EFFECTS OF DISORDER AND GEOMETRICAL CONSTRAINT ON SUPERCONDUCTIVITY IN SYSTEMS OF REDUCED DIMENSIONS

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Abstract

Experimental studies on the effects of disorder and geometrical constraints in several reduced dimensional superconducting systems have been carried out. Novel phenomena have been found, including the possible formation of an electron droplet state in the electron glass in highly disordered ultrathin Bi films prepared by quench deposition, a metallic state with an energy gap in disordered Au$_{0.7}$In$_{0.3}$ thin films, and a magnetic-flux induced superconductor-normal metal (S-N) transition in doubly connected ultrathin cylinders.

Amorphous Bi films prepared by quench deposition were studied in situ. These films exhibited a two-dimensional (2D) superconductor-insulator transition (SIT) as the film was made increasingly thicker, consistent with previous studies. In superconducting Bi films, a crossover from linear to nonlinear behavior was observed in the current-voltage ($I$-$V$) characteristic in the transition regime. The results are analyzed within the context of current-induced vortex-antivortex unbinding. Unlike the standard treatment, a finite cutoff length in the logarithmic interaction between vortex-antivortex pairs is taken into consideration. The implications of this interaction on the 2D SIT are discussed.

In subsequent studies, unexpected behavior was found in quench condensed Bi films deep in the insulating region, i.e. at the initial stage of film growth. A positive temperature coefficient of resistance ($dR/dT > 0$) emerged as the temperature was lowered, with the resistance reaching a minimum before the expected negative $dR/dT$ was obtained. This behavior was accompanied by a nonlinear and asymmetric $I$-$V$ characteristic. As the film became thicker, conventional variable-range hopping was recovered. The crossover in the electrical transport properties is attributed to an amorphous to granular structural transition. The behavior in the amorphous phase is discussed in the context of the formation of metallic droplets within the electron glass.

In superconducting Au$_{0.7}$In$_{0.3}$ films, which can be modeled as a random array of superconductor-normal metal-superconductor Josephson junctions, a magnetic field-induced metallic state was observed. The metallic state, characterized by a temperature-independent resistance, was found at temperatures much lower than where a substantial drop in resistance occurred. Whereas non-linear $I$-$V$ characteristics were found in the superconducting state, ohmic
behavior was present in the metallic state. However, tunneling studies indicated that an energy gap, similar to the superconducting energy gap, is present in the metallic phase. The implications of these observations are discussed.

Finally, electrical transport measurements in ultrathin doubly connected superconducting cylinders of Al confirmed theoretical predictions of a destructive regime, characterized by the loss of global phase coherence in the zero-temperature (T=0) limit. The phenomenon occurs in samples with diameters smaller than the T=0 superconducting coherence length, in applied magnetic flux of half-integer superconducting flux quanta (Φ₀ = ℏc/2e). In the destructive regime, a broad drop in resistance was also observed, suggesting the presence of superconducting fluctuations. Features in the resistive transition near this regime suggest that the loss of superconductivity is associated with the formation of normal metal bands.
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1. Introduction

The effect of geometry and disorder on the superconducting state in reduced dimensional systems is an interesting problem in contemporary condensed matter physics. In general, these constraints hinder and suppress the formation of a globally phase-coherent superconducting state. Studies of these effects have continued to reveal novel phenomena, challenged existing theories and provided insight into the fundamental nature of the superconducting state.

Perhaps the most notable effect of disorder in the superconducting system is the two dimensional (2D) superconductor-insulator transition (SIT) (for a review, see Goldman and Markovic, 1998). The interplay between superconductivity and localization has received considerable attention, as it involves two distinctly opposite tendencies of electronic motion: the coherent motion of electrons over the entire sample and the limitation of the spatial extent of the electron wavefunction that preempts the establishment of coherent motion. The issue is particularly interesting in 2D, as this dimension is special for both behaviors. In 2D, true superconducting long range order is only possible at zero temperature ($T=0$), while the modern scaling theory of localization predicts that even arbitrarily weak disorder will lead to localized electron states (Abrahams et al, 1979). Therefore, the interplay between the two behaviors in the same 2D experimental system can lead to unique physical phenomena.

This issue has been extensively studied in quench condensed films of metals, prepared by evaporating material onto substrates at liquid helium temperatures to substantially inhibit atomic mobility resulting, for certain materials, in amorphous films which are inherently disordered. With increasing film thickness, the disorder is reduced such that the attractive interaction responsible for superconducting pairing overcomes the localization effects and the disorder-enhanced Coulomb repulsion. A direct transition from insulating to superconducting behavior at the lowest temperatures with increasing film thickness is possible (Haviland, Liu and Goldman 1989).

Such a 2D SIT is a continuous quantum phase transition (QPT) occurring at zero temperature, where crossing the phase boundary is associated with a change in the ground state of the system. The hallmark of a QPT lies in the scaling of the system’s physical properties (for a review see Sondhi et al, 1997; Sachdev, 2001). A scaling theory and phase diagram has been
postulated, based on the assumption that the transition is fully described by interacting bosons in the presence of disorder (Fisher et al, 1990). Scaling of the 2D SIT has been experimentally demonstrated for some systems. However, the universality class of the transition remains under contention, and the applicability of a completely bosonic model has been questioned (Valles et al, 1992; Hsu et al, 1995). In addition, the question of whether an SIT truly occurs at zero temperature has also been raised.

As to geometrical constraints, it is known that sample topology has strong effects on superconductivity. The quintessential example is an effect unique to doubly connected superconducting structures: fluxoid quantization (London, 1950). The quantization is directly related to the requirement that the superconducting wavefunction be single valued. Experimentally, fluxoid quantization is most evident in the resistive transition of a superconducting cylinder in an axial magnetic field. Magnetic flux induces shifts in the superconducting transition temperature and an oscillation in the magnetoresistance at a fixed temperature (known as Little-Parks resistance oscillations) or, alternatively, modulation in the superconductor-normal metal (SN) phase boundary (Meyers and Meservey, 1971).

Current advances in micro- and nano-fabrication technology have made it possible to further the study of geometrical effects on superconductivity. Of current interest are mesoscopic superconductors, where the structures are of sizes comparable to or smaller than the zero temperature superconducting coherence length. New phenomena found in this regime include the paramagnetic Meissner effect (Geim et al, 1994), quantization of the energy of the Bose condensate (Geim et al, 1997), and the suppression of superconductivity in nanoscale samples (for a review see von Delft and Ralph, 2001). Further, studies specifically focused on sample topology on this scale have reported that the sample shape determines characteristic features of the SN phase diagram (Moschalkov et al, 1995). The mesoscopic scale has potential for more surprising phenomena.

This thesis represents work on the effects of disorder and geometrical constraints in several superconducting systems of reduced dimensions. Studies in disordered, ultrathin, quench condensed Bi films are presented, in an effort to address questions raised by previous studies on the 2D SIT. Results are also reported in another disordered thin film system of Au$_{0.7}$In$_{0.3}$, which can be modeled as a random array of superconductor-normal metal-superconductor Josephson junctions. Lastly, the effects a doubly connected geometry on the mesoscopic scale are examined in ultrathin cylinders of superconducting Al.
The organization of the rest of the thesis is as follows: Chapter 2 describes experimental techniques, including sample fabrication processes and measurement details. Chapter 3 presents results on the electrical transport properties of quench condensed Bi films in both insulating and superconducting regions. Chapter 4 reports observations in the uniquely disordered thin film system of Au$_{0.7}$In$_{0.3}$, specifically a parallel magnetic field driven superconductor-normal metal transition. Chapter 5 involves size and topology effects on the superconducting state, focusing on results found in ultrathin, doubly connected cylinders. Conclusions are given in Chapter 6.

A note on figures and references: Figures are placed at the end of each section. Citations are given in the text using parenthetical (author, year) style, with long lists (4 or more) placed in footnotes. A full reference list, arranged alphabetically by author, is included at the end of the thesis.
2. Experimental techniques

The first four sections primarily focus on sample fabrication issues. Details regarding low temperature, electrical transport measurements for all samples are discussed in the last section.

2.1. Quench condensed, ultrathin Bi films

Quench condensed films, prepared by depositing metal vapor directly onto substrates held at liquid helium temperatures (Komnik, 1982), have played an important role in elucidating the effects of interactions, disorder, and geometrical constraint on the properties of an electronic system. Films made in this manner are conducting at a thickness less than 10Å, making it a two-dimensional (2D) disordered system. Quench condensed films have been used in numerous experimental studies of superconductivity, localization, and their interplay (Liu and Goldman, 1994; and references therein). More recently, it has played an important role in the study of quantum phase transitions, such as the 2D superconductor-insulator (S-I) and metal-insulator (M-I) transitions.

Ultrathin, quench condensed films of Bi were prepared in situ in a $^3$He cryostat with a base temperature of 0.3K. The homemade quench deposition system (Zadorozhny and Liu, 1996) is installed in the inner vacuum can (IVC) of the $^3$He cryostat. A small thermal evaporator is attached to the bottom tapered vacuum seal of the IVC, directly opposite the substrate. The evaporator is composed of four ceramic-metal electrical feedthroughs, which can supply current to two independent evaporation sources. A ceramic base serves as support and electrical insulation for all electrical elements. The two homemade tungsten evaporation baskets were pre-wetted with the evaporation material in a conventional room temperature evaporator prior to cooling down. This is important as the residual strain in the tungsten wire is removed in this process to avoid uncontrolled deformation during the low-temperature deposition. A stainless sheet shields the two baskets from one another, necessary when evaporating two different materials. While up to 2 different sources can be used, for the studies reported here, both baskets were filled with Bi of 99.9999% purity. A schematic of the system is illustrated in Fig. 2.1.
As shown in Fig. 2.1, the sample stage and substrate are shielded from the evaporation sources by a copper cylinder with a shutter, both thermally anchored to the 1K pot. A rail and gear system, connected to a linear motion feedthrough on top of the cryostat, opens and closes the shutter. Since the vacuum can is immersed in a liquid helium bath, the cryopumping of the IVC walls provides an ultrahigh vacuum (UHV) environment.

Films were deposited atop a glazed alumina substrate mounted on a Cu (oxygen free high purity) sample stage. Thermal sinking of the substrate to the sample stage is achieved by mechanical means, i.e. by holding it down onto the sample stage. To enhance the thermal conduction, a small amount of Apiezon N grease was applied to the back of the substrate. The sample stage is, in turn, kept in thermal contact with the $^3$He pot.

As these films are sensitive to the initial growth conditions, care was taken to clean and prepare the substrate. The substrates were cleaned ultrasonically in acetone, rinsed in isopropanol, and blown dry. After cleaning, handling was kept to a minimum and the substrate stored in a closed sample container to avoid particle contamination.

Prior to the cool down and subsequent quench deposition, electrical leads were evaporated onto the substrate in a conventional room temperature evaporator. The lead pattern was defined by a shadow mask and composed of two Au layers. The initial Au layer was typically a >300Å thick film and meant for contact to Cu wires, which would eventually connect to the measurement instruments. To make good contact to the ultrathin Bi films, however, a thinner (<100Å) Au film was evaporated atop the thicker Au film and extending into the area where the quench condensed film would be deposited. The use of a shadow mask to lay down the thin Au layer was particularly useful in producing the gradual edge necessary to make contact to the ultrathin quench condensed film. A schematic of these Au electrical leads is given in Fig. 2.2a.

In the study involving films at the initial stage of growth, the relatively high resistivities involved lead to immeasurably high resistances in samples of conventional size. Preparing films of extremely short length but relatively large width, which was conveniently done using a two-point probe configuration, helped circumvent this difficulty. Films were deposited across a narrow gap between two Au contacts and atop the entire Au electrode. Since the Au film is significantly more conductive than the initial Bi films, the resistance of the Bi film in the gap, plus the contact resistance dominate the measured resistance. The narrow gap was created using a narrow micron-scale G.E. varnish filament as a shadow mask. The combination of the gradual slope and the good conductivity of the Au thin film are expected to minimize the contact resistance. Two film sequences were studied simultaneously, of lengths 2.5µm and 35µm, respectively, and both 0.5mm in width. A schematic of the sample configuration is shown in Fig 2.2b.
The Bi film geometry is defined by a copper shadow mask mounted < 0.5mm above the substrate. The pattern allows for four-point electrical transport measurements and is illustrated in Fig. 2.1c and 2.2a. The center electrode enables a comparison of the properties of the left and right side of the film to check for homogeneity across the sample. Additional probes allow for Hall measurements. The shadow mask used in this case and the shadow mask for the electrical leads (see above) were made to match one another precisely.

Bi was evaporated at a constant rate of 0.1-1.0Å/s, as monitored by two 6MHz quartz crystal thickness monitors mounted on the copper cylinder, adjacent to the substrate (see Fig. 2.1c). The uncovered sensor monitors the evaporation rate at all times to help ensure that the shutter will be opened only after a stable evaporation rate is established. The other sensor remains shielded until the deposition begins. The thickness monitor uses the resonant frequency of the exposed quartz crystal to sense the mass of the deposited film attached to its surface. The film thickness is computed using the known relationship between the mass and the measured frequency of the sensor crystal (Sycon Instruments, 1994), and the density of the material. The thickness values reported here are, therefore, nominal as the bulk Bi density (which does not necessarily equal the Bi film density) was used.

During the Bi deposition the substrate temperature remains below 6K as determined by a Cernox thermometer mounted on the sample stage. After deposition, the film is kept below 10K to prevent irreversible annealing.

The initial film deposition was 5Å thick, deposited at ~1Å/s. The film was then checked for signs of finite conductance (< 1 GΩ) and a voltage response to an applied bias current. Subsequent layers were 1Å thick, deposited at ~0.2Å/s. The film was checked for conductance after each deposition. At a thickness of 12Å, the deposited layer thickness was decreased to 0.5Å and deposited at 0.1Å/s. Films typically became conducting at approximately 15Å. Electrical transport measurements were carried out. After all measurements were done, more material was deposited onto the existing film, often in 2Å, 1Å, or 0.5Å increments, as desired. Transport measurements were carried out, and the process repeated. In this way, a sequence of films with ideally the same growth conditions was studied in situ. This procedure is illustrated in Fig. 2.3.

Direct morphological and structural studies of the quench deposited films created in this apparatus have not been attempted. A thorough study of the film structure would require in situ atomic force microscopy (AFM) or scanning tunneling microscopy (STM), and is beyond the scope of the current work. Ex situ (room temperature, ambient conditions) characterization are not extremely useful, as these films are known to irreversibly anneal as the temperature increases (Komnik, 1982). An inspection of just warmed films under an optical microscope at 20x
magnification reveals material beading (island formation) that is likely a result of the warm up to room temperature.

However, electronic transport behavior consistent with reentrant superconductivity, the hallmark of granular superconducting films, has been found in films nearest the SIT observed in these films (see Ch. 3.1). These observations indicate that the Bi films prepared in this system are granular, though each grain itself should be amorphous. It is of note that these films were not grown on a precursor layer of Ge, known to aid in the growth of macroscopically amorphous (as defined by the features seen near the SIT) films. However, previous attempts to grow Bi/Ge in this apparatus have not shown results indicating the growth of a macroscopically amorphous film. The Ge layer was deposited by both room temperature deposition and quench condensed just prior to the Bi deposition, conditions tried in separate runs (Zadorozhny and Liu, 1996). The granularity in these films may also be related to the source to substrate distance. A relatively short source-substrate distance (approx. 10 cm) may also result in the local substrate temperature being high, giving the deposited atoms sufficient mobility to form grains.
Fig. 2.1 Quench deposition system. (a) Schematic of the $^3$He cryostat equipped with a thermal evaporator. (b) Thermal evaporator mounted in the taper seal at the bottom of the IVC. (c) Accompanying shutter system. When closed, the shutter covers the mask, substrate, and quartz sensor 2.
Fig. 2.2 Sample configuration for quench deposited films. (a) Typical film geometry, showing both the quench deposited film and the room temperature evaporated Au electrical leads. (b) Schematic for ultrashort films.

Fig. 2.3 Flow diagram for fabricating and measuring a sequence of films (Adapted from Liu, 1991).
2.2. Superconducting Au$_{0.7}$In$_{0.3}$ films and tunnel junctions

The Au$_{0.7}$In$_{0.3}$ binary alloy system is an interesting system to study the effects of disorder on superconductivity. This system is unlike granular superconducting films which are typically characterized by a superconductor-insulator-superconductor (SIS) type array, and therefore subject to carrier localization due to charging energy and quantum phase fluctuations. In comparison, the Au$_{0.7}$In$_{0.3}$ system, though granular, is characterized by superconductor-normal metal-superconductor (SNS) type of intergrain coupling. The system is disordered as far as superconductivity is concerned, even though the carriers (Cooper pairs or electrons) are not particularly confined. It is notable that while artificial proximity-coupled Josephson junction arrays have been examined in some detail, granular materials that can be modeled as an SNS junction array have hardly been studied.$^1$

Au$_{0.7}$In$_{0.3}$ binary alloy films were prepared at ambient temperature in a conventional evaporator. The deposition is carried out in high vacuum ($< 10^{-6}$mbar) by back-to-back thermal evaporation of 99.9999% pure Au and In. The two tungsten-coil sources, separated by a shield, were 8cm apart and 25cm away from the substrate. Glazed alumina or polished quartz was used as substrates. During evaporation, the deposition rate was controlled using a quartz crystal thickness monitor.

Alternating layers of Au and In were deposited sequentially, the top and the bottom layers being Au. The respective layer thicknesses for Au and In, not exceeding 10nm each, were determined based on the desired stoichiometric ratio, in this case 70-30. The total film thicknesses $t_{Au}$ and $t_{In}$ of Au and In, respectively, for a specified ratio is given by $t_{In}/t_{Au} = 1.5412 n_{In}/n_{Au}$, where $n_{In}$ and $n_{Au}$ are the stoichiometric fractions of In and Au, respectively, reflecting the density difference between In and Au.

The initial mixing of Au and In apparently occurred during the evaporation, at the ambient temperature. Subsequent interdiffusion continued at room temperature. Resistance measurements showed no evidence for a superconducting transition at 3.4K in any film, indicating that no macroscopic fraction of pure In was present. Structural and electrical transport studies (Zadorozhny and Liu, 2002) indicate the presence of several Au-In phases in these films, including Au$_{0.9}$In$_{0.1}$ with $T_c = 77$mK; two In-rich phases with $T_c$s of 0.45K and 0.65K, that are likely compositions of AuIn; and another In-rich phase with $T_c = 0.8$K. This phase separation is directly responsible for a spatial distribution of the local superconducting transition temperature $T_c^0$. At temperatures below their onset superconducting transition temperatures $T_c^{\text{onset}}$, the In-rich
regions become Josephson coupled to one another, resulting in a random network of Josephson junctions of SNS type. A schematic of the film morphology is shown in Fig. 2.4. Further details may be found in Zadorozhny (2003).

A typical film was 6mm long and 0.5mm wide, patterned by a shadow mask for four-point electrical transport measurements. The sample configuration is very similar to that of quench condensed Bi thin films, shown in Fig. 2.2a.

For tunneling studies of Au$_{0.7}$In$_{0.3}$, both superconductor-insulator-superconductor (SIS) and superconductor-insulator-normal metal (SIN) junctions were prepared (Wang, 2002). The junctions consisted of Al or Mg as the first electrode, the native Al or Mg oxide as the insulating layer, and Au$_{0.7}$In$_{0.3}$ as the top electrode. Junctions were made in the standard cross geometry on glass substrates, as glass was found to be the best substrate for the counterelectrode (for Mg, in particular) used in these studies. Figure 2.5 shows a schematic of the tunnel junctions.

The Al (or Mg) film was the first layer created, deposited at ambient temperature in a thermal evaporator with the film geometry defined by a shadow mask. The film thickness was mainly determined by two factors. The first being that film is thick enough to be continuous and conducting. For Al on glass, this corresponds to a thickness $t \approx 100\text{Å}$; for Mg on glass $t \approx 150\text{Å}$. The second factor is that the film is thin enough that the top Au$_{0.7}$In$_{0.3}$ film remains continuous and conducting. As the cross geometry demands that the top electrode straddle the bottom electrode, having a relatively thick bottom electrode can result in a discontinuity in the Au$_{0.7}$In$_{0.3}$ film. The Au$_{0.7}$In$_{0.3}$ films under study were typically $< 250\text{Å}$. These two constraints favor a bottom electrode film thickness of 100-250Å.

The growth of the native oxide layer of Al (or Mg) was aided by the use of glow discharge. After the deposition of Al (or Mg), without breaking vacuum, O$_2$ was leaked into the chamber up to 150mtorr, and a plasma ion discharge for 5-10 minutes at 10-20% of the maximum available power of the system (4000V*30mA a.c.). It is difficult to say how these parameters ultimately affect the barrier, as a systematic trend was not found. However, by increasing all these parameters, a higher junction resistance was obtained.

After the initial Al (or Mg) deposition and oxygen plasma treatment, the evaporator was vented, evaporation sources and shadow masks exchanged, and the chamber pumped down again to deposit a Au$_{0.7}$In$_{0.3}$ film. This process was carried out in the minimum amount of time possible to help prevent any contamination of the tunnel junction surface, but varies from 15-45 minutes.

The deposition of the final Au$_{0.7}$In$_{0.3}$ layer was carried out at liquid nitrogen temperatures, as the reduced temperature helped to obtain a good insulating barrier. When the system reached high vacuum, liquid nitrogen (LN) was slowly run through copper tubing soldered to the cold

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1 For a previous study, see the work by Johnson and Kadin (1998) on niobium nitride thin films.
stage (see Zadorozhny, 2003). Thermal contact between the substrate and the sample stage was achieved by mechanical means. A thermocouple, in contact with the stage, was used to monitor the temperature of the cold stage. The sample was allowed to warm to ambient temperature before the chamber was vented to avoid water condensation. Ambient temperature N2 or He2 was run through the cooling lines to speed the warming of the sample to room temperature.

It should be noted that the $\text{Au}_{0.7}\text{In}_{0.3}$ films prepared in the procedure described above had substantially wider superconducting transitions than those prepared at ambient temperature without a counter electrode for tunneling studies. The transition width broadening may be attributed to the increased disorder. The reduced deposition temperature may inhibit the initial intermixing of the Au and In layers during deposition. However the transport properties of these films qualitatively agree with those measured previously (Zadorozhny and Liu, 2002). Alternatively, as the tunnel junctions were made on plain glass slides, as opposed to glazed alumina substrates used previously, the substrate effects may also result in differences in transport properties.

Depositing the Au-In film at reduced temperatures may have additional consequences on the junction character. LN is introduced into the cooling lines when the evaporator system reaches a pressure of approx. $10^{-6}$ torr. The reduced temperature of the sample stage cryopumps any remaining gas in the chamber onto the stage – and the substrate. It is likely that a layer of residue gases condensed on the previously deposited Mg-MgO$_x$ film. The interface is, therefore, more complicated than what is expected from a room temperature prepared Mg-MgO$_x$-$\text{Au}_{0.7}\text{In}_{0.3}$ junction.

Thin Cu wires (0.002” diameter) were attached to the electrodes by Ag epoxy. To prevent oxidation of the $\text{Au}_{0.7}\text{In}_{0.3}$ film or possible junction breakdown, the epoxy was not baked at elevated temperatures (as suggested by the epoxy manufacturer to improve the conduction and contact properties), but was instead allowed to cure at room temperature for 24 hours. Samples were stored in a desiccator for the duration of this period. If a Mg counterelectrode was involved (as in SIN junctions), Cu wires were attached with Ag paint, as Ag epoxy did not result in a measurable contact between the Cu wire and the Mg film. In this process, Ag paint was applied immediately after the Mg film was lightly scratched to expose a fresh (non-oxidized) layer of Mg.

The time between sample fabrication and cryostat cool down to liquid nitrogen temperatures was kept to less than 4 days. For longer periods of time, samples were stored at LN temperatures. The resistances of junctions stored in LN for 10 days (plus 4 days at ambient temperature and pressure) were found to be similar to the junction resistance a short time (less than 1 day) after it was made.
Samples were mounted on the sample stage of the \textsuperscript{3}He or dilution refrigerator and manually aligned to be parallel to the applied field. Thermal contact between the substrate and stage was achieved by mechanical means (screwing the substrate down with screws at the corners of the substrate) for samples on glazed alumina substrates. In the case of fragile samples, \textit{e.g.} where glass substrates were involved, the substrate was glued onto the sample stage with G.E. varnish.

