ELECTRICAL PROPERTIES OF SUPERCONDUCTING AND HYBRID SUPERCONDUCTOR-FERROMAGNET NANOWIRES

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Nitesh Kumar

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The dissertation of Nitesh Kumar was reviewed and approved* by the following:

Moses H. W. Chan  
Evan Pugh Professor of Physics  
Dissertation Advisor, Chair of Committee

Thomas E. Mallouk  
DuPont Professor of Chemistry Materials and Physics

Jainendra Jain  
Erwin W. Mueller Professor of Physics

Qiming Zhang  
Distinguished Professor of Electrical Engineering

Jayanth Banavar  
George A. and Margaret M. Downsbrough Head and  
Distinguished Professor of Physics

*Signatures are on file in the Graduate School.
Abstract

Superconductivity in reduced dimensions has attracted a lot of attention in last few decades. According to Mermin-Wagner theorem, no long-range order can be possible in strictly one-dimensional and two-dimensional systems. Strong phase fluctuations are expected to destroy superconductivity in quasi one-dimensional superconducting nanowires. This results in dissipation or resistive behavior both near and below the superconducting transition temperature. Previous electrical transport measurements in thin superconducting nanowires have reported dissipative behavior due to thermal and quantum fluctuations. However, most of the experimental and theoretical works done so far has focused mainly on studying the nature of dissipation in superconducting nanowires. The overall purpose of this research was to investigate the interaction of dissipative superconducting nanowires with its environment and vice versa.

One of the objectives of this work was to study the influence of bulk superconducting environment on the electrical properties of quasi one-dimensional superconducting nanowires. We have used electrochemical techniques to fabricate
nanowires of various metals with high crystal quality, uniformity and diameters well below the superconducting coherence length. Electrical transport measurements on Zn nanowires indicate that bulk superconductor significantly increases the dissipation in nanowires, which can result in suppression of their superconducting characteristics. These results demonstrate that the superconducting properties of nanowires are highly influenced by their environment.

In another scenario, we studied the interaction between superconducting and ferromagnetic environment in the case of hybrid superconductor-ferromagnet systems. The competition between the spin asymmetry properties of a ferromagnet and the correlations induced by superconductivity has made hybrid S-F systems an active area of research. Earlier works were done on layered two-dimensional S-F systems with granular and amorphous morphology. The second objective of this research was to explore the quasi one-dimensional hybrid S-F systems fabricated using high crystal quality nanowires. Spin polarized transport resulted in unusual magnetoresistance behavior in ferromagnetic nanowire attached to bulk superconductors. Contrary to the three-dimensional behavior, a long-range proximity effect was observed in ferromagnetic nanowires attached to superconducting electrodes. Electrical measurements were also performed on axially modulated nanowires fabricated by electrochemical deposition. Ferromagnetic properties of nanowires were observed to be strongly affected by the superconducting environment.
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Chapter 1

Introduction

In the last few decades, the advancement of nanofabrication techniques has led to the realization of electronic systems with sizes on the nanometer scale. At such small length scale, fluctuations induced by thermal or quantum mechanical effects, usually negligible for bulk systems, become significantly important. This raises a fundamental question: How the electrical properties of nanoscale systems e.g. superconductivity, are affected or altered by the confinement in reduced dimensions?

According to the famous Mermin-Wagner theorem[1], no true long-range ordering is possible in strictly one and two dimensional systems at any finite temperatures. In the case of a superconducting wire, once the diameter is made shorter than phase coherence length, ξ(T), excitations in superconducting order parameter transverse to the wire’s axis becomes energetically less favorable. Thus, the system approaches the one-dimensional (1D) limit where the role of superconducting fluctuations is more important than in three dimensional or bulk systems. This has led to a considerable interest, both theoretical and experimental, in the field of one-dimensional superconductors.

A natural question to ask is: Can superconductivity survive in 1D systems? It
is important to know the limit of superconductivity or in other words the size of a superconducting nanowire below which it cannot retain superconducting properties. This is of fundamental importance to investigate the role of superconducting fluctuations in 1D wires. From a technological point of view, it is also important in order to establish the fundamental limits of conventional devices and possible future applications. Thin superconducting wires were observed to exhibit resistive behavior below the superconducting transition temperature $T_c$ [2, 3, 4, 5, 6, 7, 8, 9]. These non-zero finite resistances has been attributed to thermally activated phase slips and quantum phase slips.

Most of the experimental and theoretical work in the field of 1D superconductors has been focused on investigating the role of phase slips in the dissipation of superconducting nanostructures. There is, however, very less amount of work done in studying the interaction of dissipative 1D superconductor with its environment. Our motivation for the current work was to study the influence of environment on the dissipative nature of superconducting nanowires. In particular, we investigated the effect of bulk superconducting environment on the electrical properties of quasi-1D superconducting Zinc nanowires. Bulk superconductors like Sn, In and Pb were observed to have strong influence on the superconducting properties of 40 nm Zn nanowires.

