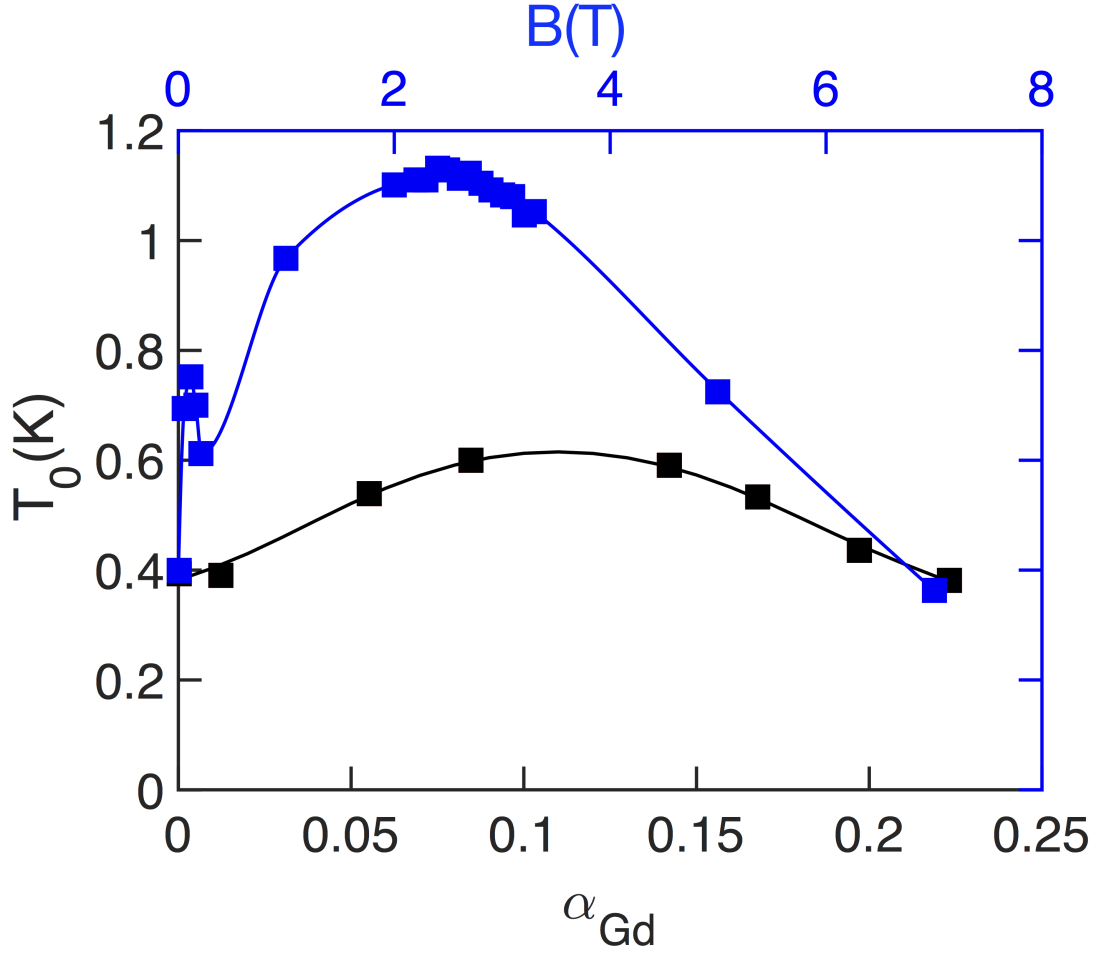


Figure 6.5.1: T_0 peak induced by magnetic field (blue) and magnetic impurity (black) in Experiment II.

SIT.

Those similarities can be understood if we think them as additive effects in terms of pair breaking. This also explains why B^{peak} moves to zero with increasing doping. The reduced field is compensated by the increased magnetic impurity.

Besides those similarities, there are also some pronounced differences between them.