Fig. 2.4 \textit{Au}_{0.7}\textit{In}_{0.3} films. (a) AFM image. Brighter areas correspond to more elevated regions. The surface height variation corresponding to the entire gray scale, \textit{i.e.} the image depth, is 5nm \textit{(from Zadorozhny and Liu, 2002)}. (b) Schematic of the film morphology.

Fig. 2.5 Schematic of \textit{Au}_{0.7}\textit{In}_{0.3} tunnel junctions.
2.3. Doubly connected, ultrathin superconducting cylinders

Ultrathin, doubly connected cylinders were used in studies of the magnetic flux induced superconductor-normal metal (S-N) transition (Liu et al., 2001). With the method described here, cylinders can be made with diameters < 150nm, and lengths on the order of a tenth of a mm. In addition, the cylindrical films typically have large zero temperature coherence lengths $\xi(0)$ – for Al this is in the range of 0.1-0.2µm.

To create doubly connected superconducting cylindrical films, filaments were drawn from a quartz melt to serve as the inner insulating core for the sample. Screening for small diameter filaments was done with an optical microscope with a magnification of ~500x. Particularly small filaments (< 1µm in diameter) were chosen for subsequent material deposition.

The selected filament was placed across a gap, around 1mm wide, in a thin glass slide, with the ends tacked down with a dab of G.E. varnish. The slide was then attached to a rotator inside a high-vacuum thermal evaporation system, and the appropriate material deposited onto the rotating filament. The material chosen for the cylinders was either Au$_{0.7}$In$_{0.3}$ or Al. Cylinders of Au$_{0.7}$In$_{0.3}$ were predominantly used in studies of disorder effects (Zadorozhny et al., 2001; Zadorozhny and Liu, 2001; Zadorozhny, 2003). Both Al and Au$_{0.7}$In$_{0.3}$ have long coherence lengths.

After deposition, the cylinder, still mounted on the glass slide, was transferred to an alumina substrate. Several fine Au wires (0.001” diameter) were attached to the cylinder using Ag epoxy for current and voltage leads, which also served to thermally and structurally anchor the cylinder to the substrate.

The cylinder was then mounted onto the sample stage of the $^3$He (or dilution) refrigerator. Thermal contact between the substrate and stage was achieved by mechanical means. The cylinders were manually aligned during the mounting process to be as parallel to the direction of the magnetic field as possible, typically within a few degrees. The sample and measurement configuration is shown in Fig. 2.6.

Diameters were inferred from the Little-Parks (1962) resistance oscillation demonstrated to occur in doubly connected superconducting cylinders. In this case, the resistance oscillates as a function of applied magnetic flux, with a period corresponding to the superconducting flux quantum, $\Phi_0 = h/2e$ (in SI units). The diameter of the cylinder may be determined by $d = (2h/\pi e H_p)^{1/2}$ where $H_p$ is the magnetic field corresponding to the oscillation period (note that $H_p = 4\Phi_0/\pi d^2$). This method does not take into account any misalignment of the cylinder with the
applied field. Given that the oscillation period is maximized when the cylinder is perfectly aligned parallel to the field, diameters determined in the manner are upper-bound values.

More details on cylinder preparation may be found in Zadorozhny (2003).

Fig. 2.6 Sample and measurement configuration for doubly connected cylinders. A schematic of the sample mounted on the substrate and lead configuration. (Adapted from Zadorozhny, 2003)
2.4. Superconducting Au$_{0.7}$In$_{0.3}$ rings prepared by e-beam lithography

The precise control over geometry given by electron-beam (e-beam) lithography techniques allows for further exploration of the effects of sample topology on superconductivity at the submicron scale. Studies on single superconducting rings would compliment the previously reported studies on superconducting cylinders (Zadorozhny and Liu, 2001, 2002), introducing an opportunity to study non-ensemble averaged mesoscopic physics.

Rings were fabricated using photolithography and e-beam lithography techniques.$^2$ Samples were made on Si or sapphire substrates. If Si was used, an oxide layer (typically 200Å thick) was thermally grown on the surface to guarantee an insulating substrate. The sapphire substrates were 1x1cm$^2$ and commercially polished to have a surface roughness of less than 10Å.

The contact pattern, shown in Fig. 2.7, was made using a standard photolithography process. Each sample chip, defined by a 1x1cm$^2$ square, had 48 possible contacts to the e-beam defined structure. Each contact was 5µm wide, with 5µm spacing between contacts. Several alignment marks are included in the pattern to allow for alignment during the e-beam write process, or for alignment to already existing (pre- e-beam-written) structures.

The contact layer was made of either Au film >300Å thick (with a 25Å Cr underlayer necessary for adhesion to SiO$_x$) or Au$_{0.9}$In$_{0.1}$ film >300Å thick. The latter material was more often used, as its preparation was easier than the Au/Cr film. In addition, the Au$_{0.9}$In$_{0.1}$ films proved to have excellent adhesion and conduction properties, as found to be common in Au-In films (Zadorozhny, 2003; Zadorozhny and Liu, 2002).

For the smaller e-beam defined structures, patterns were designed on L-Edit (software commercially available from Tanner Research) to generate the standard exchange format GDSII. This GDSII file was then converted to a machine-specific format using CATS (software from Transcription Enterprises) and transferred to the Leica EBPG-5HR e-beam lithography instrument.

The pre-patterned substrate was coated with an e-beam resist bilayer and exposed with the pattern. The bilayer consisted of a PMMA top layer and a bottom copolymer layer (PMMA-MAA). If a sapphire substrate was used, 100Å of Au was evaporated atop the bilayer to avoid charging effects during the e-beam write. The Au coating was unnecessary for Si substrates. The e-beam write was aligned to the pre-existing photolithography pattern, and exposure done at a beam energy of 50kV with a typical dose of 1100µC/cm$^2$.

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$^2$ Work done in collaboration with E. Basgall (PSU Nanofabrication Facility) and H. Russell (REU, 2003, PSU Nanofabrication Facility).
The resist layers were developed in sequence. The top PMMA layer defines the pattern and the bottom copolymer layer creates an undercut along the resist edge. The undercut is formed due to the different sensitivities and development rates for the top and bottom resist layers. The undercut is particularly useful in the liftoff process. After development, Au$_{0.7}$In$_{0.3}$ is evaporated (see above section on Au$_{0.7}$In$_{0.3}$ films) onto the patterned substrate, and lifted off. Sample characterization is done by AFM. Typical sample patterns are shown in Fig. 2.8.

The optimal dose for the $e$-beam written structures changes with the lifetime of the filament in the $e$-beam tool. As a result, test arrays of the same pattern written at different doses were done routinely on blank substrates (no predefined leads). It later proved to be efficient to expose a test array, determine the best write, and attach the contact leads to chosen structure. In this case, Au$_{0.9}$In$_{0.1}$ was always used as the lead material for improved contact to the structure.

The above process results in samples with a line width $\leq$100Å. Details are given in Appendix B.

Samples were mounted onto the sample stage of the $^3$He (or dilution) refrigerator, and oriented so that the applied magnetic field is perpendicular to the plane of the ring. Thermal contact between the substrate and stage was achieved by mechanical means (screwing the substrate down with screws at the corners of the substrate, practical when sapphire was used), or, in the case of particularly fragile samples (Si, for instance), by gluing the substrate onto the sample stage with G.E. varnish.
Fig. 2.7 Photolithographically defined leads for $e$-beam structures. Black borders are a guide to the eye, and are not included in the pattern. (a) Large scale, showing the extent of the pattern. The outer black border indicates a 1x1cm$^2$ area. (b) Central area, where contact to the $e$-beam defined structures are located. The black border indicates a 150x150 µm$^2$ area.

Fig. 2.8 AFM images of liftoff-defined $e$-beam structures. (a) Au$_{0.7}$In$_{0.3}$ ring, 100nm line width. (b) Al wire, patterned for four-point measurements of different segment lengths. The line width is 200nm.
2.5. Low temperature electrical transport measurements

Electrical transport measurements for all samples were carried out in $^3$He and dilution refrigerators. Both cryostats are equipped with a superconducting magnet, with a maximum field of 8T.

The $^3$He cryostat was manufactured by RMC Cryosystems, based on insertable $^3$He cryostats designed by E. Swartz (1986, 1987). The cryostat has a base temperature <300mK, and a hold time >24 hrs with no heat load. The system primarily consists of a continuous fill $^4$He pot and a closed $^3$He pot filled with 3 STP liters of $^3$He. The cryostat utilizes an internal charcoal sorption pump (also referred to as the sorb) to pump the condensed $^3$He and to obtain low temperatures.

The operation of the system involves cooling the insert in a helium bath to 4.2K, and pumping on the $^4$He pot with a roughing pump to cool the system to approximately 1.4-1.6K. To cool the system down to lower temperatures, $^3$He is first desorbed from the sorption pump by heating the pump. The desorbed $^3$He cools via the 1K pot and condenses in the $^3$He pot. Once the $^3$He is condensed, the sorb is allowed to cool. This cooling leads to the sorb “pumping” on liquid $^3$He, a drop temperature, and subsequent cooling down to base temperature. To speed the cooling process, a “heat switch” can be used to release a small amount of $^4$He exchange gas into a vacuum space surrounding the sorb, to provide a thermal link between the sorb and the main (liquid helium) bath.

The temperature is measured using a Cernox thin film thermometer (Lakeshore, Model CX-1030-CU, calibrated down to 0.255K) and a Conductus LTC-20 temperature controller. Temperature stability in this system can be achieved to better than 1mK.

The dilution refrigerator is an Oxford Kelvinox system, with a base temperature < 10mK, and cooling power of 200µW at 100mK. Temperature is measured and controlled using a calibrated RuOx thermometer (Oxford, RuO$_2$ thick film resistor, calibrated down to 20mK), an AVS47 resistance bridge, and a TS530 temperature controller. The system also includes a $^{60}$Co nuclear orientation thermometer applicable for $T < 50$mK, though this thermometer was not used in these studies.

All electrical leads entering the cryostat were resistive wires in twisted pairs, RF filtered with an attenuation of 10dB at 10MHz, 30dB at 100MHz, and 50dB at 300MHz. Outside the cryostat, these leads are connected to shielded cables, which, in turn, lead to a breakout boxes where each lead is assigned to a BNC connector. The BNCs provided convenient connections to the outputs and inputs of the various instruments used during the measurement.
In order to eliminate ground loops and to prevent power line ground noise from entering the system, all measurement instruments were run on an isolation transformer. The shield and measurement instrument grounds, however, were connected to a line ground separate from the power line ground. In addition, all the digital instruments involved have floating input and outputs. Lastly, an optical isolator electrically isolated the system from the computer and GPIB interface used to control the measurements.

Measurements were d.c. current biased using either a Keithley 220 current source or Keithley 2400 sourcemeter, and voltages measured with either a Keithley 182 nanovoltmeter or Keithley 2182 nanovoltmeter. For Au$_{0.7}$In$_{0.3}$ films and superconducting cylinders of Al and Au$_{0.7}$In$_{0.3}$, bias currents were chosen in the ohmic regime of the current-voltage (I-V) characteristic, characteristically $< 1 \mu A$. In quench condensed Bi films and superconducting Au$_{0.7}$In$_{0.3}$ rings, bias currents were kept below 10$\mu$A and 100nA, respectively, to prevent irreversible sample annealing or destruction. To eliminate zero current bias voltages due to thermal offset, the current at each point was reversed, or nulled, to determine the voltage offset to obtain a true voltage response to the applied current. Several readings (1-50) were averaged for each data point. The typical voltage noise level using these methods in both $^3$He and dilution refrigerators was a few nV.

In studies of ultrathin, highly resistive films, exceedingly long equilibrium times were present during the measurement cycle, due to both the large $RC$ constant and intrinsic glassy behavior present in the films. In these cases, the time response of the voltage was monitored. The values shown for these films are the limiting values of the voltage rise after adequate time was allowed for the measurement to stabilize. The voltage response was fit to a stretched exponential of the form $V(t) = V_o\{1 - \exp[-(t/\tau)^\alpha]\}$, where $V_o$ is the limiting value of the voltage, $\tau$ the time constant, and $\alpha$ the exponential constant. The time constants obtained were twice as large as expected from the $RC$ constant of the measurement system.

Studies involving tunneling spectra were carried out by measuring the I-V characteristic and taking the numerical derivative. In these cases, I-V measurements were taken with the smallest current step possible. Using the Keithley 220 d.c. current source, these steps were 500ppm of the full-scale range, e.g. for a full-scale range of 1$\mu$A the smallest step between successive points would be 0.5nA. The derivative was generated using using a forward difference scheme in Kaleidagraph (commercially available graphing software). Specifically, this scheme involves $dx_i/dy_i \equiv (x_{i+1} - x_i)/(y_{i+1} - y_i)$, and generally leads to an amplification of any noise present in the data. Alternatively, homemade code (Nelson, 2002) was also used to generate the derivative. This code was designed to fit a polynomial (of a specified order) on a (specified) number of data points around the point in question, and subsequently takes the derivative of the polynomial fit.
The two methods were consistent with one another, but with the latter resulting in a less noisy representation of the tunneling spectrum. More standard a.c. techniques for tunneling measurements were not attempted.

System control, measurement setup, and data acquisition were computerized. A personal computer (Power Macintosh) equipped with a GPIB card interfaced with all the instruments involved, including those for measurement (sources and meters) and system control (temperature controller, magnet power supplies, gas handling system, etc.). Computerized control was done using LabView (software from National Instruments). The Oxford dilution refrigerator may be run by computer during standard operation. Its gas handling system is equipped with an interface that controls the majority of the valves and pumps involved in the cryostat operation. Control programs for the dilution refrigerator were originally supplied by Oxford.

LabView programs were written to computerize the measurement cycle and data acquisition for various measurements, including (but not limited to) \( I-V \) curves at fixed \( T \) and \( H \), magnetoresistance \( R(H) \) at constant \( T \) and current bias \( I \), and resistance as function of temperature \( R(T) \) at a given \( H \) and \( I \). For all measurements at nominally constant \( T \), the temperature at each data point was also monitored and recorded, to note if any heating was present.

Further details particular to each study are given in their respective sections.
3. Electrical transport properties of quench condensed, ultrathin Bi films

3.1. Introduction to localization and superconductivity in 2D

The interplay between localization and superconductivity has been a problem of fundamental interest in the last several decades. The two phenomena represent two distinctly opposing tendencies of electronic behavior. Localization refers to the limitation of the spatial extent of the electron wavefunction, resulting in a vanishing d.c. conductance at zero temperature \(T=0\). Superconductivity, on the other hand, involves long-range phase coherence of electron-pair states, leading to a vanishing d.c. resistance at below the superconducting transition temperature, \(T_c\).

The issue is particularly interesting in two dimensional (2D) systems, as this dimension is a critical dimension for both behaviors. In 2D, true superconducting long-range order is possible only at \(T=0\), although quasi-long range order is still possible at finite \(T\). The modern scaling theory of localization (Abrahams et al., 1979) also predicts that, in 2D non-interacting systems, even arbitrarily weak disorder will lead to localized electronic states. The interplay between the two antithetical behaviors in the same experimental system may, therefore, lead to novel physical phenomena.

Quench condensed thin films of metals are particularly good systems for studying this interplay. These films are made by evaporation of metal onto substrates held at liquid helium temperatures (Shalnikov, 1938; Buckel and Hilsch, 1952, 1954). The rapid quenching of the deposited material by the cold substrate leads to substantially reduced atomic mobility and, for certain materials, amorphous films that are inherently disordered. The sheet resistance \(R\) may quantify the degree of disorder, which is a function of the film thickness. Particularly high levels of disorder can be achieved in the thinnest films so that the electron wavefunctions are localized and macroscopic scale films exhibit infinitely large resistances in the \(T=0\) limit.

As the film thickness increases, however, the disorder is reduced so that the attractive interaction responsible for superconducting pairing overcomes the effects of localization and the
disorder-enhanced Coulomb repulsion. Studies of the electrical transport properties of quench condensed films of metals have revealed a transition from insulating to superconducting behavior with increasing thickness.\(^3\)

Two classes of superconductor-insulator transitions (SIT) appear to exist, as determined by the characteristic features seen in the transport measurements. If films are grown on substrates with a thin underlayer (pre-deposited) of amorphous Ge or Sb, the films exhibit a clear separation between superconducting and insulating behavior with increasing thickness in the limit of zero temperature (see Fig. 3.1a). For Bi, the resistance at the separation is close to the quantum resistance for electron pairs, \(R_q = h/4e^2 = 6.45\,\text{k} \Omega\). Based on the electrical transport characteristics, films prepared in this manner were argued to be uniformly homogeneous and amorphous – free of clustering with disorder on the atomic scale – as a result of the underlayer promoting the wetting of the deposited material onto the substrate. The onset of conductivity can occur at a thickness less than one monolayer (Strongin \textit{et al}, 1971). \textit{As in situ} characterization remains to be undertaken,\(^4\) it is possible that these films do cluster. In this case, the role of the underlayer may prove to be more complicated – though the underlayer itself is non-conducting, it may provide a tunneling channel for coupling between clusters, allowing for measurable conductance even at the early stages.

Alternatively, films can exhibit quasireentrant superconductivity in the vicinity of the thickness tuned SIT (see Fig. 3.1b). This behavior is characterized by a local minimum in the \(R(T)\) – a resistive drop occurs at a characteristic temperature but, instead of the falling to zero, the resistance reaches a local minimum and shows insulating behavior at the lowest temperatures. With increasing thickness, the reentrant behavior is suppressed, and a fully superconducting state is obtained. However, unlike the previous case, \(T_c\) appears to be independent of thickness. These films are granular, consisting of superconducting clusters with local superconducting transition temperature \(T_c^0\) close to the bulk values. Tunneling measurements also reveal that these grains have a superconducting gap close to the bulk value (Barber \textit{et al}, 1994).

The SIT may also be traversed by applying an external magnetic field applied perpendicular to the film at a given thickness (Hsu \textit{et al}, 1995; Markovic \textit{et al}, 1998; Bielec and Wu, 2002). SITs have also been observed in other 2D superconducting systems including:

---

\(^3\) Experimental observations have been reported by Dynes, Garno, and Rowell, 1978; Orr, Jaeger, and Goldman, 1986; Jaeger \textit{et al}, 1989; Haviland, Liu and Goldman, 1989; Liu \textit{et al}, 1991; Valles, Dynes, and Garno, 1992; Kagawa, Inagai, and Tanda, 1996; Markovic, Christiansen, and Goldman, 1998; Chernevak and Valles, 1999; Merchant, Ostrick, Barber, and Dynes, 2001; Bielejec, Ruan, and Wu, 2001; Frydman, Naaman, and Dynes, 2002; and references therein.

\(^4\) These films are known to irreversibly anneal for temperatures above approx. 20K. \textit{In situ} studies of the morphology would be required – a technically difficult task. Some progress in this direction has been made (see Ekinci and Valles, 1997, 1998, 1999).
superconducting In-InO$_x$ films under applied magnetic field (Hebard and Paalanen, 1990; Paalanen, et al, 1992); granular Al films in parallel magnetic field (Wu and Adams, 1994a) or applied electric field (Wu and Adams, 1994b); and amorphous MoGe films under magnetic field (Yazdani and Kapitulnik, 1995).

Fabricated 2D arrays of Josephson junctions also exhibit an SIT as the ratio of the array’s characteristic charging energy ($E_C$) and the Josephson coupling ($E_J$) is varied (for a review, see Newrock et al, 2000). These arrays have superconductor-insulator-superconductor (SIS) type coupling. In arrays where $E_J=E_C$ an applied magnetic field drives the transition from superconductor to insulator; in insulating arrays (where $E_J < E_C$), a dissipation driven transition to a superconducting state has been demonstrated (Takahide et al, 2000). It is notable that the work in Josephson junction arrays can be used to understand the behavior previously seen in the granular systems, as the granular films can often be modeled as random arrays of SIS Josephson junctions.

The following two sections present observations in quench condensed Bi films, which exhibit a 2D SIT with increasing thickness. The majority of the work, however, focuses on films in deep in the insulating state and on films that are clearly globally superconducting. Interestingly, though the studies take place far from the critical point, the results may have implications on the nature of the 2D SIT.
Fig. 3.1 Evolution of the sheet resistance as a function of temperature, $R(T)$, with increasing thickness for (a) nominally amorphous, quench condensed Bi films (from Haviland, Liu and Goldman, 1989) and (b) nominally granular, quench condensed Ga and Pb films (from Jaeger et al, 1989).
3.2. Effect of a finite cutoff length in the logarithmic interaction between vortex-antivortex pairs on the superconducting transition in 2D

3.2.1. Introduction to the nature of the superconducting transition in 2D

The superconducting transition in 2D is considered to be described by the Kosterlitz-Thouless-Berezinskii (KTB)\(^5\) class of phase transitions. In this transition, vortex-antivortex pairs are bound at low temperatures and dissociate into free vortices above a transition temperature, \(T_{\text{KTB}}\). The interaction energy between the vortices in a pair must logarithmically depend on the separation distance for the transition to occur.

The KTB transition was originally argued not to occur in 2D superconducting films, because the vortex-antivortex interaction energy for these systems has a logarithmic dependence – which allows for the vortex pairs to be tightly bound at lower temperatures – only for separations smaller than the transverse penetration depth \(\lambda_\perp = \lambda^2/t\) (where \(\lambda\) is the bulk penetration depth and \(t\) the film thickness). For separations larger than this, Pearl (1965) has shown that the attraction between two vortices of opposite helicity in a superconducting film goes as \(1/r^2\) for large separations. Therefore, the energy to produce an isolated (free) vortex is finite, and a finite density of vortices should occur at any finite temperature.

Beasley, Mooij, and Orlando (1979), however, pointed out that the KTB transition would be applicable to sufficiently thin superconducting films where \(\lambda_\perp\) becomes comparable to the system size in the transition regime. This allows for the logarithmic interaction between vortices to extend to lengths comparable to the sample size. In order to distinguish this transition from the mean-field superconducting transition occurring at \(T_{c0}\), \(T_{\text{KTB}}\) would need to be somewhat below \(T_{c0}\). This criterion would be best met in films with high normal state sheet resistances. In the decades following this work, the observation of a KTB transition has been reported in variety of 2D superconducting systems.\(^6\)

A discontinuous jump in the \(I-V\) exponent was predicted (Halperin and Nelson, 1979) to occur as the temperature passes \(T_{\text{KTB}}\) upon cooling so that

\[
V \sim I \quad \text{for } T > T_{\text{KTB}} \quad 3.1a \\
V \sim I^3 \quad T = T_{\text{KTB}} \quad 3.1b
\]

---

\(^5\) Berezinksii, 1972; Kosterlitz and Thouless, 1973; Kosterlitz, 1974; or for a review, see Mooij, 1984.

For temperatures below $T_{\text{KTB}}$ in the $I = 0$ limit, $V \sim I^{\alpha(T)}$ with $\alpha(T) > 3$ and increasing as temperature is lowered.

Recently, however, this paradigm has come under question. The revived interest stems primarily from the behavior of the $I$-$V$ characteristic. Studies in Josephson junction arrays (van der Zant et al., 1990; Simkin et al., 1997; Hebert et al., 1998) show significant deviation from the predicted power law at low temperatures, in that an ohmic behavior was found in the low current limit. Furthermore, a universal jump in the exponent of the $I$-$V$ curve, expected from the KTB transition, was not observed. In fact, a scrutiny of the published data on the KTB transition suggests that these deviations have been quite commonly observed previously.\(^7\)

To reconcile the discrepancies between the experimental results and the theoretical expectations, an approach based on the dynamic scaling theory of Fisher, Fisher, and Huse (1991) has been proposed (Ammirata et al., 1999; Pierson et al., 1999). In this theory, the transition is assumed to be continuous, governed by a characteristic correlation length $\xi$ and characteristic time $\tau$, which diverge at the critical point with $\tau \sim \xi^z$, where $z$ is the dynamic critical exponent. All physical quantities, including $I$-$V$ isotherms, should scale in the critical regime. Using the scaling form of Fisher, Fisher and Huse, the $I$-$V$ curves should collapse onto a scaling curve following

$$V = I^z \chi_\pm(I\xi/T)$$

where $\chi_\pm(x)$ is the scaling function for temperatures above/below $T_{\text{KTB}}$. Within the dynamic scaling picture, the standard KTB transition is characterized by a diffusive exponent $z = 2$. A dynamic scaling analysis was applied to various 2D systems and an apparently universal critical exponent $z = 5.6$ has been found.