Another avenue for the study of interaction between superconductor and its environment can be explored in the case of hybrid superconductor-ferromagnet systems. Ferromagnetism and singlet superconductivity are phenomena of competing long range ordering. Ferromagnetism favors parallel spin alignment of electrons, whereas superconductivity requires Cooper pairs with antiparallel spins. This competition in spin alignment for superconductor-ferromagnet (S-F) hybrid systems has attracted considerable interest in the last few decades [10, 11].
Experimental efforts on transport properties of Superconductor-Ferromagnet (S-F) nanostructures has found many novel phenomena such as long-range proximity effects[12, 13, 14, 15], critical temperature oscillations in S-F multilayers [16], 0-π Josephson junctions in S-F-S [17, 18], and spin valve effects in F-S-F systems [19]. In another manifestation of spin polarized transport across S-F interface, point contact Andreev reflection (PCAR) has been used to estimate the degree of spin polarization in ferromagnetic materials [20, 21]. However, most of the previous experiments are performed on 2D systems in the form of thin films, using lithography to fabricate nanoscale contacts between superconducting and ferromagnetic thin films.

In the current work, our objective was to study electrical properties of quasi-1D S-F systems. We have performed electrical measurements of ferromagnetic nanowires attached to superconducting electrodes. This relatively simpler and easier lithography-free technique allowed us to study the spin-polarized transport across nanoscale S-F interface. We have observed long-range proximity effect in Co and Ni nanowires in contact with a disordered superconductor. We have also done measurements on axially modulated nanowires containing alternating S and F segments making S-F-S junctions.

This thesis is organized as follows: - Chapter 2 includes the theoretical and experimental background relevant to our work. Chapter 3 describes the experimental details and techniques used in the current projects. Chapter 4 includes the study of electrical transport properties of superconducting Zn nanowires and its interaction with the environment. Chapter 5 describes the measurements on the hybrid superconductor-ferromagnet nanostructures. It includes the measurement of Ni nanowires attached to bulk superconducting electrodes, long range proximity effect in Co and Ni nanowires with superconducting W strips and electrical prop-
erties of axially modulated nanowires with superconducting Pb and ferromagnetic Ni sections. Chapter 6 concludes the results presented in previous chapters and gives a direction for the future work.
Theoretical and Experimental Background

2.1 Introduction

This chapter is intended to give an overview of the past theoretical and experimental work relevant to the works described later in this thesis. This overview will include the work done in the field of one-dimensional superconductors and hybrid mesoscopic superconductor-ferromagnet systems. In particular, I’ll describe the existing theoretical models for dissipation in 1D superconducting nanowires based on the phase slips processes. Experiments done to investigate both thermal and quantum phase slips will be discussed and the controversies associated with them. The second half of the chapter will focus on the superconductor-ferromagnet systems. Recent experiments related to the long-range proximity effect and spin-polarized transport will be presented.
2.2 Superconducting nanowires

Superconductivity is characterized by a sudden drop in resistance to zero value for some materials below a certain temperature. It is one of the best examples of macroscopic quantum mechanical phenomenon. However, this classical definition of superconductivity doesn’t hold in reduced dimensions. Mermin-Wagner theorem states that no long-range order can be possible in a strictly 1D and 2D systems [1]. This led to the assumption that low dimensional superconductors cannot exhibit superconducting properties due to strong fluctuation effects.

However, this argument is not completely true. In case of 2D systems, due to Berezinskii-Kosterlitz-Thouless (BKT) phase transition, long range phase coherence survives at low T [22, 23]. Thus, 2D thin films can exhibit superconducting properties. In the last few decades attention has turned to the case of 1D superconductors. Also, with the advancement in fabrication techniques, it has now become possible to do measurements on high-quality ultra-thin wires. To explore experimentally the one-dimensional regime, one needs to know the relevant length scale in superconductors.

According to Ginzburg-Landau (GL) theory of second-order phase transitions, free energy density of the system can be expressed as a Taylor expansion of the energy of ordered state in powers of order parameter and its gradients close to the transition

\[ f = f_n + \alpha |\psi|^2 + \beta |\psi|^4 + \frac{1}{2m}|(-i\hbar \nabla - 2eA)\psi|^2 \]  

(2.1)

where \( \psi \) is the complex-valued order parameter, \( \alpha \) and \( \beta \) are temperature dependent parameters, \( m \) is the effective mass of Cooper pair, and \( A \) is an applied vector potential. Since, free energy has to be real, there are no terms in \( \psi \). Also, terms in \( |\psi| \) are excluded because the free energy must be analytic everywhere. Only
two terms are included in the eq. 2.1, which are sufficient when close to the phase transition temperature, $T_c$. Also, a Taylor expansion of $\alpha(T)$ about $T_c$ shows that it is proportional to $(1-t)$, where $t = T/T_c$. For zero fields and $\alpha < 0$, minimum free energy occurs when $|\psi|^2 = |\psi_0|^2 = -\alpha/\beta$. $\psi_0$ represents the ground state order parameter amplitude deep in the interior of superconductor below the critical temperature.