- The magnetic field induced peak is $T_{0B}^{peak} \approx 1.1$ K, while the magnetic impurity induced peak is only $T_{0Gd}^{peak} \approx 0.6$ K.
- Magnetic field causes frustration effects where Little-Parks oscillation are ob-

served, which does not happen with magnetic impurity doping.

- The onset of magnetic field induced peak appears deeper in the insulating state. That is, with increasing thickness, positive MR appears before magnetic impurity peak. For example, in Experiment II (see Fig. 6.3.2) at $B = 1$ T, the MR is positive but T_0 decreases with doping. More significantly, in Experiment I, we observed positive MR in the low field region but T_0 decreases monotonically with doping in the whole field range. That suggests that the magnetic fields and magnetic impurities exert opposite effects on the transport in films farther from the SIT.

Those difference implies the magnetic field is not simply pair breaking effect as the magnetic impurity. It affects the transport at least in the following three ways.

- Reduce Δ .
- Interference around each pore. (Little-Parks oscillations)
- Interference between two islands. (Fraunhofer diffraction)

The first effect is the same as magnetic impurity doping. It causes the reduction of E_C and E_J at the same time. The second effect induces frustration to the system, which contributes to the $h/2e$ oscillation at low fields. The third effect is the key factor that differentiates the magnetic field from magnetic impurity. The diffraction effect gives the envelope of the maximum I_C . It is an extra factor that reduces the Josephson coupling. Continuing with the renormalization approach we discussed in the previous chapter, T_0 can be written as,

$$T_0 = \frac{2\Delta}{3\pi^2 g} \ln(gE_{C0}/\Delta) - \beta g \Delta < \cos(2\pi f) > F(B) \quad (6.5.1)$$

where $F(B) \sim \frac{|\sin(\pi\Phi/\Phi_0)|}{|\pi\Phi/\Phi_0|}$ is the Fraunhofer effect. It decreases with increasing flux. Thus, E_J decreases faster than simply pair breaking effect which has linear reduc-

tion rate. As a result, T_0 reaches a higher value in magnetic field than magnetic impurity doping. To quantify this effect, we know $F(B)$ reaches a minimum when $\Phi = \Phi_0$. Thus, the characteristic field $B = \frac{\Phi_0}{S}$, where the area is the junction thickness times the width. The width is $W \sim 20$ nm estimated from the SEM image. The thickness can be estimated from the inter-island spacing $t = \pi D_{int}/12$. Therefore, $B = \frac{\Phi_0}{Wt} \sim 4$ T, namely the Josephson coupling is almost completely destroyed at 4 T. This value falls into a reasonable range near the MR peak. Beyond this point, E_J is negligible. Thus, the magnetic impurity and magnetic field becomes equivalent.

The frustration term, $\langle \cos(2\pi f) \rangle$, is also tricky to deal with. Plaquette disorder that comes from pore size distribution needs to be considered. It can be written as (from private discussions with Enzo Granato),

$$E_J \propto (1 - \eta) + \eta \cos(2\pi f) \exp(-(2\pi f D)^2/2) \quad (6.5.2)$$

where D is the plaquette disorder that determines how many oscillations are visible. η is the coefficient representing the interference around the pore. It is the percentage of Josephson coupling energy that contributes to the Little-Parks oscillation. From the virtual quasiparticle screening model discussed in the last chapter, our experimental data show that the oscillation amplitude is one order magnitude smaller than the value of E_J . Thus, η is a very number at the order of 0.1 from our estimate.

Fig. 6.5.3 shows a plot of the model using some reasonable parameters described in the figure caption. It captures the main features we discussed above. Specifically, T_{0B}^{peak} is higher than T_{0Gd}^{peak} . Little-Parks oscillations appears at low fields. Note that T_0 drops to zero in the high field limit which does not happen in the experiment. In the model calculation, we did not incorporate the energy barrier for quasi-particle transport which becomes dominant in the high field regime.