Alternatively, finite-size scaling for the KTB transition has been developed to analyze the superconducting transition in various 2D systems (Repaci et al., 1996; Simkin and Kosterlitz, 1997; Hebert et al., 1998). Assuming an underlying KTB transition, this approach takes into account the presence of thermally excited free vortices due to the finite system size or finite cutoff length in the logarithmic interaction. Within this analysis, the interaction beyond $\lambda_\perp$ is simplified as a constant, rather than $1/r$ as shown originally by Pearl (1965). While the effect of the $1/r$ interaction is ignored, this approach appears capable of accounting for the main features seen in the $I$-$V$ characteristic. In the present work, the effects of this cutoff length in the logarithmic interaction is quench condensed Bi films are examined.

\(^7\) See, for example, Bancel and Gray, 1981; Epstein et al., 1981; Hebard and Fiory, 1983; and Kadin et al., 1983.
3.2.2. Electrical transport measurements in quench condensed superconducting Bi films

Fig. 3.2 shows the resistance as a function of temperature for two quench condensed Bi films prepared in separate runs. Film 1 has a substantially wider superconducting transition regime than Film 2, as expected, since Film 1 is thinner and therefore more disordered. The high temperature part of the resistive transitions can be described by the Aslamasov-Larkin theory for paraconductivity effects (Aslamasov and Larkin, 1968). Fitting the data to the expression for conductance results in a mean-field transition temperature $T_{c0} = 3.90 \pm 0.02$K for Film 1, and $T_{c0} = 5.790 \pm 0.005$K for Film 2. Alternatively, values of $T_{c0}$ can be determined based on $R_{N}(T_{c0}) = R_{N}^{N/2}$, where $R_{N}$ is the normal state sheet resistance, which yields $T_{c0} = 3.94$K and $T_{c0} = 5.780$K for films 1 and 2, respectively. The values of $T_{c0}$ determined by these two methods appear to be consistent with one another.

The $I$-$V$ characteristic at various temperatures in the superconducting transition regime for Film 1 is shown in Fig. 3.3. The curves exhibit a crossover between two distinct power-law behaviors, $V \sim I^{\alpha_{1,2}(T)}$ where $\alpha_{1}(T)$ and $\alpha_{2}(T)$ are exponents in the low and high current regimes. Fitting this form to the data in the respective current regimes yields values of $\alpha_{1}(T)$ and $\alpha_{2}(T)$, which are given in Fig. 3.4 for Films 1 and 2. For all temperatures, the exponent for the high bias current part of the $I$-$V$ characteristic is larger than 1 and increases as $1/T$ as temperature is lowered. In comparison, the low current tail seen in the $I$-$V$ curves are essentially linear at relatively high temperatures and slightly super-linear at lower temperatures.

One can define a crossover current, $I_{\text{cross}}$. As illustrated in Fig. 3.3, $I_{\text{cross}}$ is experimentally obtained by extrapolating the power law behaviors in the low and high current regimes at a fixed temperature. Values of $I_{\text{cross}}$ are shown in Fig. 3.5 to be linearly dependent on temperature. At the lowest temperatures, the crossover appears to fall below the noise floor of the measurements.

Within the standard picture of KTB transition, the logarithmic interaction between a vortex-antivortex pair extends over the entire sample, so that $\lambda_{\perp} \gg W$, where $W$ is the sample size. Above $T_{\text{KTB}}$, thermally induced free vortices, as well as a number of already unbound pairs, are both present in the system. In the presence of a small applied current these free vortices produce ohmic behavior and $V \sim I$. The vortex correlation length $\xi_{\perp}(T)$, which may be thought of as the size of the largest bound vortex pair, is non-zero but significantly smaller than $W$. As temperature decreases, $\xi_{\perp}(T)$ grows and more vortices and antivortices are bound in pairs. At $T_{\text{KTB}}$, $\xi_{\perp}(T)$ diverges resulting in all vortices being bound and a zero resistance state is reached. This zero resistance state only holds in the zero current limit (Kadin et al, 1983). For $T \leq T_{\text{KTB}}$, any finite applied current unbinds pairs. The weakly interacting pairs with large separations will be broken by a small applied current, while the strongly bound, closely separated vortices can be...
unbound by a large applied current. The current-induced unbinding of pairs leads to a power law behavior of $V \sim I^{\alpha(T)}$ where $\alpha(T) \geq 3$. Traditionally, $T_{\text{KTB}}$ is defined by $\alpha(T_{\text{KTB}}) = 3$. Thus the signature of the transition, as seen in the $I$-$V$ characteristic, is a discontinuity in the $I$-$V$ behavior from ohmic to power law as temperature is lowered past $T_{\text{KTB}}$. In addition, the resistance at $T > T_{\text{KTB}}$ is governed by flux flow and may be described by

$$R \sim \exp[-2\sqrt{b(T_c - T)/(T - T_c)}]$$

where $b$ is a non-universal constant (Halperin and Nelson, 1979).

The lower part of the superconducting transition region was fit to the above expression for resistance. If the curve corresponding to $\alpha_2 = 3$ is chosen as the critical curve, then $T_{\text{KTB}} = 3.1$K. The Halperin-Nelson formula fits the data over a small temperature range near $T_{\text{KTB}}$ of roughly two orders of magnitude in the film resistance. However, a discontinuous jump in the exponent is not observed at any temperature, by tracking either the low or high current limit. Instead, the high-current exponent $\alpha_2(T)$ varies continuously with, perhaps, a kink at $\alpha = 3$ as seen in Fig. 3.4b. The disappearance of an ohmic tail at $T = 2.8$K corresponds to an exponent of 4.6. These observations suggest that a true KTB transition was not observed in these quench condensed Bi films.

![Fig. 3.2 Normalized resistance as a function of temperature for Films 1 and 2, using a measuring current of 1µA. Values of $T_c$, determined by fits to the Aslamasov-Larkin theory, are indicated. Film 1 was nominally 25Å thick with $R_N = 1.74k\Omega$. Film 2 was nominally 50Å with $R_N = 91\Omega$.](image-url)
Fig. 3.3 Current-voltage characteristic for Film 1. From top to bottom, the temperatures are 3.6K, 3.5K, 3.4K, 3.3K, 3.2K, 3.1K, 3.0K, 2.9K, 2.8K, 2.7K, 2.6K, 2.5K, 2.4K, 2.2K and 2.0K. The 3.1K curve exhibits $V \sim I^3$ dependence in the high current regime. The dashed line represents linear behavior. A crossover current, $I_{\text{cross}}$, is defined as indicated.

Fig. 3.4 (a) Exponents determined by fitting the data to a power-law in the low ($\alpha_1$) and high ($\alpha_2$) bias current regimes for Films 1 and 2, represented by open and filled circles, respectively. The lines are fits to $1/T$ dependence. (b) A discontinuous jump in $\alpha_2$ is not observed in the transition regime.
Fig. 3.5 Values of the crossover current, $I_{\text{cross}}$, as a function of $T/T_{c0}$ for Films 1 and 2. Straight lines indicate linear fits.
3.2.3. Dynamic and finite-size scaling

Assuming that the normal-superconductor transition in 2D is a continuous phase transition, the physics in the critical region is dominated by $\tau$ and $\xi$ which diverge as $\xi \sim |T - T_{\text{KTB}}|^v$ and $\tau \sim \xi^z$, where $v$ and $z$ are the correlation length and the dynamic scaling exponent, as $T_{\text{KTB}}$ is approached. The proposed scaling (Fisher et al., 1991; Pierson et al., 1999; Ammirata et al., 1999) suggests that the $I$-$V$ characteristic follows

$$ F^{-1}/(VT) = \varepsilon_x(F\xi^z/T^z) $$

where $\varepsilon_x(x) \equiv x/\chi_+(x^{1/z})$ and $\chi_+(x)$ is the scaling function above/below $T_{\text{KTB}}$, and $\xi$ is assumed to be symmetric about $T_{\text{KTB}}$ with the standard KTB form. At $T_{\text{KTB}}$, the above equation reduces to $V \sim F^{-1}$. Above $T_{\text{KTB}}$, $R(T) \sim \xi^z$ and thereby $x = I/R(T)T^z$. Varying $z$ effectively redefines the transition's universal jump from $1 \rightarrow 3$ to be $1 \rightarrow z+1$, wherein $z+1$ corresponds to the exponent of the first fully non-linear $I$-$V$ curve. In addition, the Halperin-Nelson resistance formula is modified to

$$ R \sim \exp\{-z \sqrt[b(T_c - T)/(T - T_{\text{KTB}})]\}. $$

The standard KTB features are recovered for $z = 2$.

A scaling analysis of experimental data obtained in various systems, including superconducting films, Josephson junction arrays, and superfluid $^4$He films, has been carried out by Pierson et al. (1999), who has shown an apparently system-independent critical exponent $z = 5.6$. The large $z$ has been speculated to follow from the vortex-antivortex pairs unbinding by exchanging members with neighboring pairs. In particular, a steady state recombination process involving four vortices would result in $z = 6$.

The value for $z$ and $T_{\text{KTB}}$ were obtained from the highest temperature $I$-$V$ curve that follows power law, $V \sim F^{-1}$, over all currents. By inspecting the $I$-$V$ curves shown in Fig. 3.3, we have $z = 3.6$ and $T_{\text{KTB}} = 2.70$K. A scaling collapse of the $I$-$V$ characteristic following the procedure described above with $z = 3.6$ is displayed in Fig. 3.6. Ideally, $T_{\text{KTB}}$ can be obtained independently from fitting the resistive transition to the modified Halperin-Nelson formula. The results so obtained could be used as a self-consistent check. However, the value of $z$ cannot be independently determined from this fitting. Given this, and the fact that the scaling ansatz is not explicitly dependent upon $T_{\text{KTB}}$, this fit is not attempted. Within the dynamic scaling theory, the values of resistance used in the scaling collapse should be determined in the ohmic regime. At low temperatures, an ohmic regime cannot be defined in this data. As a result, the resistance is instead treated as a fitting parameter in this analysis, with the values shown in Table 3.1. As a comparison, the resistance values obtained directly from the $I$-$V$ curves for which an ohmic regime can be identified are also listed. It can be seen that these values are similar to those
obtained from the fitting. While departure from the scaling curve at low currents is visible in several $I$-$V$ isotherms in the low current limit, the collapsing of curves appears to work, which suggest that the superconducting-normal transition in this film may indeed be a continuous phase transition. The presence of a large correlation length may explain the unusually large critical regime, from 3.5K to 2.7K.

On the other hand, the question of the usefulness of this approach remains. Shown in Fig. 3.7a, is an attempt to scale the data using $z = 5.6$ (and $T_{\text{KTB}} = 2.45\text{K}$ from Fig. 3.3), with the resistance again being a fitting parameter. It is interesting that, as shown in Fig. 3.7b, the data can also be collapsed onto a scaling curve with $z = 6.86$ (and $T_{\text{KTB}} = 2.2\text{K}$ from Fig. 3.3), using the same resistance values used for the $z = 5.6$ scaling, suggesting that collapsing data alone cannot yield a unique value for $z$.

While this uncertainty in determining the critical exponent may not mount a serious challenge to the fundamental validity of dynamic scaling theory, this suggests that caution must be taken in drawing conclusions based on the value of $z$ obtained from the scaling analysis.

Alternatively, the conventional KTB theory has been modified to take into account finite size effects (Repaci et al., 1996; Simkin and Kosterlitz, 1997; Hebert et al., 1998) to treat the experimental observations in various 2D superconducting systems. In this picture, several length scales are present in the problem. These lengths include the vortex correlation length $\xi_s(T)$, the cutoff length in the logarithmic interaction $\lambda_{\perp}$, the current length $r_c$, and the finite size of the sample $W$. An underlying KTB transition is assumed to occur at $T = T_{\text{KTB}}$. Above and below $T = T_{\text{KTB}}$, the finite size $\ell (= \min[\lambda_{\perp}, W])$ leads to a non-zero density of thermally induced free vortices, different from the conventional KTB transition. An applied current probes the dynamics of vortex-antivortex pairs with separations larger than the current length $r_c$. Therefore, sufficiently small currents probe the behavior of vortex-antivortex pairs with separations larger than $\ell$, essentially the free vortices/antivortices, resulting in an ohmic behavior.

Above $T_{\text{KTB}}$, the competing lengths are $r_c$ and $\xi_s(T)$. The use of a finite current leads to current-induced free vortices/antivortices which gives rise to a non-linear $I$-$V$ characteristic when $r_c = \xi_s(T)$. However, a finite $\ell$ introduces certain complications. Ohmic behavior is expected when $r_c >> \min[\ell, \xi_s(T)]$. In this picture, since $\xi_s(T) \ll \ell$ for temperatures well above $T_{\text{KTB}}$, a crossover from ohmic to non-linear behavior occurs at a current $I_{\text{cross}}$ which is dependent on $\xi_s(T)$. At temperatures near $T_{\text{KTB}}$, $\xi_s(T)$ diverges and the crossover is governed by $\ell$. Therefore, $I_{\text{cross}}$ is strongly temperature dependent for $T > T_c$ but weakly temperature dependent for $T = T_{\text{KTB}}$. The ohmic behavior for $T < T_{\text{KTB}}$ is solely dependent on $r_c >> \ell$, with the crossover occurring at $r_c =$
If the vortex-antivortex interaction beyond $\lambda_\perp$ is constant instead of $1/r$, the crossover should occur at $I_{cross} \sim 8k_B T_{KT} W/e \ell$ (Pierson et al, 1999).

The above-described theory qualitatively accounts for the low current ohmic behavior seen in a number of systems, in particular in finite-sized Josephson junction arrays (Simkin and Kosterlitz, 1997; Hebert et al, 1998). However, Ammirata et al (1999) has raised the objection that a transition from KTB to non-KTB behavior cannot be tuned by varying the array size, as alluded to in previous studies (Repaci et al, 1996; Hebert et al, 1998), citing that $W$ and $\lambda_\perp$ affects the density of free vortices in the same manner. In addition, this approach assumes the occurrence of a KTB transition, despite a finite sized $\lambda_\perp$. It should be noted that it is upon this finite transverse penetration depth that Kosterlitz (1974) based the argument against the occurrence of a phase transition in 2D superconducting systems.

Tab. 3.1 Resistance values used in the scaling analyses of the $I-V$ characteristic (Fig. 3.3). The values for ohmic resistances are given where applicable. $R_1$ and $R_2$ are the resistances used in the $z = 3.6$ and $z = 5.6$ and 6.86 scaling analyses, respectively. Only resistances used for scaling in the lower branch are listed.

<table>
<thead>
<tr>
<th>$T$(K)</th>
<th>$R_{\text{Ohmic}}$((\Omega))</th>
<th>$R_1$((\Omega))</th>
<th>$R_2$((\Omega))</th>
</tr>
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<tr>
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<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
</tr>
<tr>
<td>3.4</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>3.3</td>
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<td>0.0174</td>
<td>0.2</td>
</tr>
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<td>3.2</td>
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<td>0.031</td>
<td>0.047</td>
</tr>
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</tr>
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<td>2.9</td>
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<td>$3.3 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>2.8</td>
<td>$1.0 \times 10^{-7}$</td>
<td>$5.0 \times 10^{-5}$</td>
<td></td>
</tr>
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<td>$5.0 \times 10^{-6}$</td>
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<tr>
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<td></td>
</tr>
<tr>
<td>2.2</td>
<td></td>
<td>$1.0 \times 10^{-12}$</td>
<td></td>
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</tbody>
</table>
Fig. 3.6 Scaling of the $I$-$V$ characteristic (from Fig. 3.3), with $z = 3.6$ and $T_{KTB} = 2.7$ K. Both axes are in arbitrary units. Only the lower branch corresponding to $T > T_{KTB}$ is shown. Resistances used as fitting parameters are listed in Tab. 1.

Fig. 3.7 Scaling analyses corresponding to (a) $z = 5.6$ and (b) $z = 6.86$. Both axes are in arbitrary units. Only the lower branch of the transition is shown. The resistances used in the analyses are listed in Tab. 1.
3.2.4. Vortex-antivortex unbinding with a finite $\lambda_\perp$

The features observed in the $I$-$V$ characteristics in the present study may be explained by a simple treatment, which does not require the existence of a KTB transition. Within this model, the behavior is determined by the current-induced vortex-antivortex pair unbinding, wherein the members of the bound pair interact either logarithmically or as $1/r$, and are unbound by an applied current.

Beginning with the non-disordered, unrenormalized pair potential $\phi(r)$ given by Pearl (1965)

\[
2 E_{c1} - t (\Phi_0 / 4\pi \lambda)^2 \ln(\lambda/r) \quad \text{for } \xi < r < \lambda_\perp
\]

\[
2 E_{c2} - (\Phi_0 / 2\pi)^2 / r \quad \text{for } r > \lambda_\perp
\]

where $E_{c1}$ and $E_{c2}$ are constants associated with the energy of the vortex normal core, $t$ the film thickness, $\Phi_0 = h/2e$ the flux quantum, and $\xi$ the superconducting coherence length which is the effective radius of the vortex normal core. In the presence of an applied current, the potential energy of a pair changes to

\[
U(r, \theta) = \phi(r) - (J_s \Phi_0 / c) r \cos \theta \ 
\]

where $\theta$ is the angle between $J_s$ and $r$. The potential is smallest at $\theta = 0$. In this direction, a saddle point is found at $r_c$, defined as the current length with its value depending on $J_s$. Classical escape over this saddle point leads to pair unbinding and free vortices/antivortices. This situation is schematically shown in Fig. 3.8.

The electrical resistance of the film is proportional to the vortex mobility (Tinkham, 1996), which in turn is proportional to the density of free vortices $n_f$. In a steady state of a two-body recombination process, $n_f \sim \Gamma^{1/2}$ where $\Gamma$ is the rate of ionization controlled by a Boltzmann factor,

\[
\Gamma \sim \exp[-U(r_c, 0)/k_b T].
\]

Given this, the $I$-$V$ characteristic can be obtained using $V \sim I n_f \sim \Gamma^{1/2}$. As $\phi(r)$ has different forms for $r < \lambda_\perp$ and for $r > \lambda_\perp$, as does the $I$-$V$ behavior for small and large currents. At small currents, $r_c = (\hbar c / 4\pi e J_s)^{1/2} > \lambda_\perp$, leading to $\Gamma \sim \exp[2(l/I_0)^{1/2}]$, where $I_0 = (\pi k_b T)^2 A/\Phi_0^3$ (and $A$ is the cross sectional area). At large currents, $r_c = h n_s e / 2 m J < \lambda_\perp$. This leads to $\Gamma \sim \exp[(n_s h^2 / 4mk_b T) \ln l]$ where $n_s = n_{s3D} = n_{s3D} \lambda_\perp$. Therefore,

\[
V \sim l^{1+ n_{s3D}^2 / 4m k_b T} \quad \text{for } \xi < r < \lambda_\perp
\]

\[
V \sim l \exp[(l/l_0)^{1/2}] \quad \text{for } r > \lambda_\perp
\]
As shown in Fig. 3.3, the $I-V$ characteristic agrees with this finite cutoff length picture. In the high bias current region, vortex-antivortex pairs with small separations dominate the resistance. For these pairs, the interaction is logarithmic resulting in $V \sim \rho_s(T) = 1 + \pi n_s h^2 / 4 m k_b T > 1$. Furthermore, using the mean-field result $n_s = n_s(T) = n_s(0)(1/T/T_c) leads to
\[ \alpha_s(T) \sim 1/T. \]

This $1/T$ dependence is clearly seen for both films. Values of $n_s(0)$ may be determined from the slopes shown in Fig. 3.4, and are $4.4 \cdot 10^{12}/\text{cm}^2$ and $7.8 \cdot 10^{13}/\text{cm}^2$ for Films 1 and 2, respectively.

As the bias current is lowered, the cutoff length becomes important, resulting in a crossover of the $I-V$ characteristic to $V \sim I \exp[I/I_0]^{1/2}$. In this regime, an estimate of $I_0$ yields a value at least an order of magnitude larger than the applied current. Given that $I_0 >> I$, a linear $I-V$ characteristic is expected, as observed experimentally. As temperature is lowered, values of $I_0$ decrease and the exponential factor may begin to affect the $I-V$ behavior at small currents. This effect is qualitatively seen in the low temperature curves as a deviation from purely ohmic behavior.

Examining the temperature dependence of the crossover current, $I_{\text{cross}}$, further tests the validity of such a simple treatment. The crossover corresponds to $r_c \sim n_s / I_{\text{cross}}$. Using the mean-field result for $n_s$ and assuming that $\lambda_T$ is temperature independent in this small temperature range, $I_{\text{cross}}$ should be linearly dependent on temperature. A linear dependence was observed experimentally (Fig. 3.5).

If many pairs are present in the film, as expected below $T = T_c$, the pair potential for a vortex-antivortex pair of a given separation will be modified by screening effects, i.e. affected the presence of other pairs with smaller separation, leading to a renormalized pair potential. In addition, the disorder present in the film will introduce pinning forces, further altering the pair potential. A full analysis including renormalization effects would be complicated. Given that the experimental results appear to agree with the expectations of the unrenormalized theory, it seems that renormalization would not change the picture qualitatively. However, quantitative changes are expected, like modifications to the cutoff length due to the screening effects.
Fig. 3.8 (a) Vortex-antivortex interaction. (b) Modified vortex-antivortex pair potential for $\xi < r < \lambda_\perp$, in the presence of an applied current. Pair unbinding is characterized by classical escape over the saddle point at $r_c/\lambda$. A similar saddle point is present for the modified vortex-antivortex pair potential associated with $r > \lambda_\perp$. 
3.2.5. Implications of a finite $\lambda_\perp$ on the nature of the 2D SIT

These results suggest that a cutoff length is present in the logarithmic interaction between a vortex-antivortex pair and is significantly smaller than the sample size in quench condensed Bi films, and that the effects of the logarithmic and $1/r$ forms of the vortex interaction are observable. This has potential consequences on the nature of the zero temperature SIT previously shown to occur in quench condensed Bi films.

In particular, whether it is possible for a real experimental system to be self-dual, as implied by the dirty boson model proposed for the 2D SIT. Within the model, there are at least two difficulties for films of metals to be considered self-dual for the SIT in zero magnetic field (Cha et al., 1991). First, the particle-hole symmetry possessed by vortex-antivortex pairs does not exist for Cooper pairs. Mukhopadhay and Weichman (1996) have examined the issue concerning the lack of particle-hole symmetry at the SIT theoretically and concluded that although this symmetry is not present in the original Hamiltonian, a statistical version is restored at the critical point. Second, the interaction between charged pairs and that between vortices, are, in general, dissimilar. The Coulomb interaction between Cooper pairs has a $1/r$ form, while the interaction between a vortex-antivortex pair is logarithmic, up to $\lambda_\perp$.

It has been shown that in materials of high dielectric constant, the interaction between two pairs may be described as logarithmic up to a cutoff length, beyond which it recovers the $1/r$ form (Keldysh, 1979). The presence of a cutoff length in the logarithmic interaction between charges has been experimentally observed in various 2D systems.\(^8\)

The form of interaction between charges as described above is identical to that between vortices in this system, as shown above. If the effective dielectric constant for insulating Bi films is large, as may be expected (Jones and March, 1973), the interaction between Cooper pairs may also be logarithmic with a finite cutoff length. In this case, the system will be self-dual at least in principle. However, since the interaction between charges and that between vortices may be modified by the disorder and many-body effects differently, whether a particular sequence of films can actually have the same interaction form for Cooper pairs and vortices may depend strongly on the film preparation, and substrate conditions. Consequently, a self-dual system may not always be achieved even in the same material system prepared under nominally the same conditions. The characterization of the behavior of a self-dual system waits for these experimental issues to be resolved.

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\(^8\) Mooij et al., 1990; Yamada et al., 1993; Tighe et al., 1993; Liu and Price, 1994.
3.3. Evidence for a structural transition and the formation of electron droplets in quench condensed Bi films at the initial stage of growth

3.3.1. Introduction to the electron glass

The physics of interactions effects in 2D disordered electronic systems has been explored, for the most part, in two extreme limits. In the weak disorder limit, the primary effect of electron-electron interactions is to produce a logarithmic suppression of the DOS at the Fermi energy, which results in a weakly metallic ($\ln T$) conductivity. In the opposite limit, that of the strong disorder and the strongly insulating case, Efros and Shklovskii have shown that Coulomb interactions can produce a gap in the DOS, commonly known as the Coulomb gap. In 2D, this gap is expected to be linear in energy and dominates the transport behavior in the system.