GL differential equation is obtained by integrating eq. 2.1 over unit volume and minimizing to find the free energy minimum. In the absence of fields and gradients ($A=0$), GL differential equation is obtained as

$$0 = \alpha \psi + \beta |\psi|^2 \psi - \frac{1}{2m}(\hbar \nabla)^2 \psi$$

(2.2)

Since, the differential equation 2.2 has only real coefficients, one can take $\psi$ to be real. Rearranging eq. 2.2 and expressing in terms of $\psi_0$ gives

$$\frac{\hbar^2}{2m|\alpha|} \nabla^2 \left( \frac{\psi}{\psi_0} \right) + \frac{\psi}{\psi_0} - \left( \frac{\psi}{\psi_0} \right)^3 = 0$$

(2.3)

From eq. 2.3, a characteristic length scale for the variation of $\psi$ can be defined as:

$$\xi^2(T) = \frac{\hbar^2}{2m|\alpha(T)|} \propto \frac{1}{1-t}$$

(2.4)

This length scale, $\xi^2(T)$ is termed as coherence length, and represents the length scale for the spatial variation of $\psi$. Typical BCS-superconductors have coherence length in the range from 100 - 1000 nm.

Coherence length provides the relevant length scale to quantify the size of the system in order to be considered less than three-dimensional. Consider a wire whose diameter is equal to or smaller than the coherence length. This makes
the variation of order parameter amplitude over the cross section of the wire energetically unfavorable. It can only vary substantially along the length of wire, thus simplifying the eq. 2.1 and takes the form identical to the one for a one-dimensional system. So, even though the wire is not a strictly one-dimensional electronic system (there are still multiple channels of conduction), it can be considered one-dimensional as long as superconductivity is concerned. Thus, if a wire has diameter less than coherence length, the dynamics of order parameter will be one-dimensional. Hence, most of the systems discussed in this thesis are termed as “quasi one-dimensional”. One would expect that a progressive reduction of wire diameter from a value larger than coherence length to a much smaller might show a cross-over where the system’s properties will change from three-dimensional to one-dimensional. This will also lead to an increasing role of fluctuations on the electrical properties of the system.

2.2.1 Phase slips

Within the framework of Ginzburg-Landau theory, a one-dimensional superconducting wire can be described in terms of complex order parameter as:

\[ \Psi(x) = |\Psi(x)|e^{i\phi(x)} \]  

(2.5)

Thermal fluctuations can cause variations in both the modulus and phase of the order parameter from their equilibrium values. These fluctuations are described as “phase slips”. A phase slip is an event in which the amplitude of order parameter is temporarily suppressed. As soon as the amplitude is reduced to zero, the phase of the order parameter changes by \(2\pi\). After this event, the amplitude get restored, the phase becomes single valued again and the system returns to its initial state.
but with a net phase shift of $2\pi$. According to Josephson’s relation

$$\frac{\partial \Delta \phi}{\partial t} = \frac{2eV}{\hbar}$$

(2.6)

where $V$ is the voltage developed due to the phase difference, $\Delta \phi$, between the ends of wire. So each phase slip event causes a non-zero voltage across the wire. When there is no excitation current, the net average numbers of positive ($+2\pi$) and negative ($-2\pi$) phase slips are equal, thus leading to a zero net voltage drop. However, applying an excitation current

$$I \propto |\Psi|^2 \nabla \phi$$

(2.7)

results in a non-zero phase gradient along the wire and hence makes the positive phase slips more than the negative ones. This leads to a net non-zero voltage drop across the wire. For a sufficiently large rate of phase slips, a significant voltage develops along the wire resulting in a non-zero resistance $R = V/I$ of superconducting wires even below $T_c$. Since, these phase slips originated due to thermal fluctuations, they are called thermally activated phase slips or TAPS.