Furthermore, we can see how $T_0(B)$ is affected by doping. Magnetic impurity

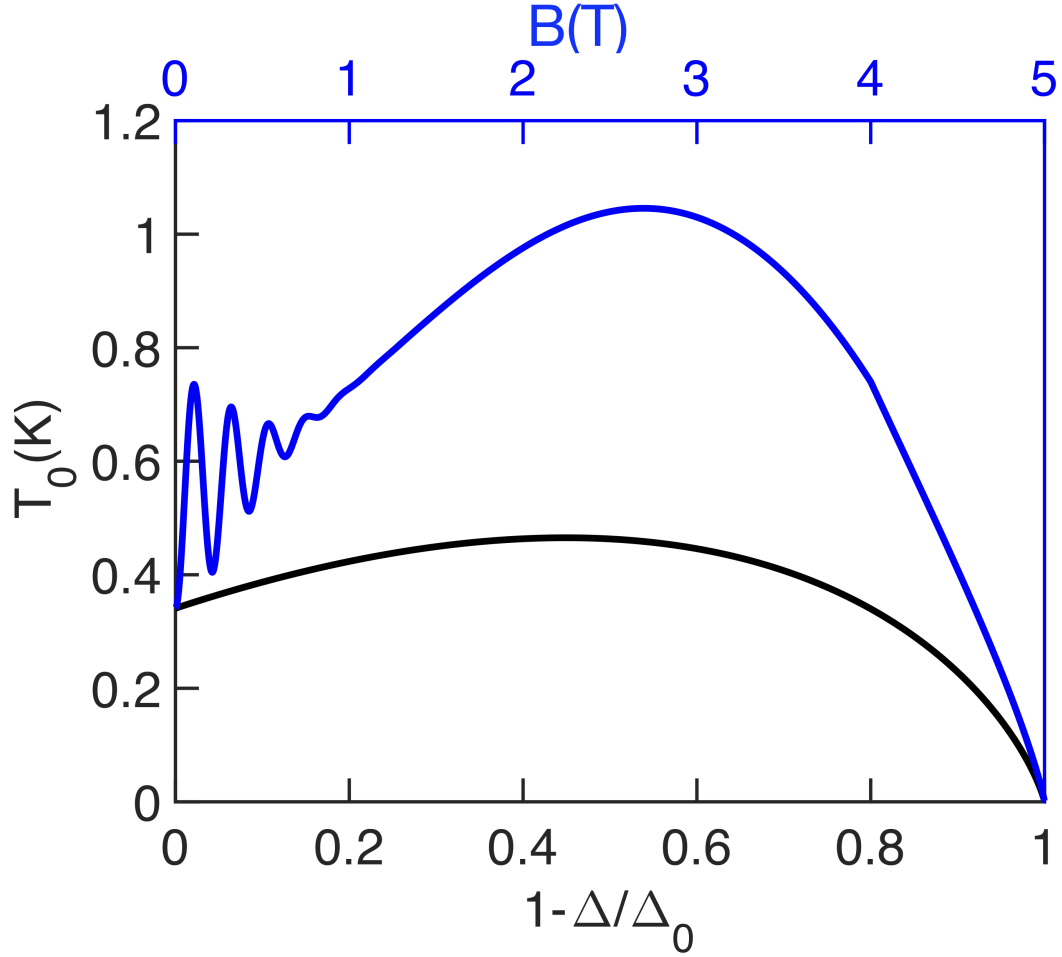


Figure 6.5.2: Model plot using Eq. 6.5.1. Parameters are set to be $g = 0.4$, $E_C = 200$ K, $\beta = 1$, $\Delta_0 = 5$ K, $B_{c2} = 5$ T, $D=0.1$, $\eta=0.1$, $\Phi/\Phi_0 = B/4$ for Fraunhofer term. The black curve is T_0 changes with doping in zero field. The blue curve is the field sweep at zero doping.

doping reduces Δ_0 and B_{C2} . The exact dependence is complicated. Arguably, we can assume B_{C2} is proportional to Δ_0 and they are reduced in the same trend. Fig. 6.5.3 shows several $T_0(B)$ curves with increasing doping. Compared to Fig. 6.3.2, for the same reason, it does not give correct shape beyond the peak. However, it succeed showing T_0^{peak} shrinks and B^{peak} moves to zero. Also, it shows the oscillation amplitude decreases with doping.