Indeed, the presence of a gap leads to modifications in the variable range hopping law that conventionally describes the conductivity in insulating systems:

$$\sigma(T) = \sigma_0 \exp[-(T_0/T)^a]$$

where $\sigma_0$ and $T_0$ are constants. In the case of non-interacting 2D systems where no gap exists near the Fermi energy, $a = 1/3$. The introduction of a linear energy-dependent gap, however, results in $a = 1/2$ with the constant $T_0$ given by $T_0 = e^2/k_B \varepsilon \xi_L$, where $\varepsilon$ is the dielectric constant and $\xi_L$ is the localization length.

This state is often referred to as a “Coulomb glass,” following the term “Fermi glass” originally coined by Anderson (1970) to describe a non-interacting, disordered insulating electron system. Interestingly, however, the Coulomb gap problem maps onto an Ising spin glass model with $1/r$ antiferromagnetic interactions in a random field, suggesting that a finite-temperature glass transition may be present. An order parameter, similar to the Edwards-Anderson order parameter used for spin glass systems, was proposed for the electron glass in an attempt to find a glass transition. Though a non-zero value of the order parameter was found, critical behavior was absent in the numerical studies. Subsequent work (Xue and Lee, 1988) revealed that a glass transition is not present at non-zero temperatures, similar to 2D Ising spin glasses (Binder and Young, 1986).

Experimental studies of the electron glass were originally carried out on lightly doped semiconductors (Monroe et al., 1987; Massey and Lee, 2000; and references therein). Recently,
field-effect experiments on strongly disordered systems\textsuperscript{12} including quench condensed films of Bi and Pb (Martinez-Arizala et al, 1997, 1998) have revealed glassy behavior (but not critical behavior associated with a glass transition). Effects such as slow relaxation, hysteresis, memory and aging are documented in quench condensed Bi and Pb. In addition, an observed minimum in the conductance as a function of gate voltage was proposed to correspond to the opening of the Coulomb gap in the DOS (Yu, 1999). Interestingly, though the conductance for the films was found to fit the general hopping form, the value for $a$ obtained from the fitting was close to 0.8 (Martinez-Arizala et al, 1997, 1998; Markovic et al, 2000), a dependence not given by any VRH theory.

Recently, in situ scanning tunneling microscopy (STM) studies on granular quench condensed films of Au and Pb revealed an unexpected scenario for film growth (Ekinci and Valles, 1998, 1999). It appears that a uniform, homogeneously disordered phase formed during the initial depositions. This precursor phase was found to avalanche into an islanded structure as the thickness reached a critical value. Results obtained on both Au and Pb films indicate that the observed structural evolution may be general, independent of substrate material and film preparation procedure. A similar amorphous precursor phase was found in in situ Raman-scattering measurements on Bi films deposited onto carbon substrates at 110K (Mitch et al, 1991). The Raman spectra indicated a distinct local structural transition from amorphous-like to nanocrystalline clusters as the film thickness increased across a critical thickness of ~8Å. This observation appears to be not inconsistent with the in situ STM studies.

These uniform, amorphous films should also form at the initial stage of film growth in Bi films quench condensed at liquid helium temperatures, even though the local amorphous to crystalline structural transformation may be incomplete because of the reduced substrate temperature. The electrical transport properties of these films at the initial stage of film growth, which have never been studied as the regular sized films are too resistive to measure, are of great interest. Transport measurements on films of macroscopic size, taken simultaneously with the in situ STM studies, showed that the onset of conductivity occurred when the films were seen to have two nearly complete layers of grains, having formed electrically connected multigrain clusters. The undetectable electrical conductivity of the initial amorphous precursor phase on a macroscopic scale suggests either electron localization at an atomic scale because of the strong disorder (Danilov et al, 1995, 1996), or structural discontinuity at a large length scale even though electrons within each connected amorphous region are not necessarily strongly localized.

\textsuperscript{11} Theoretical studies include Davies et al, 1982, 1984; Xue and Lee, 1988; Ruiz et al, 1993; Diaz-Sanchez et al, 2000.
3.3.2. Experimental results in films at the initial stage of growth

Films at the initial stage of growth exhibited exceedingly long equilibrium times, due to both the large RC constant and intrinsic glassy behavior. The glassy state previously observed in strongly disordered systems are often characterized by extremely long, non-exponential relaxation times (Adkins et al., 1984; Martinez-Arizala et al., 1997, 1998). Similar behavior was observed in these sets of films in the region where $R > 10^7 \Omega$ (corresponding to sheet resistances of $R > 10^9$), as shown in Fig. 3.9. The voltage response can be fit to a stretched exponential of the form

$$V(t) = V_0\{1 - \exp[-(t/\tau)^\alpha]\}$$  \hspace{1cm} 3.12

where $V_0$ is the limiting value of the voltage, $\tau$ the time constant, and $\alpha$ the exponential constant.

In addition to long relaxation times, films at the initial stage were found to have a non-linear, asymmetric $I$-$V$ characteristic, as seen in Fig. 3.10. The asymmetry and non-linearity were more pronounced at lower temperatures and smoothly evolved to simple ohmic behavior as temperature was increased. Non-linearity, in itself, is not unexpected in systems dominated by VRH conduction. However, an analysis of the data using theoretically predicted dependences of conductance on electric field in the VRH regime (Levin and Shklovskii, 1984) was inconclusive, as a satisfactory fit could not found. The asymmetry about zero current bias in both magnitude and curvature seen in the $I$-$V$ curves has not been theoretically predicted.

Given the nature of the $I$-$V$ characteristic, d.c. resistances were calculated by measuring the voltage across the sample at a fixed current bias of 20pA. The voltage at zero bias current is subtracted from this value to account for offset voltages. The resistance characteristic at negative current bias is similar to that measured with a positive bias.

The resistance as a function of temperature $R(T)$ of the 2.5µm long film, at a thickness $t$ of 12.5Å, is given in Fig. 3.11a. Fig. 3.11b shows a Zabrodskii plot (Zabrodskii and Zinoveva, 1984) of the data, where the function $\ln[-d(lnR)/d(lnT)]$ is plotted against $\ln T$. If the resistance is described by the hopping conduction formula,

$$R = R_0\exp[(T_0/T)^a]$$  \hspace{1cm} 3.13

this plot would exhibit a straight line. The hopping exponent $a$ would correspond to the slope of the line. A least squares line fit yielded a value $a = 0.49 \pm 0.07$, consistent with VRH with Coulomb interactions. A fit of the data specifically to this form is given in Fig. 3.11c. The localization length is estimated to be $\xi_L = 80$Å, assuming that the dielectric constant of the film is that of the substrate. Similar fits to simple activated behavior ($a = 1$) and non-interacting VRH

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12 Observations have been reported by Adkins, 1984; Ben-Chorin et al, 1993; Ovadyahu and Pollak, 1997; Vaknin et al, 2000; and references therein.
conduction \((a = 1/3, 1/4)\) were unsatisfactory. The temperature dependence of the conductivity and the slow voltage response indicate that these films may be characterized as being in an electron glass state.

As indicated in Fig. 3.11, the resistance deviated from VRH (with interactions) at low temperature. The temperature at which the deviation began was close to the temperature at which the \(I-V\) characteristic exhibited asymmetric and non-linear behavior. In thinner films, the temperature above which VRH was observed increased, with the resistance deviation persisting to increasingly higher temperatures. In the thinnest films, standard hopping conduction was no longer observed within the temperature range studied \((< 10K)\). In addition, a non-linear and asymmetric \(I-V\) characteristic was present over the whole temperature range.

Remarkably, in these thinnest films, the low temperature deviation developed into a positive temperature coefficient of resistance, i.e. \(dR/dT > 0\). Fig. 3.12 shows the \(R(T)\) of films in this regime in detail. The positive \(dR/dT\) did not extend down to \(T = 0\), but instead reached a resistance minimum and recovered insulating behavior in the limit of zero temperature. The resistance at intermediate temperatures showed a nearly linear temperature dependence. In contrast, the low temperature insulating behavior was found to rise dramatically with decreasing temperature. The precise temperature dependence in these two regimes were difficult to determine due to the small temperature range available for data fitting. The features seen in the \(R(T)\) were independent of the polarity of the current bias, with the minimum and negative \(dR/dT\) having the same relative magnitudes for negative and positive current bias measurements.

The positive \(dR/dT\) persisted to higher temperatures with increasing disorder, as indicated by the thickness dependence shown in Fig. 3.12. In contrast, the resistance minimum occurred at \(T = 2.5-3K\), for all films which exhibited a positive \(dR/dT\), regardless of film thickness. This feature disappeared at \(t = 12.0\AA\).

The evolution of the film resistance with respect to film thickness is shown in Fig. 3.13. For \(t \geq 12.0\AA\), a striking departure from the behavior of the thinnest films was seen in the resistance characteristic. Although a non-linear and asymmetric \(I-V\) characteristic was still observed at the lowest temperatures, a resistance minimum was no longer found. The films exhibited an insulating character over the whole temperature range \((T < 8K)\). For films with \(t > 12.5\AA\), the \(I-V\) curves displayed ohmic behavior over the whole temperature \((T < 8K)\) and current range \((I < 100pA)\). As more material was added the resistance was observed to enter a region where the resistance could not be fitted to any theoretically predicted dependence.

As the film was made thicker, familiar behavior for granular ultrathin films of superconducting metals, including an SIT was found, similar to what has been previously observed (Jaeger et al, 1989). On the insulating side of the transition, the resistance displayed
hopping conduction characteristics at higher temperatures, but leveled off at low temperatures. The leveling-off phenomenon has been widely observed in ultrathin insulating films (Jaeger et al., 1989; Wu and Adams, 1994). Further increases in thickness leads to a weakly localized regime where the resistance exhibited a \( \ln T \) dependence.

The kink in the \( R(T) \), below which a more rapid rise in resistance was seen, has been attributed to the opening of the superconducting energy gap in individual grains at a transition temperature \( T_{c0} \) (Haviland et al., 1989). As a result, the activation energy for single electron hops between grains is the sum of the charging and the superconducting pairing energy (Dynes et al., 1978; Adkins et al., 1980; Haviland et al., 1989). As more material was deposited, the kink developed into a resistance minimum, a well-known phenomenon of quasi-reentrant superconductivity (Orr et al., 1985; Haviland et al., 1989). In this case, although individual grains become superconducting with zero resistance which causes a resistance drop at \( T = T_{c0} \), the phases of these grains do not establish a long-range coherence (Simanek 1979, 1982). Quantum fluctuations drive the film insulating at lower temperatures (Fisher, 1986). The observed re-entrant behavior, which has become the hallmark for granular superconducting films, indicates that the Bi films prepared in the present study were granular as well.

As seen in Fig. 3.13, the evolution of the resistance as a function of film thickness is remarkably systematic: in the thinnest films, the positive temperature coefficient of resistance becomes less distinct in relatively thicker films; at intermediate thickness the films develop standard VRH behavior at higher temperatures, as well as with increasing thickness; finally, further increases in film thickness result in an SIT, consistent with previous studies. Qualitatively similar behavior was also observed in studies of the 35µm-long film.

It is important to examine the issue concerning the contact resistance, \( R_c \), between Bi and the Au contacts. Values of \( R_c \) were determined from the scaling relation \( R = rL + R_c \), where \( R \) is the measured resistance, \( r \) is the film resistance per unit length, and \( L \) is the film length. \( R_c \) can be inferred from the resistances of films with different lengths, assuming that \( r \) is the same, when the above equation is satisfied. Tab. 3.2 gives a comparison of resistances of the co-deposited 2.5µm- and 35µm-long films, and values of \( R_c \) at \( T = 8K \).

Films thinner than 11.0Å had contact resistances significantly smaller than the film resistance. For films thicker than 15.5Å, \( R_c \) was found to be a significant fraction of the film resistance. However, as noted above, the behavior was strikingly similar to what was previously observed in this system using a 4-point configuration, indicating that the measurement reflects the films’ intrinsic properties despite the relatively large \( R_c \). Finally, films of intermediate thickness were found to not scale, and a value for the contact resistance could not determined; this issue will be discussed in the following section.
As \( R_c \) is primarily determined by the tunnel barrier present at the interface of Au and Bi and by the DOS of the Au and Bi films, respectively, \( R_c \) is likely temperature dependent. Owing to the extremely long saturation time present at low temperatures, a systematic study of the temperature dependence of \( R_c \) was not attempted. However, simple physical argument suggests that the measurements reflect the films intrinsic properties. In the relatively thick films, the intrinsic nature was seen despite the large \( R_c \). This is only possible if the contact resistance was temperature independent. Furthermore, \( R_c \) in this region did not have a significant thickness dependence. Since the Au contacts and interface is the same for a set of films grown by sequential deposition, this suggests that any thickness or temperature dependence in \( R_c \) is due to the Bi film itself, likely its DOS. The systematic behavior of the resistance as a function of thickness and temperature further suggests that the features observed in the thinnest films reflects the films intrinsic properties.

<table>
<thead>
<tr>
<th>( d(\text{Å}) )</th>
<th>( R_{\text{long}}(\Omega) )</th>
<th>( R_{\text{short}}(\Omega) )</th>
<th>( R_c(\Omega) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.5</td>
<td>( 2.50 \pm 0.05 \times 10^{11} )</td>
<td>( 2.00 \pm 0.05 \times 10^{10} )</td>
<td>( 2.3 \pm 0.9 \times 10^{9} )</td>
</tr>
<tr>
<td>11</td>
<td>( 3.70 \pm 0.05 \times 10^{10} )</td>
<td>( 2.7 \pm 0.1 \times 10^{9} )</td>
<td>( 9 \pm 6 \times 10^{7} )</td>
</tr>
<tr>
<td>12</td>
<td>( 1.36 \pm 0.05 \times 10^{10} )</td>
<td>( 8.4 \pm 0.1 \times 10^{7} )</td>
<td></td>
</tr>
<tr>
<td>12.5</td>
<td>( 5.8 \pm 0.1 \times 10^{9} )</td>
<td>( 7.0 \pm 0.5 \times 10^{6} )</td>
<td></td>
</tr>
<tr>
<td>13.0</td>
<td>( 9.8 \pm 0.2 \times 10^{8} )</td>
<td>( 5.2 \pm 0.1 \times 10^{5} )</td>
<td></td>
</tr>
<tr>
<td>14.0</td>
<td>( 5.60 \pm 0.05 \times 10^{6} )</td>
<td>( 2.35 \pm 0.05 \times 10^{4} )</td>
<td></td>
</tr>
<tr>
<td>14.5</td>
<td>( 5.8 \pm 0.5 \times 10^{5} )</td>
<td>( 1.4 \pm 0.1 \times 10^{4} )</td>
<td></td>
</tr>
<tr>
<td>15.5</td>
<td>( 2.3 \pm 0.2 \times 10^{5} )</td>
<td>( 6.6 \pm 0.1 \times 10^{4} )</td>
<td></td>
</tr>
<tr>
<td>17.5</td>
<td>( 2.91 \pm 0.05 \times 10^{4} )</td>
<td>( 2.59 \pm 0.05 \times 10^{3} )</td>
<td>( 5.4 \pm 0.9 \times 10^{2} )</td>
</tr>
<tr>
<td>20.5</td>
<td>( 1.80 \pm 0.03 \times 10^{3} )</td>
<td>( 7.00 \pm 0.02 \times 10^{2} )</td>
<td>( 6.1 \pm 0.2 \times 10^{2} )</td>
</tr>
<tr>
<td>22.5</td>
<td>( 9.73 \pm 0.05 \times 10^{2} )</td>
<td>( 4.17 \pm 0.05 \times 10^{2} )</td>
<td>( 3.74 \pm 0.06 \times 10^{2} )</td>
</tr>
</tbody>
</table>
Fig. 3.9 Time response of the voltage, $V(t)$, to an applied current bias of +20pA at $T = 0.60K$. The solid line represents a fit to $V(t) = V_0\{1 - \exp\left[-\left(t/\tau\right)^\alpha\right]\}$ with $V_0 = 0.22V$, $\tau = 80s$, and $\alpha = 0.8$.

Fig. 3.10 $I$-$V$ characteristic for a film of thickness 12.5Å. Given voltages are limiting values, with the zero current bias voltage subtracted for each current. The temperatures are 0.60K, 0.80K, 0.90K, 1.20K, 1.40K, 1.80K, 2.00K, 2.20K, 2.40K, 2.80K and 4.00K. The first fully linear curve was found at $T = 2.2K$. All resistance measurements were made using a +20pA current bias.
Fig. 3.11 (a) $R(T)$ for a 12.5Å thick film (also shown in Fig. 3.10), using a +20pA current bias. (b) A Zabrodskii plot of the data indicates that a hopping conduction exponent of $\alpha = 1/2$ best describes the resistance at higher temperatures. This dependence is best seen in (c) a semilog plot of the $R$ versus $T^{1/2}$. The solid line is a fit to VRH with Coulomb interactions. The resistance deviates from this behavior at $T < 2.2K$. 
Fig. 3.12 $R(T)$ in the thinnest measurable films: (a) 10.0Å, (b) 10.5Å, (c) 11.0Å, and (d) 11.5Å. The observed minimum and negative $dR/dT$ were also present in negative current bias measurements, with the same relative magnitudes as those presented here for positive current bias. The lines are guides to the eye.
Fig. 3.13 Evolution of $R(T)$ with increasing thickness. The dashed line denotes the temperature at which resistance minima were found in the high-disorder limit. This temperature is close to the local $T_c$ near the SIT.
3.3.3. An amorphous to granular structural transition

The intriguing crossover of the resistance characteristic with respect to film thickness observed at around 12-14Å raises questions concerning its physical origin. Below it is argued that this crossover may be related to the film growth model proposed based on the in situ Raman studies on Bi films prepared at 110K ( Mitch et al., 1991). Such a model seems to be consistent with STM results obtained on quench condensed Au and Pb films (Ekinci and Valles, 1998, 1999).

The abrupt disappearance of the resistance minimum in the thinnest films, which marked a qualitative change in the resistance characteristic, appears to be related to the fact that in the range 11.5Å < t < 14.0Å, R (at T=8K) decreased particularly rapidly with increasing thickness (see Fig. 3.14a), indicating that the films underwent a qualitative change.

The above behavior suggests the existence of two distinctly different regimes, with a rapid crossover region observed over a change in film thickness of only around 2Å. In these two regions, the thickness dependences of R were similar, exhibiting a relatively slow change with increasing thickness in comparison with the transition region, though the values of R in the two limits (t < 11.5Å and t > 14.0Å) differ by more than 5 orders of magnitude. Interestingly, at t = 13.0Å, a thickness corresponding to the middle of the transition region, the film resistance does not follow any theoretically predicted dependence and, instead, appears as a boundary between the high resistance and low resistance regions. The significant difference in magnitude of the resistivity, the sharp transition, as well as the distinct difference in character between the two regimes may be explained by a change in the film's structure as the thickness is increased.

This scenario is further supported by the lack of scaling in sample resistance between the 2.5µm- and 35µm-long film in and near the transition region (see Tab. 3.2). As the films undergo the transition, a characteristic length determines the films behavior. Films whose size is larger than this length should scale whereas those smaller should not. The rapidly changing resistance found in this thickness range suggests that this length is strongly thickness dependent. As the films moved farther into the low resistance region, they were again found to scale, indicating the end of the transition, and the emergence of a stable film structure.

Within the structural transition scenario, the film develops from a uniform to granular film at a critical thickness t = 11.5Å. Assuming that the resistance in the granular film after the transition was dominated by intergrain electron hopping, further material depositions serves to decrease the tunnel barrier strength between grains, increasing the conductivity. Therefore, the resistance of the films would depend on thickness more sensitively in just-formed granular films,
and is less sensitive in the relatively thicker films after a path of grains across the film is already established, consistent with experimental observation.

In addition, within each individual grain, a local amorphous to crystalline structural transformation occurs, similar to that observed in in situ Raman-scattering measurements in Bi films deposited at 110K. In that study, the transition from an amorphous, disordered structure to a rhombohedral phase was found between 7.0Å and 8.5Å. The observed $T_{c0}$ of 2.5-3.0K near the SIT supports the presence of crystalline-like grains. Similar values of $T_{c0}$ were found in nanocrystalline Bi clusters (Weitzel and Micklitz, 1991). However, given the lower deposition temperatures used in the present study and, therefore, the lower thermal energy available for Bi atom diffusion, a larger critical thickness for the local amorphous to crystalline transition ($t \approx 11.5Å$) would be natural. Furthermore, the local transition in the present films could be incomplete for the same reason, resulting in disordered grains that are between amorphous and crystalline in nature (semi-crystalline). The thickness dependence of $T_{c0}$, i.e. that $T_{c0}$ increases with increasing thickness to a maximum value of 6.5K, provides further support that the grains after the structural transition retain a substantially amorphous character.

The proposed phase diagram for this transition is shown in Fig. 3.14b. As the thickness increases, the films pass through the following phases: uniform amorphous $\rightarrow$ macroscopically granular, locally amorphous $\rightarrow$ macroscopically granular, locally semi-crystalline. For relatively thick films, as temperature increases, a previously studied transition to a nanocrystalline phase (Komnik, 1982) is expected (not indicated in the schematic).
Fig. 3.14 (a) Semi-log plot of the sheet resistance $R$ at $T = 8K$ as a function of film thickness. (b) Proposed phase diagram for the structural transition in quench condensed Bi films at the initial stage of film growth. The shaded area indicates a locally amorphous character, and the white to semi-crystalline. The hashed area denotes the transition from a macroscopically uniform film to one that contains clusters (granular film).
3.3.4. Possible formation of droplets in the electron glass

What is the nature of the electrical transport properties of the amorphous films formed at the initial stage of film growth? It is notable that the temperature at which the resistance starts to rise in these films coincides with the \(T_{c0}\) of the locally superconducting, granular films near the SIT, as seen in Fig. 3.13. This observation can be understood if it is assumed that in the thinnest films, which should be homogeneously disordered over a large area, there may be locally superconducting regions (superconducting droplets). The resistance increase at low temperature would then be related to the opening of the energy gap in the superconducting droplets, similar to the granular superconducting film. The question is whether droplets could indeed form in these strongly insulating films.

A droplet state was proposed in a theoretical study on the 2D interacting, but highly mobile, electron system (He and Xie, 1998; Shi et al, 1999). Motivated by the recent observations of the 2D MIT (Kravchenko and Klapwijk, 2000; Abrahams et al, 2001; and references therein), it was suggested that such a system is unstable against phase separation into a high-density Fermi gas (“liquid” phase) and a low density insulating Wigner crystal (“gas” phase). The formation of a two-phase coexistence region – a droplet state – was shown to be favored by increasing potential disorder.

Similarly, droplets may form in these amorphous films at a characteristic temperature, where the formation minimizes the Coulomb repulsion energy of the system in order to be stable. However, the entropy of the system correspondingly decreases. At lower temperatures, the energy change is likely sufficient to compensate for the loss of entropy. As a result, the droplets grow in size as temperature decreases. The resistance is determined by single electron hops between droplets. As the distance between droplets decrease with decreasing temperature, as does the resistance. This results in the observed deviation from VRH as well as the positive \(\frac{dR}{dT}\). At higher temperatures, the entropy term becomes more important and droplet formation may be less favored, resulting in a “gas” (uniform electron glass) state with insulating behavior.

The droplet formation may be natural if the one-to-one correspondence of the Coulomb glass to the Ising spin glass is considered. A phenomenological scaling theory of the ordered phase of short-range Ising spin glasses was developed in terms of droplet excitations (Fisher and Huse, 1988). In this model, low lying droplet excitations, consisting of connected clusters of spins reversed from the ground state, dominate the physics of the spin glass. A similar phenomenon would not be unexpected in the electron glass.
Recently, results in quench condensed, highly disordered Be films have been reported by Butko et al (2000) and Butko and Adams (2001). They have shown that, in strongly insulating films of resistances close to the quantum of resistance, the Coulomb gap is suppressed by an applied magnetic field leading to a phase that is more metallic in character. This “quantum metal” is weakly temperature dependent and has a resistance near $R_q$. Though the Be system has substantial differences from the Bi system considered here (Be films form smooth, non-granular films; macroscopic lengths were studied; the metallic phase is field-induced), the results may have implications on the present work.

3.4. Summary

The electrical transport properties of ultrathin quench condensed Bi films have been studied. These films undergo a $T=0$ SIT tuned by film thickness and are suggested by the transport properties to be macroscopically granular, but microscopically amorphous. The results focus primarily on aspects of these films deep in the insulating state and on those that are clearly globally superconducting.

In the superconducting films, a crossover from linear to non-linear behavior was observed in the $I-V$ characteristics in the superconducting transition regime. The data can be analyzed in the context of dynamic scaling theory and, alternatively, by the current-induced vortex-antivortex unbinding involving a cutoff length in the logarithmic interaction between a vortex-antivortex pair. Dynamic scaling does not yield a unique value for the critical exponent $z$. However, the latter approach explains the results well.