A quantitative theory was first developed by Langer and Ambegaokar and later completed by McCumber and Halperin. Resulting theoretical model is known as LAMH theory [24, 25]. According to this theory, the observed non-zero resistance is given by

$$R_{LAMH} = \frac{\pi \hbar^2 \Omega}{2e^2k_B T} e^{\exp[-\frac{\Delta F_o}{k_B T}]}$$

(2.8)

$$\Omega = \frac{L}{\xi} e^{\exp[\frac{\Delta F_o}{k_B T}]} \frac{1}{\tau_{GL}}$$

(2.9)

where $\Delta F_o$ is the condensation energy in a volume $A\xi$ of the wire, $\xi$ is the coher-
ence length and \( \tau_{GL} \) is the GL relaxation time. Above equation gives a appreciable resistance value close to the \( T_c \) of superconducting wire. However, as temperature is lowered below \( T_c \), \( R_{LAMH} \) decreases exponentially and theory predicts no measurable resistance in the limit of \( T < T_c \).

This phenomenon was experimentally observed in superconducting whiskers, at temperatures very close to \( T_c \). Earlier experiments were limited to wire of relatively large diameters because modern lithographic techniques were not yet developed to allow measurements on thinner wires. Recent advancement in nanofabrication techniques allowed fabricating samples with much smaller diameters down to sub-10 nm. In such small systems, LAMH theory was still valid for temperatures close to \( T_c \). However, some new effects were observed at lower temperatures inconsistent with thermal phase slips model [3]. It was proposed that in the limit of low temperatures, phase slips events take place due to the quantum fluctuations of order parameter. The physical picture of quantum phase slips (QPS) is similar to TAPS except the order parameter get suppressed due to the quantum mechanical tunneling of the system between two macroscopic states with \( 2\pi \) phase difference.

Since, nature of QPS is quantum mechanical, one would expect that such processes would be controlled by exponent \( \sim \exp [-\Delta F_o/\hbar \omega_o] \) where \( \omega_o \) is an effective attempt frequency. A model similar to LAMH theory was developed with different attempt frequencies and substituting \( \hbar \omega_o \) in the activation exponent of eq. 2.8. A complete picture of phase slips includes TAPS dependence for \( T \sim T_c \) whereas for \( T < T_c \) dissipation is defined by QPS. Since, quantum tunneling take place even at \( T = 0 \), one can conclude that quantum fluctuations can destroy superconductivity in nanowires at any temperatures including \( T = 0 \).

QPS is observed experimentally in many experiments [2, 3, 4, 5] and the model fits well with the experimental results. However, there remained some controversy
related to the role of wire morphology in generating phase slips events. Most of the experiments were done on samples fabricated by evaporation or sputtering resulting in amorphous and granular morphology.

Tian et al. [8] measured an array of single-crystal Sn nanowires to investigate the role of QPS and TAPS. Also, the use of single crystal nanowires gets rid of the role of morphology in the measurements. Fig. 2.1 shows the R-T curves of 20 nm, 40 nm, 60 nm, 70 nm and 100 nm diameter Sn nanowires measured in an array from ref. [8]. These results clearly show the increase in dissipation of nanowire with decreasing diameter. The narrowest wire showed a pronounced broadening of transition near $T_c$ due to TAPS and a long resistive extending down to $T = 0$; a clear signature of QPS. The coherence length for Sn nanowires, $\xi_S$, was estimated to be 65 nm. Nanowires with diameter, $d > \xi_S$ showed a sharp superconducting transition and goes to zero-resistance state. On the other hand, nanowires with $d < \xi_S$ showed strong dissipation with broadening of transition and resistive tail at low temperatures. These results provided a clear picture of the crossover from
three-dimensional to one-dimensional superconducting properties.

As seen previously, superconducting fluctuations depend closely on the diameter of superconducting nanowires. Once diameter is smaller than the phase coherence length, nanowires show strong dissipative behavior. With a large coherence length ($\sim 1.5 \, \mu m$), Zn nanowires stand a better chance to show dissipative behavior or one-dimensional effects in comparison to other superconducting nanowires of the same diameter.

### 2.3 Hybrid superconductor-ferromagnet nanos-structures

Due to the incompatibility of spin ordering, singlet superconductivity and ferromagnetism do not co-exist in nature. However, we can easily achieve this in artificially fabricated hybrid superconductor-ferromagnet (S-F) systems. With the recent progress in the microfabrication techniques to fabricate high quality hybrid systems, we have the wonderful opportunity to study the interaction of these two competing ordering phenomena. In the following sections, I’ll review some of the interesting physical phenomena associated with hybrid superconducting systems.

#### 2.3.1 Proximity Effect

Proximity effect is perhaps one of the most studied phenomenon in superconductivity [26]. When a normal (or non-superconducting) metal is placed in electrical contact with a superconductor, it acquires superconducting properties. The induced superconducting correlations can extend to large distances into the normal metal. In the case of dirty normal metals, where the motion of electron is diffu-
sive, the relevant length scale is dependent on the thermal diffusion length, \( L_T = \sqrt{\hbar D/k_B T} \), where D is the electron diffusion coefficient. For a typical metallic film, \( L_T \) can be as long as few 100 nm at low temperatures.