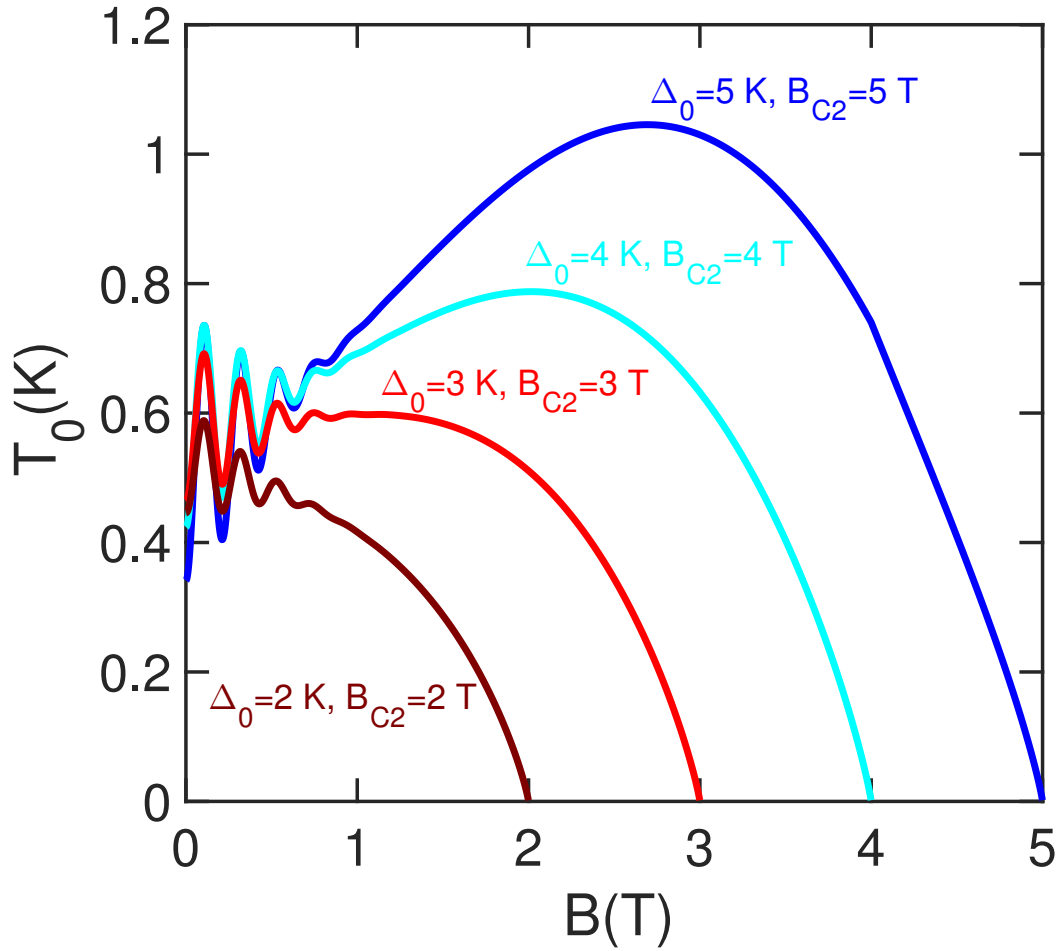


Figure 6.5.3: T_0 versus B with increasing doping. We assume Δ and B_{C2} are reduced in the same trend. Other parameters hold constant with doping.

6.6 Conclusion

To summarize, in this chapter we have shown the transport in magnetic field. The magnetic impurity provides a useful tool to study the roles of magnetic field. We have found both T_0^{peak} and B^{peak} decreases with doping. Beyond the peak, T_0 is still susceptible to magnetic impurity doping. It suggests Δ remains finite even at 7 T. The scaling features shows magnetic field and magnetic impurity are equivalent in high field region. A more detailed comparison suggests in low field region, magnetic field influences T_0 not only by shrinking the gap, but also through the phase

interference which further reduces the Josephson coupling energy. We added a Fraunhofer term to our model. It is able to capture most features in our experiment data.