In films deep in the insulating regime, unexpected behavior was seen in the thinnest films. These anomalies, specifically, a positive $dR/dT$ accompanied by a non-linear and asymmetric $I-V$ characteristic, were present only in the initial stage of film growth. As more material is deposited, the unconventional state abruptly disappears.

The evolution of the transport properties with respect to film thickness at the initial stage of film growth is attributed to an amorphous to granular structural transition in these thinnest quench condensed Bi films. The positive $dR/dT$ found in the amorphous, precursor layers are proposed to result from the formation of high electron density droplets within the insulating electron glass background.

Though this model can qualitatively account for the features seen in the conduction, the nature and implications of an amorphous precursor phase – especially that of the electron droplet state – needs further study. Simultaneous structural and electrical transport results would provide direct evidence for the above structural transition, and verify the correspondence of the
amorphous precursor phase to the unconventional transport behavior. Direct evidence for the
droplet formation may be found from low temperature, *in situ* STM tunneling studies.
4. Superconductor-normal metal transition in Au$_{0.7}$In$_{0.3}$ films

4.1. Introduction

A superconductor-insulator-superconductor (SIS) Josephson junction array can be used as a prototypical system to study the two-dimensional (2D) superconductor-insulator transition (SIT). The ground state properties of the system are dictated by the competition between Josephson coupling energy, $E_J$, and the charging energy, $E_C$. The transition may then be understood within the context of the uncertainty relation between the number of Cooper pairs, $N$, and the phase of the superconducting order parameter, $\phi$,

$$\Delta N \Delta \phi > 1.$$  \hspace{1cm} 4.1

For systems with a large charging energy ($E_J \ll E_C$), the fluctuation in the number of Cooper pairs is suppressed, leading to enhanced fluctuations in the superconducting phase, and subsequent globally insulating behavior. Conversely, systems with substantial Josephson coupling energy ($E_J \gg E_C$) will lead to a well-defined phase and a globally superconducting state.

Given that granular superconducting films can be modeled as SIS tunnel junction arrays, the above picture may also be used to understand the disorder- and field-driven SIT in these systems (Jaeger et al, 1986, 1989; Wu and Adams, 1994). The phase-number uncertainly relation may also be applicable to the SIT in homogeneously disordered systems, such as ultrathin amorphous films, where superconductivity can be suppressed by increasing disorder, leading to a reduction in the superconducting transition temperature, $T_c$, or a complete loss of superconductivity. In this case, the fluctuation in the number of electrons is suppressed by localization. Close to the SIT, the homogeneous superconducting film breaks into droplets of superconducting regions, Josephson coupled together (Zhou and Spivak, 1998). This makes it possible to understand the interplay between superconductivity and localization in both granular and homogeneous films on the same footing, although the role of fluctuations in the amplitude of the superconducting order parameter cannot be ruled out (Dynes et al, 1986; Valles et al, 1992).
The 2D SIT is regarded to be a continuous quantum phase transition (QPT). The hallmark of a QPT lies in the scaling of the system’s physical properties. The presence of a diverging length and time scales leads to scaling in the critical region (near the quantum critical point). The distance from the transition point is given by $\delta$, which is defined relative to the critical value of the tuning parameter. For a magnetic tuned transition, for example, $\delta = |B-B_c|$ where $B_c$ is the critical field. The spatial and temporal correlation lengths, $\xi$ and $\xi_\tau$, respectively, are:

$$\xi \sim \delta^{-v} \quad \text{and} \quad \xi_\tau \sim \xi^z$$

where $v$ is the correlation length exponent and $z$ is the dynamical scaling exponent. As is evident from Eq. 4.2, $\xi$ and $\xi_\tau$ diverge as $\delta \rightarrow 0$.

Though a QPT is a $T=0$ phenomenon, physical properties at finite $T$ in the critical regime are subject to the finite-sized scaling (for a review, see Sohndi et al, 1997; Sachdev, 2001). Essentially, the problem of a $T=0$ QPT in $D$ spatial dimensions can be mapped onto a thermodynamical phase transition in $D+1$ dimensions. The extra dimension represents an imaginary time axis given by $i\hbar/k_b T$, which is finite for $T > 0$.

A scaling theory of the 2D SIT in ultrathin films was introduced by Fisher et al (1990), based on a model of interacting bosons moving the presence of disorder. In this picture, the transition between the two states are driven by fluctuations in the phase of the superconducting order parameter. The superconducting state is described by a Cooper pair condensate (with localized vortices), and the insulating state by a vortex condensate (with localized Cooper pairs). A $T=0$ metallic phase is predicted, precisely at the quantum critical point between insulating and superconducting phases, with both Cooper pairs and vortices mobile. A universal conductivity of $\sigma = 4e^2/h \left( R_q = h/4e^2 = 6.45k\Omega \right)$ at the $T=0$ limit is expected if the system is self-dual.

Scaling of the field-tuned transition was experimentally demonstrated in In-InO (Hebard and Paalanen, 1990) and MoGe (Yazdani and Kapitulnik, 1995) films, indicating a critical exponent product of $vz = 1.36$. Scaling of the disorder (thickness) tuned transition yields $vz = 1.2$ (Liu et al, 1991; Markovic et al, 1998). Experimentally, scaling behavior is the strongest evidence available that the observed transitions are QPTs.

However, the applicability of the dirty boson model has been questioned. Tunneling studies show a vanishing superconducting energy gap as the SIT is approached. The latter would suggest that the phase-only physics given by the bosonic model might be incomplete for describing the SIT in 2D.

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13 Intriguingly, the field-tuned transition carried out simultaneously with studies of the disorder driven transition show $vz = 0.7$ (Markovic et al, 1998). The reason behind the discrepancy has yet to be clarified.
14 See, for example, Dynes et al, 1986; Valles et al, 1992; Hsu and Valles, 1995; Hsu et al, 1995; and references therein.
Furthermore, attention has recently been called to the existing experimental data which appears to indicate that a metallic phase intervenes in the quantum critical region between the superconducting and insulating phases. The metallic state, characterized by a temperature-independent resistance at the lowest temperatures, was first observed in early studies of ultrathin granular films prepared by molecular-beam epitaxy quench deposition (see Fig. 3.1b; Jaeger et al, 1986, 1989) and, later on, in several other systems including SIS Josephson junction arrays and ultrathin homogeneous films (see Fig. 4.1; Yazdani et al, 1995; Kapitulnik et al, 1999; Valles et al, 2000).15

In the field-driven SIT in Josephson junction arrays with $E_J/E_C$ (van der Zant et al, 1992, 1996; Chen et al, 1995), the flattening-off of the resistance at the lowest temperatures is attributed to the quantum tunneling of vortices (van der Zant et al, 1991; Tighe et al, 1991, Chen et al, 1996). Similar observations in granular thin films (Jaeger et al, 1986, 1989; Wu and Adams, 1994) may also be understood in this manner. This model, however, may not be applicable to amorphous films, where the superconducting order parameter may not be well defined, even locally (Valles et al, 1992).

The mechanism for the latter system remains to be understood, despite substantial theoretical input. The majority of these consider the system to have no free electrons present (due to Cooper pairing), using solely bosonic mechanisms (Cooper pairs or vortices) to describe the system – altogether disregarding fermionic16 mechanisms. Interestingly, these models rely on phase-fluctuation driven mechanisms for superconductivity suppression.17 In this context, the low temperature behavior has been interpreted as a novel Bose metal phase with variations on the exact mechanism behind the dissipation, disorder effects, consequences on the phase diagram, and implications on the underlying quantum phase transition.

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15 It is interesting that only observations of the presence of a metallic phase have been reported. Further studies are needed, specifically in regards to the characterization of such a state.

16 These theories primarily rely on the disappearance of Cooper pairs: disorder enhanced Coulomb repulsion leads to a decrease in pairing and a subsequent $T_c$ suppression.

Fig. 4.1 Metallic behavior observed in studies of (a) SIS Josephson junction arrays, and (b) amorphous MoGe thin films. (a) $R(T)$ for several values of magnetic field (frustration, $f$) (from van der Zant et al., 1996). (b) The curves correspond $R(T)$ at $B = 1.3, 1.26, 1.23, 1.23, 1.2$ and $1.18T$. The inset shows log$R$ vs $1/T$ for the same data set (from Mason and Kapitulnik, 1999).
4.2. S-N transition in SNS junction arrays

Recently, a theory for the quantum suppression of superconductivity has been proposed which involves both bosonic and fermionic mechanisms (Feigel’man et al., 2001; Spivak et al., 2001; and references therein). The model deals with superconductivity in an array of superconducting islands (of radius $r$ and spaced $d$ apart, where $d >> r$) coupled by a thin film normal conductor of conductance $g$ through the proximity effect. Below a critical conductance dependent on the ratio of grain radius and spacing $g < g_c(d,r)$, quantum fluctuations were found to lead to the destruction of superconductivity even at zero temperature, resulting in a transition from a macroscopically superconducting to normal metal state. This critical conductance is substantially larger than conductance corresponding to the quantum of resistance ($g = R_q^{-1} = 4e^2/h$).

Here, transport and tunneling measurements are presented of Au$_{0.7}$In$_{0.3}$ films of normal state sheet resistances $R_N << R_q$. A $T = 0$ superconductor-normal metal (S-N) transition was found to occur, driven by an applied parallel magnetic field. In this configuration, the magnetic field pair breaking effect via its influence on the electron orbital motion is minimized, allowing for the field effect on the electron spin to become dominant. So far, only Au$_{0.7}$In$_{0.3}$ films are the only SNS system in which a low temperature metallic phase has been studied. The present films are created by sequential evaporation of alternating layers of Au and In (described in Ch. 2). The interdiffusion of Au and In results in a system of In-rich grains embedded in a Au$_{0.9}$In$_{0.1}$ matrix (Zadorozhny and Liu, 2002). At temperatures below their onset superconducting transition temperatures, $T_{c_{onset}}$, the In-rich regions become Josephson coupled with one another, resulting in a random network of SNS type Josephson junctions – a disordered version of previously studied artificial arrays of SNS Josephson junctions.

Though granular, these films have vanishingly small characteristic charging energies. Au$_{0.7}$In$_{0.3}$ films not only exhibit low normal state sheet resistances, $R_N$, but also remain metallic down to $T=0.3K$ at a thickness, $t$, as low as 50Å (Zadorozhny and Liu, 2002). The carriers are, therefore, not particularly localized. In the context of the phase-number uncertainty relation, this corresponds to where the number of carriers on an individual grain varies substantially.

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18 Provided that the spin-orbit scattering rate is sufficiently small. For a review of field effects in thin films see Fulde (1973).
19 While artificial proximity-coupled, i.e. SNS, Josephson junction arrays have been examined in some detail (for a review see Newrock et al., 2000), granular materials that can be modeled as an SNS junction array – such as niobium nitride films (Johnson and Kadin, 1998) – have not been studied in the context of the existence of a metallic phase in 2D.
Therefore, fluctuations in the superconducting order parameter, if found, has to come from a different mechanism, for example, from phase slips in 2D.
4.3. Experimental observations of a parallel magnetic field induced metallic state

4.3.1. Resistance as a function of temperature in finite applied $H_\parallel$

Figure 4.2 shows the temperature dependence of the sheet resistance, $R (T)$, in applied parallel magnetic field, $H_\parallel$, for several superconducting Au$_{0.7}$In$_{0.3}$ films with or without tunnel junctions. As expected, $T_c$ decreased with increasing $H_\parallel$. For relatively small $H_\parallel$, the $T_c$ suppression was accompanied by a fully superconducting state at sufficiently low temperatures. For a range of $H_\parallel$, however, despite the presence of a resistance drop signifying the onset of a superconducting transition, the zero resistance superconducting state was absent. Instead, a temperature independent resistance extended down to the lowest temperatures, spanning nearly a decade in temperature. The metallic behavior exhibited increasingly higher limiting resistances with increasing $H_\parallel$. In sufficiently high fields, where the resistance drop was completely suppressed, weakly insulating behavior was found at the lowest temperatures.

The field driven transition appears to be common in the Au$_{0.7}$In$_{0.3}$ film system. The flattening-off of the resistance consistently emerged in fields of roughly 0.1T. The behavior was also present in doubly connected cylindrical films (Zadorozhny et al., 2001; Zadorozhny and Liu, 2001) where the cylinder axis is aligned parallel to the applied field (see Fig. 4.2d). The phenomenon is found even in films with $R_N < 10\Omega$ – very far from the 2D SIT which occurs at $R_N \approx 6.5k\Omega$ (see, e.g., Goldman and Markovic, 1998). For Au$_{0.7}$In$_{0.3}$ films, it is possible that although $R_N$ is low, the disorder in the superconducting state is high, as pointed out earlier.

Can sample heating or external microwave noise be the cause of this behavior? The limiting ($T \to 0$) resistance is greatly affected by the applied field. As sample heating is expected to be the same for all $H_\parallel$, this suggests that heating is not the source of the behavior. External microwave noise may also affect the leveling-off of the resistance. Effective elimination of microwave noise requires filtering at cryogenic temperatures, for which the current system is not equipped. However, the metallic behavior in Josephson junction arrays was observed in studies carried out in carefully shielded environments (van der Zant et al., 1992, 1996). Therefore, the observed leveling-off of the resistance should be intrinsic to Au$_{0.7}$In$_{0.3}$ films.

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20 Substantial work on this project was done by Zadorozhny (2003).
21 Likely due to weak localization effects (for a review see e.g. Bergmann, 1984; Lee and Ramakrishnan, 1985).
It is also relevant to note that the behavior may be present in perpendicular applied field. The only existing data for the same film taken in both perpendicular and parallel applied fields, shown in Fig. 4.3, are taken down to $T=0.3K$. Fig. 4.3a shows a tendency towards only a suppression of $T_c$, at least up to $H_\perp=160G$. Measurements in parallel field (Fig. 4.3b), on the other hand, may indicate of a flattening-off of the resistance at lower temperature, as suggested by the trend in the concavity of the $R(T)$ with increasing $H_\parallel$. Fig. 4.4 shows a film in perpendicular field taken down to 25mK. No sign of a flattening off in the resistance (after an initial drop at $T_{c0}$) was observed. A finer field scale between the 100G and 118G curves, which was not carried out, would be needed to resolve this issue.

Fig. 4.2 Sheet resistance as a function of temperature, $R(T)$, of superconducting Au$_{0.7}$In$_{0.3}$ films for several thicknesses, $t$: (a) 7.5nm thick planar film, (b) 10nm thick planar film, (c) 30nm thick planar film, and (d) cylindrical film with $t=30nm$ and diameter $d=550nm$. Applied parallel magnetic fields, $H_\parallel$, are as indicated. For a range of $H_\parallel$, a temperature independent resistance was found at the lowest temperatures. (Adapted from Zadorozhny, 2003)
Fig. 4.3 Resistance as a function of temperature, $R(T)$, of a 30nm thick film at several values of (a) perpendicular and (b) parallel magnetic fields. For (a), from top to bottom, $H_\perp = 300, 170, 160, 150, 120, 110, 100, 75, 50, 25, 10, \text{ and } 0 \text{G}$. For (b), from top to bottom, $H_\parallel = 4900, 3920, 2940, 2450, 2960, 1500, 980, \text{ and } 0 \text{G}$. Measurements were taken in two separate cooldowns; measurements for this film below 0.3K are not available. (From Zadorozhny and Liu, 2002.)

Fig. 4.4 Resistance as a function of temperature, $R(T)$, of a 20nm thick film at several values of perpendicular field. From top to bottom, $H_\perp = 118, 100, 88, 78, 58, 38, 28, 18, 17, \text{ and } 0 \text{G}$. Measurements in parallel field for this film are not available. (Adapted from Zadorozhny, 2003)
4.3.2. Current-voltage characteristics in finite applied $H_{//}$

The zero field superconducting state of Au$_{0.7}$In$_{0.3}$ can be further defined by the $I$-$V$ characteristic,\textsuperscript{22} shown in Fig. 4.5a. Non-linear, power law behavior was observed at the lowest temperatures in the low current limit, suggestive of a Kosterlitz-Thouless-Berezinskii (KTB) transition\textsuperscript{23} and current-induced vortex-antivortex pair unbinding expected in superconducting thin films (Kadin et al, 1983). With increasing temperature, the power law evolved into primarily linear behavior, representative of thermally activated unbinding of vortex-antivortex pairs and the introduction of dissipation in the system. The ohmic response emerged at a temperature consistent with the appearance of measurable film resistance ($T = 0.1$K, see Fig. 4.5a). With decreasing temperature, the nonlinearity in the $I$-$V$ curves increased. However, a superconducting state characterized by $V \sim I^{\alpha(T)}$ (where $\alpha(T) \geq 3$) was not observed down to the lowest temperature, implying that $T_{KTB} < 25$mK.

The effect of applied parallel magnetic field on the $I$-$V$ curves is similar to that of increased temperature at zero field. Fig. 4.5b shows the $I$-$V$ characteristic in finite $H_{//}$ at low temperatures. In the low current limit, the $I$-$V$ curves evolved from power-law to ohmic behavior with increasing $H_{//}$. The ohmic behavior appears to be well established at $H_{//} = 0.20$T. Therefore, if there does indeed exist bound vortex-antivortex pairs in the (zero field) globally superconducting state, these pairs have either become fully unbound or the vortices themselves disappear altogether by the time the metallic phase is reached. If unbound pairs are truly present, they are likely the dominant contributor to the finite dissipation in the zero temperature limit.

\textsuperscript{22} An in-depth discussion of the $I$-$V$ characteristic in the Au$_{0.7}$In$_{0.3}$ system is in Zadorozhny (2003).

\textsuperscript{23} Berezinskii (1970), Kosterlitz and Thouless (1973), or see Ch. 3.2 for a review.
Fig. 4.5 $I$-$V$ characteristic of the $\text{Au}_{0.7}\text{In}_{0.3}$ film given in Fig. 4.2b. (a) Zero field at several temperatures. From right to left, the curves correspond to $T = 20\text{mK}$, $90\text{mK}$, $0.1\text{K}$, $0.125\text{K}$, $0.175\text{K}$, and $0.20\text{K}$. (b) At the lowest temperature available for several values of field as indicated and at $T=25\text{mK}$, with the exception of the $0.1\text{T}$ curve which was taken at $70\text{mK}$. The dashed line indicates linear (ohmic) behavior.
4.4. Tunneling spectroscopy of Au$_{0.7}$In$_{0.3}$ films

Tunneling spectra were taken in superconductor-insulator-normal metal (SIN) junctions of Au$_{0.7}$In$_{0.3}$/MgO$_x$/Mg, as well as in SIS junctions of Au$_{0.7}$In$_{0.3}$/AlO$_x$/Al (Wang, 2002). Results in two SIN junctions, with junction resistances of approximately $10^2\,\Omega$, on the same Au$_{0.7}$In$_{0.3}$ film show results that are quantitatively very close to one another. Results in two SIS junctions with junction resistances $~10^3\,\Omega$, on different Au$_{0.7}$In$_{0.3}$ films, also show quantitatively similar results with each other, and qualitatively similar$^{24}$ to the results in SIN junctions. Here, the discussion focuses on results in SIN junctions.

Fig. 4.6 shows the Au$_{0.7}$In$_{0.3}$/MgO$_x$/Mg junction resistance as a function of temperature, $R_J(T)$, in zero field. The resistance of the Au$_{0.7}$In$_{0.3}$ film (part of the junction) is also given on a semi-logarithmic scale for comparison. In the normal state at $T=0.85\,\text{K}$, $R_J = 115.1\,\Omega$, while the film resistance is $R = 55.7\,\Omega$. The resistance of the Au$_{0.7}$In$_{0.3}$ film in finite $H_{//}$ is given in Fig. 4.2b. The junction consists of one square of the film (Fig. 2.5). Therefore, the junction resistance and film resistance are comparable, which is undesirable for tunneling studies. In addition, the step features in the Au$_{0.7}$In$_{0.3}$ $R(T)$, typically associated with film inhomogeneity, likely results from the low temperature (77K) deposition of Au and In.$^{25}$ Despite all this, the field induced metallic behavior was observed for the range $3T > H_{//} > 0.20\,T$, and the tunneling spectra showed systematic behavior, as shown below.

Fig. 4.7 shows the single particle tunneling density of states (DOS) in zero applied field. A coherence peak accompanied by the opening of an energy gap at approximately 0.28K were found. However, complete suppression of the DOS at the lowest energies was not observed. Both $R_J(T)$ and the temperature evolution of the tunneling spectra indicated a limiting value of about 35% suppression of the normal state DOS. This proved to be junction dependent (other samples showed 25-80%), but always present. This suggests a substantial population of quasiparticles in the Au$_{0.7}$In$_{0.3}$ film. As Au$_{0.7}$In$_{0.3}$ behaves as a random array of SNS Josephson junctions, the large number of quasiparticles is not unexpected. However we cannot rule out the contribution of the leakage current, specific to each junction, which affects the conductance at zero bias voltage, $G_j(V=0)$.

The evolution on the tunneling spectra with $H_{//}$ is shown in Fig. 4.8a. The gap in the DOS fills with quasiparticle excitations with increasing field until it closes at $H_{//} \approx 0.55\,T$. The effect is

$^{24}$ In terms of the Au$_{0.7}$In$_{0.3}$ film properties, specifically including observations of an energy gap in the metallic phase. The tunneling spectra in the SIS junctions show two gap features – one consistent in magnitude and temperature dependence with Al, and the other with Au$_{0.7}$In$_{0.3}$. 
similar to that of increasing temperature in zero field. The tunneling spectra, further, displayed both coherence peak and gap features well into the field range of the metallic phase. These features are qualitatively similar to the zero field case. Indeed, as shown in Fig. 4.8b, the evolution of the tunneling spectra with increasing temperature at a fixed field ($H_{/\parallel} = 0.40\text{T}$, well into the field range of the metallic phase) is also similar to the zero field case.

Fits\textsuperscript{26} of the BCS-expected DOS (for a review see Wolf, 1985; or Tinkham, 1996) to the tunneling spectra obtained in both zero and finite fields were unsatisfactory, due to the absence of a sharp gap edge. Neither can finite temperature effects (thermal smearing) introduced by the $T$-dependence of the Fermi function in the BCS form account for the observed broadening.

In finite applied magnetic field, the broadening of the density of states may be accounted for by pair breaking effects of the field, theoretically considered in detail by Maki and others (1969; and references therein). These effects also yield a finite $G_j(V=0)$\textsuperscript{27} – although not to the extent as seen in the present case.

Comparable behavior in the tunneling spectra has been previously reported in other systems under applied perpendicular fields. Hsu and Valles (1994) reported that granular Pb films with high normal state resistance $R^N$ exhibited a DOS (in applied field) that can be described completely by pair breaking effects. For low $R^N$, the DOS in applied field showed a substantial number of states in the gap, which they propose indicates the presence of vortex cores. In PbBi/Ge films near the SIT in applied magnetic field, substantial broadening of the DOS was reported and suggested to result from fluctuations in the amplitude of the order parameter (Hsu \textit{et al}, 1995). They estimate that the average number of Cooper pairs in a coherence volume is on the order of 1 – small enough that it is likely to fluctuate. An analysis along these lines has not been attempted for Au$_{0.7}$In$_{0.3}$ films

Fits of the spectra to the DOS form proposed to account for finite quasiparticle lifetime broadening effects (Dynes, Narayanamurti and Garno, 1978) worked well for both zero and finite field cases. In this picture, quasiparticles at or near the gap edge recombine into pairs that become part of the superfluid condensate. It was proposed that the addition of an imaginary term to energy would account for the broadening and smearing of the gap edge. In the present analysis, the lifetime-broadened form of the DOS was further modified to include a constant term to offset the zero-bias conductance.\textsuperscript{28} Although the fits appeared to agree with the measured spectra,

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\textsuperscript{25} See Ch. 2.2 for further discussion.

\textsuperscript{26} All fits carried out by Wang (2002), using code written by Nelson (2002). The fitting program allows four adjustable parameters [the energy gap $\Delta$, the quasiparticle lifetime term $\Gamma$, the normal state conductance $G^N$, and a constant $\zeta$] to be included in a modified BCS form of the DOS.

\textsuperscript{27} See, \textit{e.g.}, results by Rasing \textit{et al} (1981).

\textsuperscript{28} The constant is added in “by hand” and is not part of quasiparticle lifetime broadening (Nelson, 2002).
values the energy gap determined from the fits as a parameter showed a distinct drop at the lowest temperatures, suggesting that this is not appropriate for these Au$_{0.7}$In$_{0.3}$ films.