The microscopic mechanism of proximity effect is based on Andreev reflection. It provides the elementary mechanism for converting single electron states from normal metal to Cooper pairs in the superconducting condensate. An electron in the normal metal with an energy less than the superconducting gap is reflected at the NS interface as a hole. To maintain charge conversion, a charge \( 2e \) is transferred to the Cooper pair, which appeared in the superconducting side of the interface. Andreev reflection is a phase coherent process. This implies that the phases of the incident electron and the reflected hole are related through the macroscopic phase of the superconductor. Thereby, inducing superconducting correlations inside the normal metal.

The electron transfer mechanism is same in S-N and S-F systems. However, since ferromagnetism favors a parallel spin alignment, it is reasonable to expect that the injection of spin polarized electrons from F into S will lead to a stronger pair-breaking effect than in the case of S-N structures. On the F side, the Fermi surface is split into up and down spin due to the presence of an exchange field, h. Thus, a singlet Cooper pair going from S to F acquires a non-zero centre of mass momentum which leads to the oscillation of the order parameter inside the F, on a length scale given by \( L_F = \sqrt{\hbar D/2\pi h} \). This results in the length scale of proximity effect in transition metals to be as small as few nm. However, several experiments on nanoscale S-F systems have reported proximity effect on length scale longer than the theoretical value.

Petrashov et al. [14] reported a strong mutual influence of superconductor and ferromagnet in hybrid Ni/Al nanostructures. They observed a proximity-induced
conductance two orders of magnitude larger than that predicted by theory. They attributed it to the long-range proximity effect in Ni due to superconducting Al.

Giroud et al. [13] investigated the proximity effect in Co/Al system. They observed that superconducting Al islands could induce proximity effect to a distance of 180 nm in the ferromagnetic Co. In a similar experiment, Aumentado et al [15] studied Ni/Al systems. They found no long-range superconducting correlations in the Ni part. They concluded that the proximity effects are only present in the interfaces between superconducting Al and ferromagnetic Ni.

2.3.2 Charge Imbalance

Another phenomenon relevant to the electrical properties of S-N or S-F systems is “Charge Imbalance”. When a current I carried by quasiparticles is injected from a normal metal to superconductor, it gives rise to a non-equilibrium distribution of quasiparticles and Cooper pairs in the superconductor near the NS interface. This, in turn, leads to different electrochemical potentials $\mu_{qp}$ and $\mu_{cp}$ of quasiparticles and Cooper pairs, respectively near the NS interface. $\mu_{cp}$ relaxes to the electrochemical potential in the bulk of superconductor $\mu_0$ over the length scale determine by phase coherence length, $\xi_S$. This is typically of the order of few 100 nm for conventional superconductors. On the other hand, $\mu_{qp}$ relaxes to $\mu_0$ over the charge imbalance length $\Lambda_{Q*}$, which can be much longer than $\xi_S$. If the potential at NS interface is assumed zero, $\mu_{qp}$ has a spatial dependence inside the superconductor given by equation $\mu_{qp}(x) = e\Lambda_{Q*}\rho_S I \tanh(x/\Lambda_{Q*})$ where x is the distance from the interface and $\rho_S$ is the resistance per unit length of the superconductor in its normal state.

If the voltage in the superconductor near the NS interface is measured by a
superconducting electrode, it will probe $\mu_{cp}$. Also, beyond a distance $\xi_S$ from the interface it will essentially be $\mu_0$. However, a normal metal electrode placed on the superconductor will measure $\mu_{qp}$. This results in a difference $\mu_{qp}(x) - \mu_0$ measured in superconductor by a normal electrode and a superconducting electrode beyond a distance $\xi_S$ from the interface. An enhancement in voltage results in an increase in resistance. Since, $\mu_{qp}(x)$ decays with distance $x$ from the interface, the enhancement in resistance also decays as $\Delta R(x) = \rho S \Lambda_{Qs} (1 - \tanh(x/\Lambda_{Qs}))$.

$\Lambda_{Qs}$ is expected to diverge at $T \sim T_c$ [27]. Also, the charge imbalance contribution goes to zero in the low temperature limit. So, at higher temperatures near $T_c$, charge imbalance effect can play a crucial role in the transport properties of hybrid systems.