Bibliography

- [1] H. Q. Nguyen, S. M. Hollen, M. D. Stewart, J. Shainline, Aijun Yin, J. M. Xu, and J. M. Valles. Observation of Giant Positive Magnetoresistance in a Cooper Pair Insulator. *Physical Review Letters*, 103(15):1–4, oct 2009.
- [2] Yen-Hsiang H Lin, J Nelson, and A M Goldman. The role of mesoscopic disorder in determining the character of the field-induced insulating regime of amorphous ultrathin films. *Physica C-Superconductivity and Its Applications*, 497:102–109, 2014.
- [3] G. Sambandamurthy, L. W. Engel, A. Johansson, and D. Shahr. Superconductivity-Related Insulating Behavior. *Physical Review Letters*, 92(10):107005–1, 2004.
- [4] G. Kopnov, O. Cohen, M. Ovadia, K. Hong Lee, C. C. Wong, and D. Shahr. Little-parks oscillations in an insulator. *Physical Review Letters*, 109(16), 2012.
- [5] M Steiner and A Kapitulnik. Superconductivity in the insulating phase above the field-tuned superconductor-insulator transition in disordered indium oxide films. *Physica C-Superconductivity and Its Applications*, 422(1-2):16–26, 2005.
- [6] MA Paalanen, AF Hebard, and RR Ruel. Low-temperature insulating phases of uniformly disordered two-dimensional superconductors. *Physical review letters*, 69(10):1604, 1992.

- [7] K H S Tan, K A Parendo, and A M Goldman. Evidence of spatially inhomogeneous pairing on the insulating side of a disorder-tuned superconductor-insulator transition. *Physical Review B*, 78(1), 2008.
- [8] T. I. Baturina, A. Yu. Mironov, V. M. Vinokur, M. R. Baklanov, and C. Strunk. Localized superconductivity in the quantum-critical region of the disorder-driven superconductor-insulator transition in TiN thin films. *Physical Review Letters*, 99(25):257003, dec 2007.
- [9] S M Hollen, G E Fernandes, J M Xu, and J M Valles. Fate of the Bose insulator in the limit of strong localization and low Cooper-pair density in ultrathin films. *Physical Review B*, 90(14), 2014.
- [10] S Okuma, T Terashima, and N Kokubo. Anomalous magnetoresistance near the superconductor-insulator transition in ultrathin films of $\text{a-mo-x-si } 1-x$. *Physical Review B*, 58(5):2816, 1998.
- [11] M A Steiner, G Boebinger, and A Kapitulnik. Possible Field-Tuned Superconductor-Insulator Transition in High- T_c Superconductors: Implications for Pairing at High Magnetic Fields. *Physical Review Letters*, 94(10):107008, 2005.
- [12] Amit Ghosal, Mohit Randeria, and Nandini Trivedi. Inhomogeneous pairing in highly disordered s-wave superconductors. *Physical Review B*, 65(1):014501, 2001.
- [13] S. M. Hollen, G. E. Fernandes, J. M. Xu, and J. M. Valles. Collapse of the Cooper pair phase coherence length at a superconductor-to-insulator transition. *Physical Review B - Condensed Matter and Materials Physics*, 87(5):11–14, 2013.