If the value of the energy gap $\Delta$ may be estimated by the position of the peak, then $\Delta = 0.1$ meV for $H_{\parallel} < 0.4$T at low temperatures ($T \leq 0.24$K).$^{29}$ With the experimentally defined $T_c^{\text{onset}}$ of 0.82K, this leads to $2\Delta/k_B T_c = 2.9$, slightly lower than the BCS result of 3.53.

An additional unexpected feature occurs at higher energies. Figs. 4.7 and 4.8 suggests that the feature moves towards lower energies with increasing temperature or increasing field. Fig. 4.9 has a larger energy range and best shows the development. At the lowest temperature measured ($T=25$mK), the feature is present at approximately 10\Delta. With increasing temperature or field, the feature moves in to lower energies, finally disappearing at precisely where the gap feature associated with superconductivity in Au$_{0.7}$In$_{0.3}$ also disappears. The anomalous behavior appears to be associated with a kink seen in the $R(T)$, see Fig. 4.10.

Quantitatively similar behavior was found in another Au$_{0.7}$In$_{0.3}$-MgO$_x$-Mg junction, as well as in an SIS junction of Au$_{0.7}$In$_{0.3}$-AlO$_x$-Al junction, where the normal state junction resistances are comparable ($10^2\Omega$). However, the feature was not observed in Au$_{0.7}$In$_{0.3}$ junctions with substantially higher junction resistances ($10^3\Omega$) – making it difficult to attribute the behavior as something intrinsic to the Au$_{0.7}$In$_{0.3}$ film system. The feature likely corresponds to a current redistribution process$^{30}$ in part of the Au$_{0.7}$In$_{0.3}$ film in the vicinity of the tunneling area. In this scenario, the feature would be more pronounced in low resistance junctions – where the Au$_{0.7}$In$_{0.3}$ film resistance may be comparable to the junction resistance – and less distinct in high resistance junctions where $R_j$ is dominant, consistent with experimental observations.

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$^{29}$ Similar treatments of tunneling spectra include Valles et al (1992), Hsu and Valles (1994), and Hsu et al (1995).

$^{30}$ Resulting, for example, from an area with a locally lower $T_c$ (or critical current $I_c$) than the rest of the film. (J. M. Rowell, personal communication.)
Fig. 4.6 Au$_{0.7}$In$_{0.3}$/MgO$_x$/Mg junction resistance as function of temperature, $R_J(T)$, in zero applied field and using a d.c. bias current of 20nA. The Au$_{0.7}$In$_{0.3}$ film sheet resistance is also given on a semilog scale for comparison. This is the same film for which $R(T)$ and $I$-$V$ characteristics are given in Fig. 4.2b and 4.5, respectively.
Fig. 4.7 Tunneling spectra of the film shown in Figs. 4.2b, 4.5 and 4.6. Tunneling conductance as a function of voltage, $G_J(V)$, at several temperatures in zero field. $T>25\text{mK}$ curves are shifted up from the $25\text{mK}$ curve for clarity. The development of the high energy feature [e.g. at $0.2\text{mV}$ for $0.28K$ in (a)] is best seen in Fig. 4.9.
Fig. 4.8 Tunneling spectra of the film shown in Figs. 4.2b, 4.5 and 4.6. (a) $G(I(V))$ curves at finite $H_{\parallel}$ and $T = 25\text{mK}$. $H_{\parallel} > 0$ curves are shifted up from the zero field curve. (b) $G(I(V))$ curves at $H_{\parallel} = 0.40\text{T}$ at several temperatures. $T > 75\text{mK}$ curves are shifted up from the 75mK curve for clarity. The development of the high energy feature is best seen in Fig. 4.9.
Fig. 4.9 Tunneling spectra of the film shown in Figs. 4.2b, 4.5 and 4.6, larger energy scale to illustrate the high energy feature. (a) Tunneling conductance as a function of voltage, $G_J(V)$, at several temperatures in zero field. $T>25\text{mK}$ curves are shifted up from the $25\text{mK}$ curve for clarity. (b) $G_J(V)$ curves at finite $H_{||}$ and $T=25\text{mK}$. $H_{||}>0$ curves are shifted up from the zero field curve.
Fig. 4.10 Au$_{0.7}$In$_{0.3}$/MgO$_x$/Mg junction resistance as function of temperature, $R_J(T)$, in several values of applied field, as indicated.
4.5. Discussion

Recently, theoretical models for a metallic state of Cooper pairs have been proposed. In the original dirty boson Hubbard model (Fisher et al., 1990) – where the superconducting state is described by a Cooper pair condensate with localized vortices and the insulating state by a vortex condensate with localized Cooper pairs – a $T=0$ metallic phase was predicted, but only precisely at the quantum critical point between insulating and superconducting phases, and characterized by a universal conductivity ($\sigma = 4e^2/h$).

An extension of the original boson Hubbard model has predicted a metal phase composed of phase-disordered Cooper pairs, prevented from condensing by dissipation (Das and Doniach, 1999, 2001). This phase lies between the superconducting and insulating phases and the SIT, thereby, consists of a transition from a superconducting state to a Bose metal phase to an insulating state. In another work, it was demonstrated that the phase disordered Bose state has a finite conductivity as $T\to 0$, in the absence of disorder and dissipation (Dalidovich and Phillips 2001). An extension of this study indicated that the addition of disorder leads to a Bose glass state that also possesses nonzero conductivity as $T\to 0$ (Dalidovich and Phillips, 2002). Alternatively, a dissipative Bose system has been considered which does not indicate the existence of a Bose metal, but instead reveals a crossover region at finite temperatures to metallic behavior (Ng and Lee, 2001). It has been further suggested that the metallic behavior arises from the system coupling to a dissipative heat bath (Mason and Kapitulnik, 1999; Kapitulnik et al., 2001). The coupling introduces a new axis to the standard phase diagram for the 2D SIT where, for sufficiently strong coupling, a metallic phase emerges.

Shimshoni et al. (1998) suggested that the metallic behavior results from vortex tunneling between superconducting droplets, even in a homogeneously disordered system, with a globally superconducting state obtained only when the Josephson coupling between superconducting regions percolates. The model appears consistent with studies of the field-tuned SIT in InO$_x$ (Hebard and Paalanen, 1990) and MoGe (Yazdani and Kapitulnik, 1995) thin films which reveal a critical correlation length exponent $\nu = 1.3$, as the correlation length exponent in 2D classical percolation is $4/3$ (for a review see Stauffer, 1992).

In another droplet scenario, Zhou and Spivak (1998) proposed a theory based on mesoscopic fluctuations in disordered superconducting thin films in parallel magnetic fields. It was demonstrated that, at sufficiently low temperature and high field, the system exhibits a

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31 In the amorphous thin film system, the dissipation is suggested to result from vortex tunneling (see specifically Yazdani and Kapitulnik, 1995; Shimshoni et al., 1998).
transition into a state where the fluctuations of the local superfluid density, $n_s(r)$, are larger than the average – the probabilities of having a positive or negative $n_s(r)$ become comparable. These fluctuations, further, can lead to an inhomogeneous state of superconducting droplets. In this case, a globally superconducting state would be obtained if the coupling between droplets is sufficiently strong.

Given the morphology and structure of Au$_{0.7}$In$_{0.3}$ it is natural to model the system as an SNS Josephson junction array, as pointed out earlier. In this case, the observed gap and coherence peak features in the tunneling spectra results from the existence of grains with a well-defined superconducting order parameter.

Feigel’man et al (2001; and references therein) have considered a superconductor-normal metal transition in a 2D SNS Josephson junction array. Their system consists of an array of superconducting grains of radius $r$, coupled by a 2D normal metal conductor (of dimensionless conductance $g = [h/e^2]/R_q$), and with distance between neighboring grains $d >> r$. The interface resistance between the superconducting grains and the normal metal matrix is low, and the grains themselves are large. The theory predicts that the macroscopically superconducting state is unstable with respect to quantum fluctuations if $g < g_c = [(1/\pi)\ln(d/r)]^2$, where a transition to a normal metal state is found. Here, $g_c$ corresponds to a critical sheet resistance $R_c = h/e^2g_c$ much less than the quantum resistance $R_q = h/4e^2$.

The results obtained in Au$_{0.7}$In$_{0.3}$ may be analyzed in this context. For a Au$_{0.7}$In$_{0.3}$ film with spatially varying local $T_c$ (Zadorozhny and Liu, 2002), the applied parallel magnetic field serves to drive local areas of the film with lower $T_c$ normal. As a result, the concentration of superconducting grains decreases, effectively increasing the distance between the neighboring grains. A transition from a fully superconducting state to one exhibiting normal metal behavior is observed at a critical field. The resistances involved here are well below $R_q$ (see Tab. 4.1 for $R^N$), in agreement with theory. Also within this scenario, the observed coherence peak and gap features in the tunneling spectra are understandable – the tunneling measurements are sampling the energy gap in the superconducting grains with the highest $T_c$s.

However, the theory may be incomplete for Au$_{0.7}$In$_{0.3}$ films, as suggested by an estimate of the critical concentration of grains necessary to drive the S-N transition. An estimate of $d/r$ can be made given the result $g_c^{1/2} = (1/\pi)\ln(d/r)$. Values of $R^N$ are listed in Tab. 4.1 for the films shown in Fig. 4.2. Using, for example, $R^N = 9.96\Omega$ as the critical resistance and the associated dimensionless conductance $g_c = 404$, the distance between grains is $d = re^{63}$. The predicted concentration of grains is, therefore, exponentially small.$^{32}$

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$^{32}$ Also pointed out by Spivak et al (2001).
The $I-V$ characteristics (Fig. 4.5) indicates that quasi-long range phase coherence is achieved at $T_{\text{KTB}} < 25\text{mK}$; the same sample, in comparison, has an estimated mean field superconducting transition temperature $T_{c0} = 0.48\text{K}$, where $T_{c0}$ is determined by $R(T_{c0}) = 0.5R_N$.\textsuperscript{33} A more conservative estimate of $T_{c0}$ is the onset of the coherence and gap features in the tunneling spectra; in this case this would correspond to $T_{c0} = 0.28\text{K}$, still well above $T_{\text{KTB}}$. The large difference between values of $T_{c0}$ and $T_{\text{KTB}}$ suggests that the phase fluctuation in the Au$_{0.7}$In$_{0.3}$ films is large.

Spivak et al\textsuperscript{(2001)} have addressed a system akin to that of Feigel’man et al, though specifically in the limit of small grain size ($r < \xi$). They also predict a quantum S-N transition can take place at a large conductance. The critical concentration of grains, in this case, appears to be relatively large.

Although a direct observation of amplitude fluctuation is difficult, the broadening of the tunneling spectrum has previously been argued to corroborate the existence of amplitude fluctuations in disordered superconducting films.\textsuperscript{34} Spectrum broadening is evident here and comparable to those previously reported. For Au$_{0.7}$In$_{0.3}$ films with superconducting grains of varying size, the amplitude fluctuations may be significant. With increasing field, substantial fluctuations are induced in the smaller grains. The situation is consistent with the dependence of $G_j(V=0)$ on applied field. As shown in Fig. 4.11, the increase in $G_j(V=0)$ suggests that the area between the robust superconducting grains grows linearly with $H_{//}$.

In summary, the transport properties and tunneling spectra of Au$_{0.7}$In$_{0.3}$ thin films have been studied. Under applied parallel magnetic field, a transition from a superconducting to normal metal state was found to occur in the $T=0$ limit. Measurements of the $I-V$ characteristics suggest that the normal state may be populated by free vortices. Tunneling spectra in both superconducting and normal states exhibit a gap feature and coherence peak, though substantially broadened.

The experimental results qualitatively agree with a quantum S-N transition predicted to occur in a system of superconducting grains coupled via a normal metal. However, quantitative agreement with theory is lacking, but may be reconciled if the effects of both phase and amplitude fluctuations are taken into account.

\textsuperscript{33} Values for the films shown in Fig. 4.2 are given in Tab. 4.1.

Tab. 4.1 Parameters for the Au$_{0.7}$In$_{0.3}$ films shown in Fig. 4.2. $T_{c0}$ is defined by $R(T_{c0}) = 0.5 R^N$. The listed values for $g^N = [R^N/(\hbar/e^2)]^{-1}$ are dimensionless.

<table>
<thead>
<tr>
<th></th>
<th>$R^N$ (Ω)</th>
<th>$g^N$</th>
<th>$T_{c0}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.5nm thick planar film (Fig. 4.2a)</td>
<td>89.2</td>
<td>44.8</td>
<td>0.25</td>
</tr>
<tr>
<td>10nm thick planar film (Fig. 4.2b)</td>
<td>55.7</td>
<td>71.8</td>
<td>0.45</td>
</tr>
<tr>
<td>30nm thick planar film (Fig. 4.2c)</td>
<td>9.9</td>
<td>404</td>
<td>0.48</td>
</tr>
<tr>
<td>30nm thick cylindrical film (Fig. 4.2d)</td>
<td>9.96</td>
<td>402</td>
<td>0.31</td>
</tr>
</tbody>
</table>

![Graph](image.png)

Fig. 4.11 Tunneling conductance at zero bias voltage, $G_j(V=0)$, as a function of $H/J$. 
5. Novel phenomena in ultrathin, doubly connected superconducting cylinders

5.1. Introduction to geometry, mesoscopics and superconductivity

Recent advances in nanotechnology have led to dramatic progress in mesoscopic superconductivity. Fascinating phenomena have been found when the size of a superconducting sample becomes comparable to, or smaller than, the zero temperature superconducting coherence length, $\xi(0)$.\(^{35}\) Phenomena observed in this regime include the paramagnetic Meissner effect in micron-sized structures (Geim et al, 1994), quantization of the energy of the Bose condensate in submicron superconductors (Geim et al, 1997), the suppression of superconductivity in nanoscale samples (Anderson, 1959; for a review see Tinkham et al, 1996 or von Delft and Ralph, 2001), and the effect of sample topology.

Independent of sample size, the fluxoid in a doubly connected superconductor is quantized. This quantization is a consequence of the global phase coherence among Cooper pairs, which allows the system to be described by a wavefunction $\psi(r) = |\psi(r)| e^{i\varphi(r)}$. In the case of a superconducting ring (see Fig. 5.1a), the single valuedness of $\psi$ requires that the phase factor $\varphi(r)$ return to itself (modulo $2\pi$) as it goes around the ring

$$\int_C \nabla \varphi \cdot ds = 2\pi n$$

As a result, the fluxoid $\Phi'$, which is the applied magnetic flux $\Phi$ enclosed by the ring and a term related to the superfluid velocity $v_s$, is quantized:

$$\Phi' = \Phi + \left( \frac{m^* c}{e^*} \right) \int_C v_s \cdot ds$$

$$\Phi' = n h c / e^* = n \Phi_0$$

\(^{35}\) In bulk superconducting Al, $\xi(0)$ is approx. 1µm. In small samples, this length can still be a substantial fraction of a micron (~0.1µm for small Al samples).
where $m^*$ and $e^*$ are the effective mass and charge of the Cooper pairs, respectively, $C$ is a closed contour in the superconductor, and $\Phi_0 = \hbar c / 2e$ is the superconducting fluxoid quantum$^{36}$ (London, 1950).

The supercurrent $v_s$ in the ring flows only in the surface layer of thickness comparable to the penetration depth $\lambda$ (Meissner effect). If the ring is thick compared to $\lambda$, then contour can be taken where $v_s = 0$. In this case, the fluxoid is the same as the magnetic flux ($\Phi' = \Phi$). Therefore, the flux itself is also quantized (Deaver and Fairbank, 1961; Doll and Nabauer, 1961).

In sufficiently thin rings or thin-walled cylinders (see Fig. 5.1b), where the width of the ring is less than $\lambda$, $v_s$ can be uniform in the sample. The quantization of the fluxoid, leads to

$$v_s = (2\hbar / m^* d)(n - \Phi / \Phi_0)$$

where $d$ is the diameter of the sample, and $n$ is an integer which minimizes $v_s$. The supercurrent velocity, and its associated kinetic energy, is then a periodic function of $\Phi / \Phi_0$ (see Fig. 5.2). It follows that the free energy of the superconducting state in the ring is also periodic in flux, and so is the transition temperature – $T_c$ exhibits minimum values precisely where $v_s$ is maximized (Little and Parks, 1962, 1964). In a superconducting cylinder in an axial magnetic field, this effect may be seen in the resistance as a function of magnetic field, $R(H)$, as an oscillation of period $h/2e$ (Fig. 5.3a). Alternatively, as given in Fig. 5.3b, measurements of the $H-T$ phase boundary show $h/2e$ oscillations (Meyers and Meservey, 1971).

In the following, results on ultrathin, doubly connected superconducting cylinders in external applied magnetic flux are presented. The samples involved are nearly an order of magnitude smaller than those previously studied (Deaver and Fairbank, 1961). New physical phenomena were observed, which appears to directly result from the size and geometrical constraints on the superconducting state.

$^{36}$ in CGS units = $2.07 \times 10^{-7}$ G·cm$^2$. In SI units, $\Phi_0 = h/2e = 2.07 \times 10^{-15}$ Wb.
Fig. 5.1 (a) Superconducting ring. The dashed line denotes a closed contour. (b) Schematic of the experimental configuration used in the present studies: a doubly connected cylinder in an applied flux, $\Phi$.

Fig. 5.2 Supercurrent velocity, $v_s$, and $v_s^2$ as a function of applied flux. The depression of $T_c$, and the increase of resistance in the experiment, is proportional to $v_s^2$. 

\[ v_s^2 \sim \Delta T_c(\Phi) \]
Fig. 5.3. (a) Little-Parks resistance oscillation. Resistance of a \( \text{Sn} \) cylinder as function of applied magnetic field. The straight line is the magnetic field variation, with zero being the center of the picture. (From Little and Parks, 1962). (b) \( \Phi - T \) phase diagram for an \( \text{Al} \) cylinder. An oscillation, of period \( h/2e \), is present at the superconductor-normal metal phase boundary. (From Meyers and Meservey, 1971)
5.2. Existence of a destructive regime in ultrathin, superconducting cylinders

5.2.1. Theoretical prediction

de Gennes (1981) considered a superconducting loop with a dangling arm and predicted two very different physical regimes should emerge for different ring diameters. For large rings, the conventional Little-Parks effect, with a small oscillation in $T_c$, should be found, and superconductivity should exist at zero temperature in all magnetic fields up to the critical field. However, for $d < \xi(0)$, where $\xi(0)$ is the zero temperature superconducting coherence length, a destructive regime should occur. For a simple ring, without the arm, the solution of the Ginzburg-Landau equation leads to

$$\cos(2\pi\Phi/\Phi_0) = \cos(\pi d/\xi(T))$$

where $\xi(T) = \xi(0)[T_c/(T_c-T)]^{1/2}$. Eq. 5.4 does not have a solution when $d < \xi(0)$, for $\Phi$ given by

$$(k\Phi_0 - \Delta\Phi)/2 < \Phi < (k\Phi_0 + \Delta\Phi)/2$$

where $k$ is an odd integer and $\Delta\Phi = (1 - d/\xi(0))\Phi_0$. The S-N phase boundary (see Fig. 5.4b), derived from Eq. 5.4, is

$$(n - \Phi/\Phi_0)^2 = [d/2\xi(0)]^2(1 - T/T_c).$$

The destruction of superconductivity at zero temperature is directly related to the sample-size induced increase in $v_s$ in a doubly connected superconductor. Within the Ginzburg-Landau free energy, the kinetic energy density of the supercurrent $1/2n_s^*m^*v_s^2$ can be compared with the superconducting condensation energy density in an applied field (Tinkham, 1996),

$$H_c^2/8\pi + H^2/8\pi = n_s^*\hbar^2/4m^*\xi^2(T) + H^2/8\pi$$

where $H_c$ is the thermodynamic critical field, and $H$ is the applied field. The doubly connected sample geometry demands that the supercurrent increase towards its maximum value of $v_s^{\text{max}} = \hbar/m^*d$ at half-integer flux quanta, as long as global phase coherence is present in the sample (see Fig. 5.2). If $d$ is made sufficiently small, the kinetic energy would be pushed so high as the flux nears half-integer quanta, that it would be impossible to compensate this energy by the condensation energy, making the globally phase coherent superconducting state energetically

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37 For a follow up, see Straley and Visscher (1982), where an extension of the theory, as well as a detailed summary of the original work, is included.
unfavorable. This way of suppressing superconductivity is fundamentally different from that by strong disorder or Coulomb repulsion (see Ch. 3.1; and references therein).

Fig. 5.4 (a) Configuration originally considered by de Gennes (1981). (b) Predicted phase boundary for a ring ($L=0$).
5.2.2. Experimental results

The destructive regime predicted by de Gennes is difficult to observe experimentally. If rings are used, the condition \( d < \xi(0) \) requires the rings be extremely small in diameter and, subsequently, line width. These types of samples typically have short coherence lengths because of the unavoidable disorder introduced by structural defects and boundary roughness. Santhanam et al. (1989) attempted to measure the predicted destructive regime in small Al superconducting loops.\(^{38}\) However, the sample sizes were too large to reach the regime considered theoretically. The samples studied had \( d = 0.76\mu m \), substantially larger than the estimate on \( \xi(0) \) of \( 0.1\mu m \). Studies by Moschalkov et al. (1995) may also probe the effect, though – again – the samples size were too large (sizes \( \sim 1\mu m \), \( \xi(0) = 0.1\mu m \)).

Ultrathin, doubly connected cylinders of Al and Au\(_{0.7}\)In\(_{0.3}\) were used in the present study. These samples have advantages over the rings as they can have both sufficiently high critical fields and reasonably long superconducting coherence lengths.

Figures 5.5 and 5.6 show the resistance of an Al cylinder with \( d = 150\)nm as a function of \( \Phi \) and \( T \). At the lowest temperatures, the sample was superconducting for a substantial range of magnetic field below \( H_{c2} \). However, zero resistance was absent for a range of \( \Phi \) around \( \Phi = \pm 1/2 \) and \( \pm 3/2 \Phi_0 \), resulting in narrow resistance peaks. At the lowest temperature, \( T = 20\)mK, the resistance peaks at \( \Phi = \pm 1/2 \Phi_0 \) had a magnitude \( R \approx 310\)Ω, a significant fraction of the normal-state resistance \( R^N \approx 930\)Ω, and a width of approximately \( 0.18\Phi_0 \), as measured at the onset of nonzero resistance.

As shown in Fig. 5.7a, the temperature dependence of the resistance measured in zero and finite fields corresponding to integer and half-integer flux quanta shows that, at zero field, the sample became superconducting at \( T \approx 1.3\)K. At \( 1/2 \Phi_0 \) the resistance showed a broad drop starting around \( 1\)K, in strong contrast with \( R(T) \) at \( \Phi = \Phi_0 \) where a sharp transition to zero resistance was seen at \( 1\)K even though the applied field was higher. Similar behavior was also observed in an ultrathin cylinder of Au\(_{0.7}\)In\(_{0.3}\) with \( d = 154\)nm (see Liu et al., 2001; Zadorozhny, 2003). For these cylinders, \( R(T) \) at \( 1/2 \Phi_0 \) leveled off to a substantial fraction of \( R^N \), showing almost no change from \( 200\)mK down to \( 20\)mK. In contrast, the temperature dependence of a larger Al cylinder, with \( d = 357\)nm, displayed a conventional \( T_c \) oscillation with no essential difference in the shape of \( R(T) \) at integer and half-integer flux quanta, as seen in Fig. 5.7b.

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\(^{38}\) One loop included a dangling arm, as originally addressed by de Gennes (1981).
The systematic behavior observed in all samples suggests that a sample with a sufficiently small diameter may remain non-superconducting around half-integer flux quanta even at zero temperature. A phase diagram can be obtained from the magnetoresistance measurements. As shown in Fig. 5.8, a normal phase extends deep into the region where superconductivity would be expected for cylinders of a conventional size.

To compare experimental results with theory, values of $\xi(T)$ are estimated from

$$H_{c1}(T) = \sqrt{3}\Phi_0/\pi t\xi(T)$$

where $t$ is the film thickness (Tinkham, 1996). Using the onset $H_{c1}(T)$, $\xi(T)$ are found to be 161 nm for the smaller Al cylinder ($d = 150$ nm) at 20 mK, 160 nm for the Au$_{0.7}$In$_{0.3}$ cylinder ($d = 154$ nm) at 20 mK, and 60 nm for the larger Al cylinder ($d = 357$ nm) at 0.39K ($\xi(0) < 60$nm). Therefore, $d < \xi(0)$ for the two smaller cylinders, while $d > \xi(0)$ for the larger Al cylinder, as expected.