Another interesting point to note here is that charge imbalance is not only related to hybrid systems like S-N or S-F. It can appear in any system with a non-equilibrium distribution of quasiparticles and Cooper pairs. One good example is the case of quasi one-dimensional superconducting nanowires discussed in previous section. The resistive (or dissipative) state of a 1D superconducting nanowire is governed by phase slips induced by thermal and quantum fluctuations. This resistive state is a dynamic process consisting of discreet phase slips events repeatedly occurring with an average rate. As we know, during each phase slip, the magnitude of order parameter goes to zero and phase changes by $2\pi$. All this action occurs in the core region of phase slip, usually on the size of $\xi(T)$ since that governs the spatial variation of order parameter. Each phase-slip event gives rise to a “quasi-normal” region with non-equilibrium quasiparticles. This leads to a conversion from non-equilibrium quasiparticles to equilibrium Cooper pairs. The charge imbalance created by this conversion process is pinned to the each phase slip and decays in time and space. This regime is reminiscent of the case of hybrid S-N
and S-F systems. The decay length of charge imbalance is similar in both cases. In the case of superconducting nanowire, due to this process a region of length equal to charge imbalance length $\Lambda_{Q^*}$ becomes normal. This has been observed as multiple voltage steps in the current-voltage characteristics measured above the critical current of thin and long superconducting filaments [28, 29]. Recently, similar voltage steps are observed in the measurements done on quasi one-dimensional superconducting nanowires [6, 8].

Most of the works mentioned above are done in layered systems. The S-F structures were fabricated using evaporation and sputtering in conjunction with e-beam lithography. The samples were either amorphous or granular in morphology. Also, the lateral dimensions of the system are usually more than 100 nm making it a 2D system. In our technique using electrochemical deposition, we can fabricate high crystal quality nanowires. Also, nanowire’s diameter can be as small as 30 nm. The small size of the nanowire along with a better morphology may shed more light on the interesting electrical properties of hybrid S-F systems.
Experimental Procedures

3.1 Synthesis of nanowires

Nanowires used in the present study were fabricated by template-based electrochemical deposition. Porous membranes with non-intersecting channels of diameters in tens of nanometers and lengths in microns were used as templates for the synthesis of nanowires. There are two types of porous membranes used in the process, namely Polycarbonate membranes (PCM) and Anodized Alumina membranes (AAM). Preparation and physical characteristics of the used templates are described below.

3.1.1 Templates

3.1.1.1 Polycarbonate membranes

There are two types of PCM used for the synthesis of nanowires, PC1 and PC2, purchased commercially from Structure Probe, Inc., USA and it4ip, Belgium, respectively. Both types are track-etched membranes manufactured by irradiating a polycarbonate film with energetic heavy ion. These irradiation leads to the
formation of linear damaged tracks across the film, which are then revealed into pores using appropriate wet-chemical etching. The open pores in these membranes are aligned parallel to each other and perpendicular to the surface of membranes within a dispersion of $17^\circ$. Fig. 3.1 shows the SEM picture of a PC1 membrane. The pore density of these membranes is about $6 \times 10^8$ pores/cm$^2$, but pores are distributed randomly. The physical dimensions of both types of PC membranes are very different. PC1 membranes comes in four different pore sizes with the same thickness of 6 $\mu$m. However, the actual diameter of the resultant nanowires obtained by using these membranes as templates are found to be usually larger than the pore size quoted by the manufacturer. The quoted pore sizes of 10nm, 30 nm, 50 nm and 80 nm results in nanowires of diameters 40 nm, 70 nm, 100 nm and 160 nm, respectively. On the other hand, PC2 membranes comes in pore sizes of 30 nm and 50 nm with a thickness of 20 $\mu$m. These membranes results in longer nanowires and hence are better for the purpose of single nanowire measurements. Since both polycarbonate membranes, PC1 and PC2, are very flexible and don’t break on squeezing; they are well suited for electrical measurements done on array of nanowires. However, the limited availability of pore diameters and length restricts use of PC membranes to some extent. To overcome this problem, I have
used homemade AAM.

### 3.1.1.2 Anodized Alumina Membranes

Porous AAM are another commonly used template for the electrochemical deposition of nanowires. The nano-channels in AAM are formed by anodization of high-purity Al foils or films in an acidic electrolyte. Relative to other porous templates, such as PCM describe in previous section, well-fabricated AAM possess a much higher pore density, around $10^{11}$ pores/cm$^2$ and a narrower distribution of pore diameters. Also, the pore channels of a good AAM are well-aligned parallel to each other. The diameter and density of the pores are controllable by varying the anodization conditions. Figure 3.2 (a)-(f) outlines the steps involved in the fabrication of AAM templates.

The starting Al plates was purchased from either Sigma-Aldrich or Alfa Aesar, depending on the desired dimensions and purity. To avoid any contamination, we used high quality and purity 99.999 % Al plates. The dimension of plates are usually 100 mm $\times$ 100 mm with thickness around 0.5 mm.