- [14] U Givan and Z Ovadyahu. Compositional disorder and transport peculiarities in the amorphous indium oxides. *Physical Review B*, 86(16), 2012.
- [15] V F Gantmakher, M V Golubkov, V T Dolgoplov, A A Shashkin, and G E Tsydynzhapov. Observation of the parallel-magnetic-field-induced superconductor-insulator transition in thin amorphous InO films. *Jetp Letters*, 71(11):473–476, 2000.
- [16] Adam Doron, Idan Tamir, Tal Levinson, Franzisca Gorniaczyk, and Dan Shahaar. The temperature dependence of the magneto-resistance peak in highly disordered superconductors. *arXiv preprint arXiv:1804.08471*, 2018.
- [17] I Shammass, O Cohen, M Ovadia, I Gutman, and D Shahaar. Superconducting correlations in thin films of amorphous indium oxide on the insulating side of the disorder-tuned superconductor-insulator transition. *Physical Review B*, 85(14), 2012.
- [18] SV Syzranov, Andreas Moor, and KB Efetov. Strong quantum interference in strongly disordered bosonic insulators. *Physical review letters*, 108(25):256601, 2012.
- [19] M Muller. Magnetoresistance and localization in bosonic insulators. *Epl*, 102(6), 2013.
- [20] BI Shklovskii and BZ Spivak. Scattering and interference effects in variable range hopping. *Hopping Transport in Solids*, 28:271, 1991.
- [21] Hui Lin Zhao, Boris Z Spivak, Martin P Gelfand, and Shechao Feng. Negative magnetoresistance in variable-range-hopping conduction. *Physical Review B*, 44(19):10760, 1991.

- [22] Thuong T Nguyen and Markus Müller. Magneto-oscillations of the mobility edge in coulomb frustrated bosons and fermions. *arXiv preprint arXiv:1606.07747*, 2016.
- [23] V M Galitski, G Refael, M P A Fisher, and T Senthil. Vortices and quasiparticles near the superconductor-insulator transition in thin films. *Physical Review Letters*, 95(7), 2005.
- [24] Y Dubi, Y Meir, and Y Avishai. Theory of the magnetoresistance of disordered superconducting films. *Physical Review B*, 73(5), 2006.
- [25] M Tinkham. Introduction to Superconductivity. *The McGraw-Hill Companies, Inc.*, 1996.
- [26] M D Stewart, H Q Nguyen, S M Hollen, A J Yin, J M Xu, and J M Valles. Enhanced suppression of superconductivity in amorphous films with nano-scale patterning. *Physica C-Superconductivity and Its Applications*, 469(13):774–777, 2009.
- [27] M Ovadia, D Kalok, I Tamir, S Mitra, B Sacépé, and D Shahar. Evidence for a Finite-Temperature Insulator. *Scientific Reports*, 5:13503, 2015.
- [28] Allen Miller and Elihu Abrahams. Impurity conduction at low concentrations. *Physical Review*, 120(3):745, 1960.
- [29] V. F. Gantmakher. *Electrons and Disorder in Solids*. Oxford University Press, aug 2007.
- [30] T. I. Baturina, C. Strunk, M. R. Baklanov, and A. Satta. Quantum metallicity on the high-field side of the superconductor-insulator transition. *Physical Review Letters*, 98(12):127003, mar 2007.

- [31] B Sacepe, J Seidemann, M Ovadia, I Tamir, D Shahar, C Chapelier, C Strunk, and B A Piot. High-field termination of a Cooper-pair insulator. *Physical Review B*, 91(22), 2015.

Chapter 7

Summary and Outlook

This thesis has primarily focused on two projects. One is the film growth on nano-patterned substrates with varying temperatures. The theory behind sets the foundation for the quench condensation method we use in low temperature experiment. The other project is the study of Cooper pair insulator state near SIT using magnetic impurity as a probe. In this chapter, I will discuss the main results we found. In the last part, I will talk about some possible future experiments that can help address the open questions.

7.1 Summary

We are able to make AAO templates with varying inter-pore spacings by different combinations of anodizing voltage, acidic electrolyte, concentration and temperature. Among them, 100 nm AAO shows the best ordering. In some experiments, the ordering was intentionally made worse by covering the aluminum sheet with a piece of teflon tape [1]. In the other limit, improving the ordering is not easy. Lithography can be used to create nano-indents [2], but it suffers from cost and scalability problems. The pore size is also controllable by etching the template in phosphoric acid after the regular anodization procedures. We can manipulate the island size or the width of inter-island links by varying the etching time. SEM and AFM are primarily used to characterize the template. SEM is helpful to check the large area properties, like the ordering, inter-pore spacing, porosity etc. AFM provides more information in the vertical direction. It can be used to calculate the roughness of the surface.