![Fig. 5.5](image)

Fig. 5.5 $R(T, \Phi)$ for an Al cylinder with $d = 150$ and film thickness $t = 30$nm. At $T = 20$mK the resistance peak at $\Phi = \pm 1/2\Phi_0$ has a width of $\Delta \Phi = 0.18 \Phi_0$, and a magnitude $R = 0.33 R^N$, where $R^N (= 930 \Omega)$ is the normal state resistance. Values of resistance were taken every 0.01$\Phi_0$ from -2.5$\Phi_0$ to +2.5$\Phi_0$, at 20mK and every 100mK starting from 0.10K up to 1.30K. The solid red line connects data taken at 20mK.
Fig. 5.6 Same data shown in Fig. 5.5, looking only at the $R, H$ plane. For clarity, only the $T = 20\text{mK}, 0.4\text{K}, 0.6\text{K}, 0.8\text{K}, 1.0\text{K}, 1.2\text{K},$ and $1.3\text{K}$ curves are shown.

Fig. 5.7 $R(T)$ for Al and Au$_{0.7}$In$_{0.3}$ cylinders, at several fixed values of $\Phi$ as indicated. (a) Al cylinder with $d = 143\text{nm}, \xi \approx 161\text{nm}$ at $T = 20\text{mK}$. (b) Al cylinder with $d = 357\text{nm}, \xi \approx 60\text{nm}$ at $T = 0.39\text{K}$. In (a), a broad drop in resistance is seen at $\Phi_0/2$, followed by a leveling off of the resistance at the lowest temperatures. This is in contrast with the resistive transitions seen at integer multiples of $\Phi_0$, as well as what is exhibited by the cylinder shown in (b).
Fig. 5.8 Phase diagram for an Al cylinder with $d = 143\,\text{nm}$, $\xi = 161\,\text{nm}$ at $T = 20\,\text{mK}$. Disconnected phase coherent superconducting regions are found in the limit of zero temperature. Solid lines are a fit to theory. A value of $R(T_c) = 0.05\,\text{R}^S$ was chosen to determine the phase boundary.
5.3. Superconducting fluctuations in the destructive regime

In the destructive regime, $R(T)$ measurements showed a broad drop in the resistance at the relatively higher temperatures. The temperature dependence of the excess conductivity $\Delta \sigma \, (= \sigma - \sigma_N$, where $\sigma_N$ is the normal state conductivity) in this region is found to exponentially grow with decreasing temperature. The behavior may be a result of superconducting fluctuations present in the destructive regime.

At integer flux quanta, the resistive transitions exhibited the expected $T_c$ shift, with very little broadening of the resistive transition. In comparison, a relatively broad drop in resistance was found for half-integer flux quanta. This behavior is different from the transition broadening resulting from flux motion, as the field in the parallel orientation does not induce vortices in thin cylindrical films. If a small misalignment of the cylinder does lead to field-induced vortices, a higher field would generate a higher number of vortices and result in a wider transition. Nevertheless, the $\Phi = \Phi_0, 2\Phi_0$ curves showed significantly narrower resistive transitions than what is seen at $1/2 \Phi_0$ and $3/2 \Phi_0$.

It is clear, however, that the substantial drop in resistance is related to superconductivity. As the finite resistance at the lowest temperatures only indicates the loss of global phase coherence, it is possible that local pair formation may still survive. In particular, it is reasonable to ask whether the behavior is consistent with the presence of superconducting fluctuations.

In this case, the temperature dependence of the conductance is given by the Aslamasov-Larkin theory (1968) for fluctuation-enhanced conductivity. The normal state conductivity is supplemented by superconducting fluctuations, such that the excess conductivity (for a review, see Tinkham, 1996)

$$\Delta \sigma = \rho^{-1} \cdot \rho_N^{-1} \approx (2e^2/m^*) \Sigma <\psi_k|^2 \tau_k/2$$

where $\psi_k$ is the Fourier coefficient of the superconducting order parameter in momentum ($k$) space, and $\tau_k$ is the relaxation coefficient in the time-dependent Ginzburg-Landau equation. The temperature dependence of $\Delta \sigma$ is found by integration of Eq. A.2 over $k$ space, which leads to

$$\Delta \sigma \sim [T/(T - T_c)]^{3/2}$$

in 1D.

As can be seen in Fig. 5.9, the excess conductance at half-integer $\Phi_0$ does not exhibit the behavior predicted by the standard AL theory, but instead showed an exponential dependence on temperature. This dependence may still be consistent with fluctuation-enhanced conductivity. The AL temperature dependence directly results from the $T$-dependence of $\tau_k$ and $|\psi_k|^2$, determined by
assigning an energy of $k_b T$ to each orthogonal mode, i.e. each $k$ value (Tinkham, 1996). In the present case, this energy may not be assumed to be $k_b T$, as done in the standard calculation at relatively high temperatures. The Bose-Einstein distribution must be included in the temperature range considered. While a thorough calculation of $\Delta \sigma$ in this case remains to be carried out, it is reasonable to expect that this consideration would introduce an exponential $T$-dependence to the expression for $\Delta \sigma$, consistent with the experimental data.

Fig. 5.9 Semilog plot of the excess conductance ($= R^{-1} - R_N^{-1}$) as a function of temperature at $\Phi = \frac{1}{2} \Phi_0$ and $\frac{3}{2} \Phi_0$. 
5.4. Zero-temperature, flux-tuned superconductor-normal metal phase transition

5.4.1. Experimental results on the resistive transition in the vicinity of Φ₀/2

Fig. 5.10 shows $R(T)$ at several values of applied field for an Al cylinder, with $d = 150\text{nm}$ and $\xi(T) = 161\text{nm}$. As previously noted, the superconducting transition exhibited the conventional $T_c$ shift followed by zero sample resistance at sufficiently low temperatures, for small values of $\Phi$. Furthermore, as $\Phi$ neared 1/2 $\Phi_0 (H_{//} = 585.5\text{G})$, a finite resistance emerged in the $T = 0$ limit.

Curves near 1/2 $\Phi_0$ also exhibited pronounced step-like features at certain values of the resistance, as indicated in Fig. 5.10. Such features in the resistive transition are frequently attributed to sample inhomogeneity. However, the features fall into regularly spaced positions as the normal state was approached, as shown in Fig. 5.11a. At fixed $\Phi$ with increasing $T$, the first step ($n=1$) appears, followed by the second ($n=2$), and so on. The resistance at each step ($R_b$) is defined by where the relatively rapidly decreasing resistance meets the relatively slow plateau behavior (see Fig. 5.11b). The regularity exhibited in Fig. 5.11a is difficult to understand in an inhomogeneity scenario. Moreover, these features became less distinct at $H=420\text{G}$ and were not observed at $H=295\text{G}$, suggesting that the steps are induced by the applied field.

The steps in the resistive transition may be explained by the emergence of normal regions in the form of bands, as shown in Fig 5.12. At fixed $\Phi$ with increasing $T$, the uniformly superconducting cylinder breaks down with one normal band emerging, followed by the formation of two additional normal regions, and so on. The number of normal metal bands increases as $N = 2^n-1$. Given that the coherence length in this sample is much lower than that in the bulk, it is reasonable to expect that this Al cylinder is a type II superconductor. This is not inconsistent with estimates of the relevant lengths ($\xi=161\text{nm}$ and $\lambda=115\text{nm}$ at $T=20\text{mK}$, which leads to $\kappa \geq 1/\sqrt{2}$). Therefore, the S-N interface energy should be negative. (Note that the field is perpendicular to the interface, so the interface energy in this case, which has not been treated theoretically, is different from the bulk case.) The presence of normal regions then lowers the overall free energy of the system, similar to the formation of the Abrikosov vortex lattice in higher dimensional systems. In this scenario, the resistance of the sample is determined by...
number of normal metal bands, $R_0 = N R_0$ where $R_0$ is the resistance of a single band, and leads to roughly evenly spaced steps on a logarithmic scale, as seen experimentally.\textsuperscript{39}

It is notable that an inhomogeneous superconducting state was not predicted for the superconducting ring (de Gennes, 1981). The additional degree of freedom introduced by the finite length of the cylinder, however, introduces the possibility of an inhomogenous superconducting state, with additional features accompanying the destruction of superconductivity.

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\textsuperscript{39} Although a sequence beginning with an even number of bands (e.g. $N = 2, 5, ...$) should also be possible the initial formation of two bands likely corresponds to a higher free energy barrier than the formation of just one band and is, therefore, unfavorable.
Fig. 5.11 (a) The resistance at each step as a function of step number, $R_b(n)$ where $n=1$ corresponds to the lowest step at $R=10.2\,\Omega$. Error bars indicate the resistance range for each step; points without error bars have errors smaller than the point size. (b) How $R_b$ was determined.

Fig. 5.12 Schematic of the normal band formation with increasing $T$ at fixed $\Phi$. 

$n = 1, 2, 3$
5.4.2. Theoretical models of the resistive transition in 1D: Flux controlled thermally activated phase slips

The standard model for 1D wires is given by the Langer-Ambegoakar-McCumber-Halperin (LAMH) theory (Langer and Ambergoakar, 1967; McCumber and Halperin, 1970) wherein dissipation results from the superconducting order parameter $\psi$ fluctuating to zero at a section in the wire of length of the zero temperature superconducting coherence length, allowing the relative phase across the section to slip by $2\pi$. This process is associated with the thermal activation of the system over a free energy barrier. The resistance is predicted to follow

$$R_{\text{LAMH}}(T) \sim (\Omega/T) \exp(-\Delta F/k_B T)$$

where $\Delta F$ is the free energy barrier height, $\Omega = (\Delta F/k_B T)^{1/2} L/\xi_{\text{G-L}}$ is a weakly temperature dependent attempt frequency, and $\tau_{\text{G-L}} = h/(16k_B(T_c - T))$ is the characteristic time scale in the time dependent Ginzburg-Landau (G-L) theory. Adopting the G-L theory implies that the superconducting order parameter, strictly not present for 1D systems due to the lack of long-range phase coherence (Hohenberg, 1967), is well defined locally.

The explicit expression for $R_{\text{LAMH}}(T)$ was obtained in the absence of an applied magnetic field. In finite fields, the determination of $\Delta F$ involves, in principle, solving coupled G-L and Maxwell equations, where the latter describes the field outside the sample. Corresponding boundary conditions at the inner and outer cylinder surfaces, as well as infinitely far away, must also be considered. As a result, the explicit expression of $R_{\text{LAMH}}$ obtained in the original work cannot be applied directly to the current experimental configuration.

However, the general form given by Eq. 5.11 should still be applicable for thermally activated phase slips even when an external magnetic flux is present. $\Delta F$ can be estimated from the energy associated with the formation of a normal band of length $\xi(T)$ (see Fig. 5.13). The G-L expression for the free energy density is given by

$$f = f_n + \alpha|\psi|^2 + 1/2 \beta|\psi|^4 + 1/2 m^* v_s^2 |\psi|^2 + \hbar^2/8\pi$$

$$\Delta F = \int (f_1 - f_0) dV$$

where $\alpha = -e^2 H_c^2 \lambda^2/m^* c^2$, $\beta = 4\pi e^4 H_c^2 \lambda^4/m^* c^4$, $H_c$ is the thermodynamic critical field, and $\lambda$ is the penetration depth. For a given $v_s$, the minimum of $f$ corresponds to the free energy density of the superconducting state in a magnetic field. The free energy densities of the superconducting state with and without the normal band of length $\xi(T)$ are $f_1$ and $f_0$, respectively. If the energies associated with the field and the interfaces between the superconducting and normal regions are omitted,

$$\Delta F \approx (f_n - f_n^0) A \xi(T)$$
where \( A \) is the cross sectional area. Then from Eq. 5.11,

\[
R_{TA}(T, \Phi) \sim (\Omega/T) \exp\{a_1(1-r^2)^{3/2}(1+r^2)^{1/2}[1 - a_2v_s^2(\Phi)(1+r^2)/(1-r^2)]/k_b T\}
\]

5.14

where the phenomenological temperature dependences for bulk superconductors were used for \( \xi(T) \), \( \lambda(T) \), and \( H_c(T) \). In the above, \( a_1 = \hbar c A H_c(0)/16\sqrt{\pi} e^* \lambda(0) \), \( a_2 = [m^* c/2e^* H_c(0) \lambda(0)]^2 \), and \( t = T/T_c(\Phi) \). A \( \Phi \) dependence also results from the constraint imposed by the fluxoid quantization,

\[
v_s(\Phi) = (n - \Phi/\Phi_0) \hbar m^* d
\]

where \( n = 1 \) for the range of \( \Phi \) studied. The \( \Phi \) dependence of \( T_c \) and \( v_s \) leads to a phase slip rate controlled by the applied magnetic flux.

It is notable that as the temperature is lowered far below \( T_c \), the number of thermally activated phase slips decreases exponentially (see Eq. 5.11). Nevertheless, previous experiments (Giordano, 1994; and references therein) have clearly demonstrated finite resistance far below \( T_c \), as well as deviations from the predicted LAMH behavior in ultrathin wires (Sharifi et al., 1993). It was suggested that the observed resistance may be from quantum fluctuations. The fluctuations would result in quantum phase slips, corresponding to tunneling through the free energy barrier (as opposed to going over the barrier as discussed above). Recently, this problem has received renewed attention.\(^4\)

Would quantum phase slips be applicable to the current study? The original proposal originated from observations of a weakly temperature dependent tail in the resistive transition at the lowest temperatures in thin In and Pb wires (Giordano, 1988). Subsequent experimental work (Lau et al., 2001) appears to demonstrate that the process should be more pronounced in very thin wires (10-22nm in width), where a substantial broadening of the transition with decreasing wire width could not be explained by the conventional LAMH expression. Though smaller than \( \xi(0) \), the diameter of the cylinders studied here are large in comparison. Further experiments are needed to resolve this issue.

\(^4\) For experimental studies see, e.g., Giordano (1988, 1991, 1994); Bezryadin et al., (2000); Lau et al. (2001); and references therein. For theoretical work see, e.g., Duan (1995); Zaikin et al. (1997); Golubev and Zaikin (2001); and references therein.
Fig. 5.13 Schematic of the thermally activated phase slip process in a doubly connected cylinder.
5.4.3. Analysis of the resistive transition

At the lowest temperatures, below the first resistance plateau, the resistive transition appears to be described by thermally activated phase slips quite well. In Fig. 5.10, solid lines indicate results of two-parameter fits using the above expression to the lower part of the resistive transitions. To reduce the number of fitting parameters, $\Omega$ was taken to be constant as the results were insensitive to its temperature dependence, and $T_c(\Phi)$ was taken to be the temperature at which the lowest step in the resistive transition was observed ($R(T_c)=10.2\Omega$).

In the $T=0$ limit, Eq. 5.14 has an $\exp(-T_0/T)$ dependence where $T_0 = a_0[1-a_2\nu_s^2(\Phi)]^2/k_b$. $T_0$ may represent the relevant energy scale for the thermally activated phase slips, analogous to $\Delta F$ given in Eq. 5.11. Values of $T_0$ can be found from the fits to Eq. 5.14. As shown in Fig. 5.14, $T_0$ decreased as $\Phi$ increased, indicating a reduced free energy barrier height with increased flux. The physical mechanism behind the decrease in $\Delta F$ is related to the reduced condensation energy in applied field, as noted in Ch. 5.2.1. An enhanced phase slip rate results from the lowered barrier height. This effect is also explicitly seen in Eq. 5.14, where $T_c$ and $\nu_s$ have distinct $\Phi$ dependences.

While curves up to 526G show agreement with the theory, significant deviation emerged at 527G ($\Phi \approx 0.45 \Phi_0$). This value of the flux can be identified as a critical value $\Phi_c$ (see Fig. 5.10). For $\Phi < \Phi_c$, the curves exhibited a distinctly negative curvature consistent with the phase slip model, particularly in the lowest part of the resistive transition. For $\Phi \geq \Phi_c$, however, the curves could not be described by the above expression. More precisely, as shown in Fig. 5.15, the curves for $\Phi \geq \Phi_c$ are best described by a linear $T$-dependence. The transition between the behaviors occurs over 1G, or $< 1\cdot10^{-3}\Phi_0$.

Interestingly, a linear dependence has been predicted (Giamarchi and Schulz, 1988; Fisher et al, 1990) for a metallic state at the critical point of the superconductor-insulator transition (SIT) in 1D. Is the transition observed here a quantum phase transition (QPT) in a 1D system? QPTs have attracted intense theoretical and experimental attention in the past two decades (see, e.g., Sohndi et al, 1997; Sachdev, 2001). These transitions occur at zero-temperature, where crossing the phase boundary represents a fundamental change in the ground state properties of the system. In superconducting systems, the problem of a QPT in $D$ dimensions can be mapped onto an XY model in $D+1$ dimensions. The XY model in 2D possesses only quasi-long range order, as described in the Kosterlitz-Thouless-Berezinskii (KTB) theory (Berezinskii, 1971; Kosterlitz and Thouless, 1973; Kosterlitz, 1974), consistent with the fact that true long-range superconducting phase coherence is not possible in 1D, even at $T=0$.
(Hohenberg, 1967). Systems of finite length, however, can possess KTB order over the entire sample, opening the possibility of observing a true superconducting state in a 1D system.

QPTs have previously been reported in 1D superconductors. So far, however, only one study (Kuo and Chen, 2001) has reported scaling behavior, the hallmark of a QPT. At the quantum critical point, the presence of a diverging length and time scales lead to the scaling of the physical properties in the critical region. In mapping a $D$ dimensional QPT onto a $D+1$ dimensional classical phase transition, the size of the extra dimension (given by $\hbar/k_B T$) is finite for any $T>0$. In 1D samples, both the sample size and the experimental temperature impose cutoffs for scaling. The theory of finite-size scaling states that physical quantities follow the scaling form

$$O(k, \omega, K, T) = \left(\frac{1}{z}\right) L_\tau^{d_O} O(k L_\tau^{1/\nu}, \omega L_\tau, L_\tau/\xi_\tau)$$  \hspace{1cm} (5.15)

where $L_\tau \equiv \hbar/2\pi k_B T$ is the finite length of the imaginary time axis (Sachdev, 2001). The correlation length in the time dimension is $\xi_\tau$, which is related to the spatial correlation length $\xi$ by a dynamical scaling exponent $z$, such that $\xi_\tau \sim \xi_\tau^z$. The wave vector $k = 0$, the scaling dimension $d_\phi = 2 - D = 1$, and $\omega = 0$ for d.c. measurements. The resistance then scales as $R(T, \Phi) = (T^{1/2}) R(1/T\xi_\tau)$. As $\xi_\tau = |\delta|^{-v}$, where $\delta = \Phi - \Phi_c$ and $v$ is the spatial correlation length exponent, the resistance follows

$$R(T, \Phi) = T^{1/2} R(|\delta|^{1/v}/T) = T^{1/2} R(|\Phi - \Phi_c|^{1/v}/T)$$  \hspace{1cm} (5.16)

An attempt scale the data was unsuccessful. This may imply that critical region for the transition is quite small (as expected for a weakly disordered superconducting sample) and that the thermally activated phase slip model does not apply to the critical regime. Alternatively, the lack of scaling may suggest that the observed transition is not a QPT controlled by quantum fluctuation, but a first order transition in nature.

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41 Therefore, the superconducting order parameter is strictly not well defined in 1D.
42 See, for example, Sharifi et al, 1993; Chow et al, 1998; Bezryadin et al, 2000; Kuo and Chen, 2001.
Fig. 5.14 $T_0$ as a function of $\Phi$.

Fig. 5.15 $R(T)$ for fields nearest $\Phi_c$. Solid lines are fits to linear $T$ and $R_{TA}(T)$ dependences for the two higher and three lower curves, respectively.
5.4.4. The S-N phase transition

Figure 5.16 shows the $\Phi$-$T$ phase diagram determined in the context of the normal band formation discussed above where, for a given $\Phi$, several characteristic temperatures are defined by the steps observed in the $R(T)$. The curves in Fig. 5.10 then represent traversing the phase diagram at fixed $\Phi$. Each step in the $R(T)$ represents the crossing of a phase boundary where, with each crossing, normal regions nucleate within the superconducting cylinder. This transition is similar to the classical liquid-vapor phase transition (see Huang, 1987) wherein the transition from liquid to gas occurs by passing through a liquid-gas coexistence regime. In this regime, as $T$ is increased, the vapor phase may form within the liquid as bubbles. The liquid may also be in a superheated metastable state under appropriate conditions. In the present system, the liquid phase would be analogous to the superconducting state, and the gas the normal state.

The phase diagram may be also traversed at fixed $T$ and varying $\Phi$. At finite temperature, this also crosses several phase boundaries. The boundaries obtained from the $R(T)$ curves may extend down to the $T=0$ limit. In this case, the zero temperature, flux-tuned transition to the destructive regime might be accompanied by normal band formation occurring with increasing $\Phi$.

To address the $\Phi$-tuned transition in more detail, however, requires additional magnetoresistance measurements. Existing data, carried out in increments of 5G, showed extremely sharp behavior in this region. In comparison, the spacing between the $n=1$ and $n=6$ boundaries at $T=0.3K$ is only 0.04$\Phi_0$ (approx. 46G). More precise measurements are needed verify that similar steps are indeed present for increasing $\Phi$ at fixed $T$. 

Fig. 5.16 Φ-T phase diagram. The boundaries are defined by steps seen in the resistive transition, $R_s(n)$. The solid line connects data points taken from magnetoresistance measurements at fixed $T$ (Fig. 5.5) using $R(T_c) = 10.2\,\Omega \approx 0.01R_N$. The inset shows the phase diagram over a larger range. The solid line denotes the phase boundary defined by magnetoresistance measurements. The box indicates the area depicted in the main graph.
5.5. Summary

Experimental results in doubly connected cylinders of Al reveal the existence of the predicted destructive regime in cylinders with $d < \xi_0$. The destructive regime is characterized by the absence of global phase coherence in the $T=0$ limit, around applied magnetic flux equal to half-integer multiples of $\Phi_0$. The destructive regime is related to the sample-size induced increase in the supercurrent velocity imposed by the sample’s doubly connected geometry. The increase makes the superconducting state energetically unfavorable in a range of $\Phi$ near $1/2 \Phi_0$. Several questions of fundamental interest are raised by these results.

The first lies in the nature of the destructive regime found at $1/2 \Phi_0$. The $R(T)$ in this regime exhibited a broad drop as temperature was lowered, followed by a temperature independent resistance at the lowest temperatures. An examination of the temperature dependence in this region indicates that the excess conductivity exponentially grows with increasing temperature. This dependence does not suggest any conventional transport mechanism, though it may be consistent with the presence of superconducting fluctuations. It is thereby reasonable to ask whether local pair formation is present, leading to a novel resistive state of Cooper pairs. Further work, both theoretical and experimental, is needed.

The second lies in the zero-temperature flux-tuned transition. Measurements of the resistive transition, at applied flux close to the boundary of the non-superconducting state at $1/2 \Phi_0$, were found to be described by thermally activated phase slips, with the phase slip rate controlled by the applied flux. Features in the resistive transition at a given flux – namely regularly spaced steps in the transition – may be associated with the formation of normal metal regions. The $T=0$ flux-tuned phase transition may be associated with a similar process. However, direct evidence for the formation of such an inhomogeneous superconducting state, as well as its possible formation in singly connected superconducting 1D wires, remains to be found. A better understanding of the transition – whether it is continuous, quantum in nature or of first order – is desired.

Finally, the results may have implications on the physics of 1D superconducting systems. In particular: what would happen if the cylinder were even smaller, so that the circumference was less than $\xi_0$? In this limit, the G-L formulation is presumably invalid and a theory has not been advanced. Experimentally speaking, the preparation of this type of sample challenges the existing processes and technologies. Will these results have an impact on the question of superconductivity in carbon nanotubes, the smallest known doubly connected cylinder?
Superconductivity in single walled carbon nanotubes has been reported (Kociak et al., 2000; Tang et al., 2001), however single carbon nanotubes have yet to be measured.
6. Conclusions

This thesis has examined the effects of disorder and geometrical constraint in several superconducting systems of reduced dimensions. Novel phenomena have been found, including the possible formation of an electron droplet state in the electron glass in highly disordered ultrathin Bi films prepared by quench deposition, a S-N transition in disordered Au$_{0.7}$In$_{0.3}$ thin films of particularly low $R^N$, and a magnetic-flux induced S-N transition in doubly connected ultrathin cylinders.