The fresh aluminum plates procured from the vendors are usually smooth but not good enough for anodization (fig. 3.2 a). So, firstly the Al plates are mechanically polished by hand using wet silicon carbide sand paper. The mechanically polished Al plate was then thoroughly cleaned with water, acetone and Iso propyl alcohol (IPA).

After this, Al plate was electro-polished to obtain a mirror-like finish, ideal for good anodization. The resultant quality of AAM depends closely on this process, making it one of the most crucial steps. The plate was immersed in a freshly prepared acid solution containing 60 vol% phosphoric acid and 40 vol% sulfuric acid with total volume of 4L. The glass beaker containing acid solution was kept
Figure 3.2. Steps involved in the fabrication of AAM: (a) Rough surface of the as-purchased aluminum plate with native oxide layer, (b) Aluminum plate after mechanical and electro-polishing. (c) Initial ramping of voltage results in pit formation on the surface. (d) Simultaneous anodization and acid etching results in vertical pores. (e) Slowly decreasing voltage results in branching of pores and thinning of barrier oxide layer. (f) AAM is detached from the base Aluminum plate by etching in a strong acidic solution.

on a hot plate to maintain temperature between 75° - 80° C with constant stirring by a magnetic stir bar. Stirring is very crucial in order to maintain a uniform temperature throughout the volume of the solution. A clean lead (Pb) plate of similar area is suspended parallel to the Al plate acting as the cathode. Both the plates were suspended in the acid solution using metallic clamps and electrically connected to a current source while avoiding any contact to the liquid. Al plate
Table 3.1. Parameters for anodization of Al plates.

<table>
<thead>
<tr>
<th>Pore Size (in nm)</th>
<th>Acid</th>
<th>Concentration</th>
<th>Voltage</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>$H_2SO_4$</td>
<td>6 wt.%</td>
<td>20 V</td>
</tr>
<tr>
<td>40</td>
<td>Oxalic Acid</td>
<td>0.3 M</td>
<td>40 V</td>
</tr>
</tbody>
</table>

act as a anode and connected to the positive end of current source. The current was slowly increased and maintained at a constant current $\sim 12 \pm 2$ A. The current should be increased slowly in order to avoid pitting of the Al surface. The temperature was monitored periodically to ensure stability since the joule heating of the acid solution could sometimes raise the temperature above the acceptable range. If temperature exceeded above 80°C, process is momentarily stopped and the solution is left to cool itself. Electro-polishing is usually carried out for 30-40 minutes and is stopped when Al plate shows, upon visual inspection, a haze-free-mirror-like finish (fig. 3.2 b). After this, the plate is again cleaned with water, acetone and IPA. Next step is the anodization of the polished Al plate.

Anodization process is carried out in cooled acidic bath at temperatures close to 0°C. AAM of different physical dimensions (i.e. pore size and membrane thickness) can be fabricated by choosing appropriate anodization conditions: Acid bath, voltage and time. Table 3.1 lists some of the parameters for the commonly used AAM in the current study. A large beaker, 4 L volume, containing freshly prepared acidic solution is put inside an ice bath maintained inside a insulated box for cooling. A magnetic stir bar inside the beaker gently circulates the solution. As mentioned in Table 3.1, high voltages are used for the anodization and hence it becomes necessary to prevent Al plate from overheating locally. For this reason, the acidic solution is continuously stirred throughout the process and solution is kept cold by ice bath. Since ice chunks are not very small in size, a small amount of water is added to the ice bath to ensure good thermal contact with the glass
beaker. Prior to anodization, acidic solution is left in ice bath for several hours to get it cooled to around 1-2°C.

For anodization, the electro-polished Al plate is immersed in the acidic bath acting as the anode. A clean Pb-plate of similar area is suspended parallel to the Al plate and connected to the negative terminal. Both the plates are electrically contacted above the liquid level using alligator clips, connecting them to a computer-controlled DC voltage source. Since the pore structure and barrier layer thickness depend sensitively on the local currents and potentials, it is required to change these values gradually so that the anodization can be achieved uniformly over the whole area. The applied potential was gradually increased by hand until the desired anodization potential is reached. A sudden increase in voltage or too high rate of change of voltage results in a rapid increase of current leading to the preferential anodization of Al plate at one location. This often ends up in etching of a hole in Al plate rather than a uniform anodization. A slow ramping of potential with frequent halts to let the current stabilize, always results in a uniform anodization. Once the desired potential is reached, current was observed to stabilize and changed very little through the anodization process. Since, both sides of the Al plate are exposed to the acid solution, anodization was done uniformly on both sides of the entire plate. The whole process of anodization is a mix of 2 processes going on simultaneously; Al plate is steadily oxidized and the resulting alumina layer is etched into a porous membrane. The thickness of the membrane depends on the time of anodization. As seen in 3.2 (d), there is always a barrier oxide layer between the bottom of pores and the unanodized base aluminum. This insulating barrier layer usually has a thickness of 10 - 100 nm depending on the anodization potential. It can thus restrict the conducting electrical path between the pores and the base conducting substrate required for the DC electrodeposition
of nanowires.