One of the primary uses of AAO is providing the templates for nano-material fabrication. We studied the film growth on the surface of AAO. Ordered nano crystal arrays are achieved using several different evaporating materials. We also investigated the influence of substrate temperature. With sufficiently high temperature, the adatoms obtain enough energy to diffuse. If it satisfies some specific surface tension relations, the film becomes granular. By contrast, if the substrate temperature is low, the evaporated atoms will stay where they landed. The film will follow the same structure as the substrate. This is the foundation of quench condensation we used in the low temperature transport measurement experiment, where the evaporation takes place below 10 K.

In the other project, we studied the Cooper pair insulating state near the SIT probed by magnetic impurity doping. It is based on our previous investigations of

the thickness tuned Insulator-superconductor transitions on AAO substrates. There were two major experiments done. One is on a film farther and the other one is on a film closer to the transition. We studied the activation energy T_0 of the system. It is the characteristic energy scale on the insulating side. At zero field, they show contrasting behaviors with Gd doping. The film closer to SIT shows a peak with doping while the other one monotonically decreases with increasing Gd concentration. For $f = 1/2$, both of the experiments show the reductions of T_0 by doping. Those behaviors lead us to consider the dissipative process along with Cooper pair tunneling. In the theoretical model, the Cooper pair charging energy E_C is renormalized by virtual quasi-particle tunneling. It helps avoiding the huge bare charging energy set by the geometry of the substrate, and it also renders the dependence of T_0 on the superconductivity gap. Our results agrees well with this model with some reasonable parameters.

We also inspected how the activation energies in magnetic field change with doping. The two experiments behave similarly in this case. T_0 peaks in magnetic field, similar to the giant magnetoresistance. On the right side of the peak, T_0 is still susceptible to doping, indicating that the gap remains finite even in the high field region. T_0 versus α_{Gd} for different fields scale well into a single curve. This suggests the magnetic field and magnetic impurity are equivalent in the high field region. Both T_0^{peak} and B^{peak} decreases with doping. By careful comparison of the effects of magnetic field and magnetic impurity, we find that the magnetic field is not purely pair breaking when the field is low. In addition, it introduces the interference along the pore which contributes to the Little-Parks oscillation in our system. Also, it causes the interference between the neighboring superconducting islands, known as Fraunhofer diffraction. Plugging those terms into the expression for T_0 , we are able to capture the major features observed in our experiments.

7.2 Future Experiments

Despite a lot of work done in this area, there still some open questions and some interesting projects are can to be done in our lab.

First, the AAO fabrication process involves several parameters to vary. To have more controllable and consistent substrate, we need to carry out systematic studies of each parameter. Specifically, it is very useful if we can manipulate the roughness of the system. It will help us determine the amount of inhomogeneities that is necessary to localize Cooper pairs [3, 4]. Another project related is to fabricate ordered 500 nm substrate. It involves new design of the anodizing cell that has better heat dissipation. Because of the limit from the peak, we can only observe limited $h/2e$ oscillations. 500 nm substrate can reduces the oscillation period by a factor of 25. It enables us to achieve high frustration number and study some interesting physics behind.

For the SIT experiment, first we need to pay attention to the thickness of the Sb wetting layer. Although the system is supposed to be unaffected as long as the wetting layer is sufficiently thick, some experimental results differ for varying Sb thickness. A careful study of Sb's influence will be helpful. Keeping it a constant for different experiments is always a good idea. Also, we have observed double low field oscillations in some experiments. We assume it is because the inter-island link is too wide. Experiments with substrates of various pore diameters can help test that idea.