The electrical transport properties of Bi films prepared by quench deposition were studied \textit{in situ}. These films exhibited a 2D SIT in the limit of zero temperature as the film was made increasingly thicker, consistent with previous studies and typically considered to be a QPT. In superconducting films, a crossover from linear to nonlinear behavior was observed in the $I-V$ characteristic in the transition regime. The results are analyzed within the context of current-induced vortex-antivortex unbinding. Unlike the standard treatment, a finite cutoff length in the logarithmic interaction between vortex-antivortex pairs is taken into consideration. It would be interesting to push this study to the regime close to the SIT. If it is revealed that the interaction between the vortex-antivortex pairs in the superconducting side and that between charges on the insulating side of the SIT in the same sequence of films have the same form, the system will be self-dual and thereby address an outstanding question on the nature of this $T=0$ phase transition.

Subsequent studies of these quench condensed Bi thin films revealed unexpected behavior deep in the insulating regime. A $dR/dT > 0$ emerged as the temperature was lowered, with the resistance reaching a minimum before the expected negative $dR/dT$ was obtained. This behavior was accompanied by a nonlinear and asymmetric $I-V$ characteristic. As the film became thicker, conventional variable-range hopping was recovered. The crossover in the electrical transport properties is attributed to an amorphous to granular structural transition. Further verification of this would involve simultaneous \textit{in situ} structural and transport measurements, a technically challenging endeavor. Also deserving additional study is the metallic behavior found in the amorphous phase at the initial stage of the film growth, presently discussed in the context of the formation of metallic droplets within the electron glass. The evidence for the existence of the droplets requires substantially more experimental and theoretical input. Regardless of the
origin of the metallic behavior – but particularly if droplet formation is present – the above observations point out that the understanding of electron interactions and correlations in strongly disordered systems remains an open problem.

In superconducting Au$_{0.7}$In$_{0.3}$ films, which can be modeled as a random array of SNS Josephson junctions, a magnetic field-driven S-N transition was observed at $R^N \ll R_q$. The metallic state, characterized by a temperature-independent resistance, was found at temperatures much lower than where a substantial drop in resistance occurred. Whereas non-linear $I$-$V$ characteristics were found in the superconducting state, ohmic behavior was present in the metallic state. Tunneling measurements indicate that an energy gap is present in the metallic phase, and is substantially similar to the energy spectra found in the zero field superconducting state. The behavior is discussed in the context of a quantum S-N transition predicted to occur in a system of superconducting grains coupled via a normal metal. However, quantitative agreement with theory is lacking, but may be reconciled if the effects of substantial phase and amplitude fluctuations are taken into account.

Finally, electrical transport measurements in ultrathin doubly connected superconducting cylinders of Al confirmed theoretical predictions of a destructive regime, characterized by the loss of global phase coherence in the $T=0$ limit. The phenomenon occurs in samples with $d < \xi_0$, around half-integer $\Phi_0$. In the destructive regime, a broad drop in resistance was also observed, implying the presence of superconducting fluctuations. Features in the resistive transition near this regime suggest that the loss of superconductivity is associated with the formation of normal metal bands.

In conclusion, the work presented here emphasizes that the effects of strong disorder and geometric constraints in superconducting systems of reduced dimensions remains an intriguing problem in contemporary condensed matter physics. Additional work in the area promises new discoveries, the understanding of which can provide insight into answering fundamental questions.
Appendices

A. Quench deposition

An estimate of the substrate temperature during the quench deposition was determined by measuring the resistance of a La_{1/2}Ba_{1/2}MgO_3 (LBMO) film mounted adjacent to the substrate. The temperature dependence of the resistance for the LBMO film was measured in the same ^3He cool down. The LBMO film was within line of sight of the evaporation sources, with the film center situated approximately 0.5” away from the center of the quench condensed film. In comparison, the Cernox thermometer is mounted on the sample stage, at least 1cm away from the substrate\textsuperscript{43} and not within the line of sight of the evaporations sources. It is, therefore, possible that the actual substrate temperature is different from that reported by the Cernox thermometer.

Fig. A.1 shows the resistance as a function of temperature, R(T), of the LBMO film. The resistance, and correspondingly temperature, of the LBMO film during the deposition of Bi is given in Fig. A.2. These calibrations are taken during the initial Bi depositions, where the Bi film resistance is substantially higher than that of LBMO. The resistance of the LBMO film was also measured after 30Å of Bi was deposited onto both the glazed alumina substrate, and the LBMO film itself – the resistance in this case and was found to be the same as the initial measurement. The resistances are, therefore, taken to be solely from LBMO.

The temperature given in this calibration cannot be said to be exactly that of the Bi film substrate surface. Factors which may lead to a discrepancy between the two temperatures include: differences in substrates – LBMO is grown on an NdGaO\textsubscript{3} (NGO) substrate, in comparison to the glazed alumina substrate for the Bi film; the heat capacity of the LBMO film itself, in comparison to the quench condensed Bi; thermal sinking of the two samples also differ, as the substrate of the LBMO film is G.E. varnished into place, whereas that of the quench condensed Bi is mechanically pressed onto the sample stage. Despite these considerations, the temperatures

\textsuperscript{43} If the thermometer is mounted exactly on the other side of this segment of the sample stage. The thermometer may be mounted as far as 2.5” away, depending on the space allowed by the placement of other mounted samples.
reported here may serve as a guide. It is notable, however, that the temperature reported by the Cernox and by the LBMO film are agree to within < 1K.

![Fig. A.1 Resistance as a function of temperature $R(T)$ of the LBMO film. The film is grown on an NGO substrate, by pulsed laser deposition. (Sample from E. T. Wertz, The Pennsylvania State University.)](image)
Fig. A.2 Resistance and temperature as a function of time, $R(t)$ and $T(t)$, for the LBMO film mounted adjacent to the quench deposited Bi thin film. The deposition rates were (a) 0.1Å/s, (b) 0.2Å/s, and (c) 0.5Å/s. Events occurring during the deposition are as indicated.
B. Micro- and nano-fabrication

This appendix outlines micro- and nanofabrication procedures. The information given here is, for the most part, meant only as a guide. Good, in-depth, references on micro- and nanofabrication include: Moreau (1988) and Rai-Choudhury (1997) for a general and exhaustive discussion, Levinson (2001) for a good introduction, while Brodie and Muray (1992) and Valiev (1992) are more physics oriented. Finally, excellent, but often overlooked, sources of information are the manufacturers and distributors of the photo- and e-beam resists (PSU Nanofabrication Facility supplier is Microchem, Newton MA, website: www.microchem.com).

The basic process consists of first defining the contact layer by photolithography, then creating the smaller structures by e-beam lithography. Overall, the structures were defined by liftoff (additative) processes. The order of the photolithography and e-beam processes is reversible, depending upon (1) the robustness of the e-beam defined structures, and (2) the quality of the alignment marks and contact edges at the end of the photolithography process. If there is any question regarding the fragility of the e-beam defined structures, it is best to keep the e-beam process as the final process, as any subsequent photolith processing may lead to sample damage. If, however, the small structures prove to be hardy, and either the quality of the alignment marks in the photolith process are poor, or the edges of the contact layer are particularly “spiky,” then it is possible (and advisable) to carry out the photolith process last. If the photolith process results in ill-defined alignment marks, the e-beam alignment procedure will be more involved (though not impossible, see B.3). In addition, particularly sharp step edges in the photolith layer may result in inadequate contact to post-written e-beam structures, if the film thickness of the e-beam written structure is significantly less than the height of the step edge in the contact area. Initial attempts at making the contact layer should be inspected using an AFM or profilometer to characterize the edge at the contact area before subsequent e-beam processing is attempted.

B.1. Photolithography procedures

The photolithography pattern used to define the contact layer is shown in Fig. 2.6. The mask is Cr on soda lime glass with a minimum feature size of 5µm. The following procedures are meant for use with a positive photoresist and a liftoff process. The majority of the work was done in at the PSU Electronics Materials and Processing Research Laboratory (EMPRL), with initial work undertaken at the PSU Nanofabrication Facility. A Karl Suss mask aligner was used.
Chemicals used
1. Shipley 1811 photoresist
2. MF351 developer
3. Isopropanol (IPA), acetone, deionized water (DI)

Photolithography process
1. Spin resist onto the substrate: 40s @ 4krpm gives a 1.1µm thick resist.
2. Bake 60s @ 100C.
3. Align and exposed for 1.3 min at 3mW.
4. Develop in 1:5 MF351:DI water for 40s
5. Rinse in DI water, blow dry.

Material evaporation
1. For Au/Cr contacts, thermal evaporation of Cr 25Å, Au 300-500Å
2. For Au$_{0.9}$In$_{0.1}$ contacts, Au and In were thermally evaporated sequentially for a total thickness of 300Å (see Ch. 2.2 for more details.)

Liftoff
1. Liftoff in acetone, heated
2. Ultrasonic agitation for a short period of time (< 5s).
3. Rinse in IPA, blow dry.

B.2. e-beam lithography procedures

The following is a bilayer liftoff process. The majority of the work was done in at the PSU Nanofabrication Facility. A Leica electron-beam pattern generator (EBPG) –5HR was used. To use a different resist thickness, check the spin speed-thickness charts supplied by the manufacturer with each resist. Different concentrations can be made by diluting the resist with the appropriate solvent. Check each product’s (technical) specifications sheet or contact the manufacturer for details. [Modified from process conditions by M. Cabassi, Electrical Engineering Dept., PSU. Initial development procedures obtained from the supplier (Microchem, Newton MA, website: www.microchem.com).]

Chemicals used
1. Polymethyl methacrylate: PMMA, molecular weight 950K, in anisole (3%)
2. co-polymer, methyl methacrylate-methacrylic acid in ethyl lactate: MMA(8.5)MAA, [note that 8.5 refers to the methacrylic acid concentration]
3. methyl-isobutyl-ketone: MIBK
4. Microposit 1165 resist remover
5. IPA and acetone

Resist application to the substrate
1. Spin the co-polymer [MMA(8.5)MAA] to the desired thickness, 40s @ 5krpm gives 4000Å.
2. Bake for 2min @ 150C on a hotplate
3. Spin PMMA to desired thickness, 40s @ 5krpm gives 1200Å
4. Bake 2min @ 180C on a hotplate
5. For insulating substrates (e.g. glass, sapphire, or quartz), 100Å of Au was (thermally) evaporated atop the resist bilayer. This coating film was etched away prior to resist development.

Alignment and exposure (see B.3)

Development
1. Develop in a 1:1 solution of IPA:MBIK for 60s @ 20°C. To keep the temperature well regulated, a water bath was used.
2. Rinse in IPA, 60s
3. Hard bake at 100C for 90s on a hotplate
4. Descum in a reactive ion etcher (RIE) (optional)
   i. Cleans the trenches opened in the resist and smoothes the resist edge.
   ii. Parameters for the Plasmatherm RIE at the PSU Nanofabrication Facility: 100W, 100mT, 40sccm O₂ flow for 15s.

Material evaporation
1. 300Å thick Au₀.₇In₀.₃ films were studied. Films were deposited by thermal evaporation sequential layers of Au and In, beginning and ending with the Au layer (see Ch. 2.2 for more details).

Liftoff
1. Liftoff 1165 remover, heated to 80C. This process can take up to 1hr.
2. If 1165 remover was unavailable, heated acetone was used. Care was taken to make sure that all the acetone did not evaporate.
3. In difficult liftoff cases, short (< 5s) ultrasonic agitation was carried out.
4. Rinse in IPA, DI, blow dry.

B.3. e-beam pattern design, writes, and details
This section primarily deals with issues regarding the design and write of the e-beam pattern/layer. These notes are specific to design, fracturing and machine commands involving L-Edit, CATS, and the Leica EBPG-5HR.

**L-Edit design**

This is the initial pattern/design step. The e-beam writer does not, itself, have an interface adequate to design anything more than a simple rectangle. Anything more complicated requires use of a more user-friendly interface, *i.e.* a CAD program.

L-Edit (software available from Tanner Research) is a graphics editor, designed with lithography in mind. It can output GDSII format, which is a binary format widely used for lithography. L-Edit supports the use of layers, with each layer typically representing one mask or e-beam exposure step in a process.

In designing the pattern, using (and heeding) a grid is particularly helpful, since the following step (CATS fracturing) typically snaps to a user-defined grid – objects not on the grid will either be snapped to grid, or ignored. Stick to polygons or rectangles. If an object has a hole, design the object so that it is a polygon that comes around and meets itself (see Fig. A.3a). Alternatively, the object may be designed in two layers, which are later subtracted from one another (see Fig. A.3b).

A note on AutoCAD – AutoCAD was not designed for lithography and cannot output GDSII format. Its output is DXF, which must be converted into GDSII. This process does not always result in the original design, and significant time might have to be invested in analyzing the resulting GDSII pattern to assure the correctness of the conversion.

![Diagram](image)

Fig. A.3 (a) A doubly connected object, drawn as a polygon (b) A doubly connected object, defined as a two objects on two separate layers.
CATS fracturing

The above GDSII format is still an intermediate format which must be converted to a machine specific format. Generally, this involves the “fracturing” of the GDSII defined polygons into primitive shapes (the lowest level shape understood by the e-beam writer, generally a square), and splitting the pattern into fields and subfields (the entire pattern is not written at one time; it writes in divisions).

This conversion can be done using CATS (available from Transcription Enterprises). Certain parameters must be known in order to convert the GDSII file to machine format – the machine (Leica EBPG-5HR) and the beam energy (for the EBPG-5HR, this is 20kV, 50kV, or 100kV) must, in particular, be defined.

In the fracturing process, a grid is defined. This grid can be (but is not necessarily) the same as the grid in the initial (L-Edit) design, and determines where the e-beam will be placed. For example, for a 6x10µm² rectangle, a 2µm grid will result in a 3x5 object that is defined by 2µm blocks (see Fig. A.4). These blocks are where the beam writer will place a beam. It will place a beam there, regardless of how large (or small) the beam actually is. For a “single pass” write, the grid is set to equal the feature size of the object to be written in single pass (e.g. a 20nm line is set to a 20nm grid).

Objects that are off grid can either be snapped to the nearest grid or ignored (this is user defined during the fracture process). This point is important in the case of arcs or polygons drawn at an angle. To better define these objects, a smaller grid can be used, keeping in mind how this will affect the e-beam write process.

Separate layers of the GDSII design may be fractured simulatenously (at the same grid spacing, etc.) or separately. This is useful in separating particularly large objects from particularly small ones, which are generally written using different beams and doses. GDSII layers may be subtracted from one another, reversed in tone, scaled, or mirrored using the CATS software, prior to the actual fracturing.

Once the pattern is fractured, CATS can output the machine palatable (and Leica specific) IWFL format. This output can be directly viewed in CATS for verification. Note that there is currently no comparable viewer on the e-beam writer. The IWFL file is then transferred to the e-beam machine for the subsequent write process.

It is also of note that geometrical shapes (defined by size, for instance) can be identified in the fracture process and tagged to specify individual doses. A single IWFL file can have tagged objects that are written at different doses from the main pattern (usually defined as a multiple of the primary dose).
Fig. A.4 Rectangular object defined on a grid.

**Leica EBPG-5HR machine notes**

The current operating system for the Leica EBPG-5HR is VAX/VMS, supplemented by a number of machine specific commands. An exhaustive explanation of these commands is given in the command book supplied by Leica.

An e-beam writer is, at its core, an e-beam source with a significant number of (highly expensive and sensitive) electronics and hardware devoted to beam focusing and placement. Each machine has a defined set of parameters associated with a set of beam demagnifications (demags). For a given source filament at a given time in its life and a given beam energy, these demagnifications correspond to set of beam sizes and currents.

For the e-beam to write a pattern, it must be told a specific beam (defined either by the current or the size) and a dose (also known as resist, in units of μC/cm² – this effectively sets the amount of time the beam sits at each particular spot). The beam size is generally chosen to approximately agree with the grid spacing defined during the fracture. The dose is primarily determined by the e-beam resist and the designed pattern. For the patterns and bilayer resists in the present studies, a dose of ~1000μC/cm² was used. The required dose varies, and primarily depends on the resist scheme, substrate, and pattern design. The dose must be empirically determined, usually by writing a dose array. In this procedure, the pattern is written at several different doses (say every 50μC/cm² in the 100-1000μC/cm² range). The resulting patterns are inspected, and the optimal dose (lowest dose at which a complete pattern is present, and not overexposed) determined. The e-beam machine itself defines the dose using the beam current and the grid spacing defined in the pattern.
The other bit of important information the e-beam needs in order to write a pattern is where to write it. The main point of reference used by the e-beam is a set of (immovable, permanent) alignment marks on the substrate holder. Note that although the alignment marks are the point of reference, they are not the origin of the e-beam position grid (although they could be, it is more practical to use the lower left corner or center of the substrate holder to be zero).

If there is no previous layer on the substrate and no alignment is necessary, then the easiest defined spot is the center of the substrate holder. This “center” is defined uniquely for each substrate holder, and referenced to the substrate holder alignment marks. The next easiest position is one that is very roughly defined by using an optical microscope equipped with a X-Y coordinate (rail) system. In this case, the chosen position is referenced to a known spot on the substrate holder (an alignment mark, the faraday cup, etc). This method of alignment can be accomplished to within 20µm.

Generally, life is not so easy, and reference to a previously defined pattern is needed. The “where” task relies on the use of previously defined alignment marks, and, of course, knowing where the pattern should be written with respect to said alignment marks. The Leica EBPG-5HR recognizes rectangles as alignment marks, with the exact dimensions and tone (positive corresponds to raised features; negative to sunken features e.g. etched marks) being user defined. The best places for alignment marks are outer corners of the pattern; three corners out of four are sufficient. If only one alignment mark can be placed, it is best for it to be in the lower left corner of the pattern.

For a single alignment to a single pattern, one defined alignment mark will account for general pattern placement; two marks for substrate rotation; and three for pattern distortion (keystoning, for example). For a series of the same pattern (e.g. the same pattern repeated in a 5x5 array), one alignment mark (per pattern) is sufficient to account for placement and rotation; three per pattern is still necessary for distortion. In a series of exposures, it is possible to align just once, at every exposure, or at user defined intervals.

Although the e-beam can accommodate substrate rotation, it can only do so to within 2°. This angle is specific to the Leica EBPG-5HR at the PSU Nanofab; other machines may be more or (horribly) less. A coarse rotation adjustment must be made during the substrate mounting. Some substrate holders are specifically equipped with a rotation adjustment (generally “small substrate” and GaAs sample holders), although this is not standard.

In order for the e-beam to use the alignment marks, it must recognize them. In general, this means that there must be significant contrast between the mark and the surrounding area and that the sides which define the mark be straight. Definitions of “significant contrast” and “straight” are controllable – there are about 20 adjustable parameters to quantify these two words.
What may pass as an alignment mark on one substrate/resist system, may not pass on another – hence the tweakable (and savable) parameters.

Generally, if any distortions in the sides of the mark can be seen under an optical microscope with a 50x objective, the e-beam will not be able to recognize the object as an alignment mark. Bad marks may, however, still be used for alignment. This requires the user to manually tell the machine (during the write) where the mark is, using the beam-writer’s SEM mode. This user input definition must be made at every mark the writer tries to find. Though time consuming and requiring the presence of a user, this method will get the write done, regardless.

The command files used for alignment are given below. The write relies on 8x8µm² positive alignment marks on the photolith-defined layer, situated in the corners of the pattern. The centers of the marks lie at the vertices of a 152x152µm² square, which defines the write area. The lower left corner of the lower left alignment mark is (80µm, 80µm) in the (x, y) direction away from the center of the e-beam written pattern. It is meant to write the pattern in a series grid, with a step and repeat distance of (1cm, 1cm) in the (x, y) direction. If the e-beam writer cannot identify the initial set of alignment marks, the user is prompted to manually identify them using SEM mode.

Some notes: $ indicates a new command line; ! denotes the start of comment area. “mariannedw2.com” is the main command file. “mardw.com” is a command file, called by the main file.

main command file:

$ !mariannedw2.com
$ !looks for user defined positive markers (8umx8um) within a rectangular area.
$ !if markers aren't found, looks for joy defined markers
$ !adjusts global wafer alignment and distortion
$ !
$ !
$ marker create rect pos 8,8 user !the user defined markers
$ marker create rect pos 8,8 joy !the joy defined markers
$ archive restore beam f##_###_### !restores beam to use for writing
$ adjust beam local !focuses
$ move marker !finds markers on holder
$ adjust table coordinates !adjusts coordinates via marker
$ set on
$ on error goto tryagain
$ move marker posx, posy user
$ vdu "found markers!"
$ layout wafer rectangle sizex, y posx, y /net /center
$! $! $!
$ select patternname
$ adjust srd 10mm, 10mm
$ adjust dwoffs -80um, -80um 8um
$ layout dw_marker #, # user
$! $! $!
$ adjust resist #
$ adjust ebpg
$ adjust wafer alignment
$ adjust wafer distortion user
$ do "@mar2dw" matrix_field
$ exit
$ tryagain:
$ vdu "didn't find markers! try joy!"
$ move marker posx, posy joy
$! $! $!
$ layout wafer rectangle sizex, y posx, y /net /center
$ select patternname
$ adjust srd 10mm, 10mm
$ adjust dwoffs -80um, -80um 8um
$ layout dw_marker #, # joy
$ adjust resist #
$ adjust ebpg
$ adjust wafer alignment
$ adjust wafer distortion joy
$ do "@mar2dw" matrix_field
$ exit

command file called in the above:

$ !mardw.com
$ !file to expose
$ !uses three marks within the die to correct for gain, rotation and position errors
$ adjust wafer distortion /cell 152um,152um  !center to center distance between marks in x,y
$ expose matrix_field  !exposes

B.4. Comments

The $e$-beam processing work initially involved only a single PMMA resist layer. However, the structures often had “fencing” along the edges, associated with the film either depositing on the edges of the resist layer or being lifted away during the liftoff process – both undesirable consequences. Furthermore, early attempts often showed structures only for relatively high doses. It is possible that the resist profile was so gradual that the film within the resist trench remained connected to the film sitting above the resist and was, therefore, also effectively removed during the lift off. The two scenarios are likely (and common) causes of the observed symptoms, though were never verified. Direct verification requires extensive SEM and AFM studies of the resist (post development, but prior to evaporation) and resulting structures. Switching to a bilayer system, however, appears to sidestep these problems.

Initial structures also exhibited rough edges, as well as substantial granularity in the final structures (though the film deposition was carried out at appropriate and often used conditions which is known to result in smooth films). A descum in the RIE, prior to film evaporation, appears to have solved both problems. The line edges are smoother, and the graininess has disappeared. The granularity may have been a result of remnant resist in the trenches. Evidence of this can be seen in AFM studies of sufficiently wide trenches in PMMA (post-development). Any remnant resist in the “developed” areas may also be examined by SEM, though this takes considerable skill (and very preferably an FESEM) for the feature size desired here.
There is substantial room for improvement in the process described above (B.2 and B.3).

With regards to the bilayer scheme, the main problem is the possible over-development of the lower (copolymer) layer, leading to the top (image) layer to fall. It has been suggested that switching to a bilayer of PMMA of differing molecular weights may solve this issue. The development rates between the two layers, in this case, would not differ as much, leading to less undercutting of the top layer. Another problem with the present bilayer is a shadowing effect resulting from the use of 2 sources (Au and In) deposited from different positions. At present, reducing the resist thickness and positioning the substrate appropriately during the deposition (to make use of any symmetry present in the geometry) minimizes the shadowing. A better solution would be to maximize the substrate-source distance for the evaporation or to rotate the sources, or the position of the substrate, so that the two evaporations are done from nominally the same angle and distance.

In addition, given that the substrates of choice were thoroughly insulating, a conducting top coat was evaporated to avoid resist charging. At present, 10nm of Au is evaporated for this film. No systematic study has been done to optimize this. It is best to minimize this film thickness as much as possible, or perhaps switch to Al (a lower Z metal to minimize e- scattering). In choosing a metal, it is useful to keep in mind that the top coat must be etched away before the development of the resist – a metal with a commercially available etchant (or one that is easily prepared and understood) would be convenient.

With regards to the e-beam write, PSU’s EBPG-5 has recently (in the last 6 months) been re-tuned to be relatively more stable at higher energies – i.e. at 100kV (historically been optimized at 50kV). The higher energy makes it easier to achieve smaller beam sizes at correspondingly higher currents – allowing for smaller and faster writes. Optimal conditions need to be looked for.

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45 Without the coat, the resist has been seen to crack (H. Russell, 2001).
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