For magnetic impurity doping, we have shown two experiments in the insulating regime. The model is still valid on the superconducting side near SIT where E_J is slightly larger than E_C . A future doping experiment on the film that just pass the critical point will be helpful to further support the theory. Also, deep into the insulating regime, the transport is fermionic. We expect $T_0 = \Delta + E_C/4$ [5]. T_0

should go down approximately linearly with increasing doping. It will also be an interesting experiment to do. Moreover, for the scaling of high field data, we found $B = 1 \text{ T} \leftrightarrow \alpha_{Gd} = 0.04$. More data points at various high fields are needed to verify that.

There are also some other transport experiments that attract great attention. Recently, several groups have reported metallic state which is forbidden in the scaling theory [6, 7, 8, 9]. The origin of the new phase is widely debated. It is interesting to see if it can be observed in quench condensed system. Also, some other groups have observed superinsulating state where the conductance is zero at finite temperature and related it to charge Berezinskii-Kosterlitz-Thouless transition [10, 11, 12]. They have shown a lot of unconventional features, including non-linear IV characteristics and non-activated transport at extremely low temperatures. It is worth trying in our system. Those measurements are carried out in the extremely high resistive regime. In order to do that, new measurement circuits with low noise current amplifiers are required.

Bibliography

- [1] HQ Nguyen, SM Hollen, J Shainline, JM Xu, and JM Valles Jr. Driving a superconductor to insulator transition with random gauge fields. *Scientific reports*, 6:38166, 2016.
- [2] Hideki Masuda, Haruki Yamada, Masahiro Satoh, Hidetaka Asoh, Masashi Nakao, and Toshiaki Tamamura. Highly ordered nanochannel-array architecture in anodic alumina. *Applied Physics Letters*, 71(19):2770–2772, 1997.
- [3] James Joy. *Studies on the Bose Insulator to Fermi Insulator Crossover Near the Two-Dimensional Superconductor-Insulator Transition*. PhD thesis, Brown University, 2017.
- [4] S M Hollen, G E Fernandes, J M Xu, and J M Valles. Fate of the Bose insulator in the limit of strong localization and low Cooper-pair density in ultrathin films. *Physical Review B*, 90(14), 2014.
- [5] P Delsing, C D Chen, D B Haviland, Y Harada, and T Claeson. Charge solitons and quantum fluctuations in two-dimensional arrays of small Josephson junctions. *Physical Review B*, 50(6):3959, 1994.
- [6] AW Tsen, B Hunt, YD Kim, ZJ Yuan, S Jia, RJ Cava, J Hone, Philip Kim, CR Dean, and AN Pasupathy. Nature of the quantum metal in a two-dimensional crystalline superconductor. *Nature Physics*, 12(3):208–212, 2016.
- [7] T. I. Baturina, C. Strunk, M. R. Baklanov, and A. Satta. Quantum metallicity on the high-field side of the superconductor-insulator transition. *Physical Review Letters*, 98(12):127003, mar 2007.

- [8] Yongguang Qin, Carlos L Vicente, and Jongsoo Yoon. Magnetically induced metallic phase in superconducting tantalum films. *Physical Review B*, 73(10):100505, 2006.
- [9] Philip Phillips and Denis Dalidovich. The elusive bose metal. *Science*, 302(5643):243–247, 2003.
- [10] Valerii M. Vinokur, Tatyana I. Baturina, Mikhail V. Fistul, Aleksey Yu. Mironov, Mikhail R. Baklanov, and Christoph Strunk. Superinsulator and quantum synchronization. *Nature*, 452(7187):613–615, apr 2008.
- [11] M Ovadia, D Kalok, I Tamir, S Mitra, B Sacépé, and D Shahar. Evidence for a Finite-Temperature Insulator. *Scientific Reports*, 5:13503, 2015.
- [12] Alexey Yu Mironov, Daniel M Silevitch, Thomas Proslier, Svetlana V Postolova, Maria V Burdastyh, Anton K Gutakovskii, Thomas F Rosenbaum, Valerii V Vinokur, and Tatyana I Baturina. Charge berezinskii-kosterlitz-thouless transition in superconducting nb_{1-x}tin films. *Scientific reports*, 8(1):4082, 2018.