To overcome this problem, after anodization the voltage was reduced in logarithmically spaced steps of three-minute duration. This step-wise decrease in voltage causes pores to branch in a uniform way, etching the barrier layer between Al and pores and thinning the pore walls [30, 31, 32]. The anodized Al plate was then immersed in a 20 vol % sulphuric acid solution for 60 - 90 minutes. The strong acid solution preferentially etched the narrow branched pore structures between AAM and residual aluminum layer and also slightly enlarged the pores in the process. The etching resulted in the detachment of AAM from the underlying aluminum plate. The detached AAM is rinsed in water 3- 4 times to get rid of any remaining acid inside the pores, followed by a thorough rinsing with acetone and IPA. The remaining Al plate gets further polished during this removal procedure. Anodization is carried out on the remaining plate without electro-polishing, resulting in higher quality AAM than the first anodization, probably due to the impressions of pore array from previous membranes etched on the Al plate. A single Al plate is good for several times of anodization until it becomes too thin and fragile to handle.

An initial check for the quality of AAM can be done by visual inspection. Good quality AAM are usually clear, flat and doesn’t curl up on drying. On the other hand, bad quality AAM are cloudy in appearance, curl up on drying and too brittle to handle. Pore size and membrane thickness are confirmed by examining AAM in a Field Emission Scanning Electron Microscope (FESEM) JEOL 6700F. Fig. 3.3 shows the SEM images of an AAM with pores of diameter 25 nm. Fig. 3.3 (a) shows the top-view with pores etched in the membrane. Fig. 3.3(b) shows the cross-sectional view of the AAM. The nano-channels are almost parallel with uniform diameter of 25 nm.
Above mentioned process of anodization is ideal for fabricating thick AAM typically on the order of 30-50 µm. However, free standing AAM with thickness less than 10 µm becomes too fragile to be used for the fabrication of nanowires. An alternative method was employed to fabricate thin and fragile AAM supported on rigid silicon substrates[33]. A 4” thermally oxidized silicon wafer is taken as the starting substrate. The substrate is loaded in a Semicore e-gun evaporator chamber with multiple crucible pockets. First, an adhesion layer of titanium (Ti) is deposited on the substrate. The thickness of the film is typically kept between 50-100 nm. Without breaking the vacuum, an aluminum film of desired thickness is deposited making a multilayer structure Al/Ti/SiOx/Si. Since the deposited Al film is already very smooth, it is directly anodized without any polishing. Anodization is carried out as before at temperature close to 0°C in an acidic bath. The process is continued until the whole Al layer is anodized, indicated by a sudden decrease in electrical current. A thin barrier layer, similar to the one in previous case,
is present between the bottom of the pores and Ti adhesion layer. Since, AAM has to be supported on the substrate, the previous solution of etching barrier layer in strong acid cannot be employed here.

To penetrate in-situ oxide barrier layer, immediately after the completion of anodization, a reverse-bias voltage (-3.5 to -5.0 V) was applied to the sample in the same acidic bath. Bubbles of $H_2$ were observed coming out from the pores at the AAM surface. The bias voltage was reduced slowly and held where the bubbles stopped. This reversing process was done for a few minutes. The bias voltage was tuned off when plenty of bubbles evenly spread out on the AAM surface. At this point, oxide layer was completely removed, opening the pores to the Ti layer. Voids and cracks are developed along the interface of AAM and Ti layer due to the over-etching of barrier layer by reverse-biasing. By careful adjustment of reverse-bias voltage and the etching time, one can selectively etch the bottom oxide barrier layer vertically but not destroy the oxide walls transversely between the neighboring pores at the bottom. The initial value of reverse voltage and the total time to penetrate the barrier layer depend on the thickness of barrier layer. Generally, both increase with an increase in the anodization voltage.

The reverse bias may actually result in an increase in the local concentration of $H^+$ ions at the barrier layer. Since a reverse bias was applied, the $H^+$ ions can migrate to the bottom of the pores due to the electric field. This locally higher concentration of $H^+$ facilitates the dissolution of the oxide barrier layer and thus open the pores. The dissolution reaction can be expressed as

$$Al_2O_3(s) + 6H^+(aq.) \rightarrow 2Al^{3+}(aq.) + 3H_2O(l) \quad (3.1)$$

After the dissolution of barrier layer, $H^+$ ions reach the Ti cathode, where they
leave the electrolysis cell in the form of $H_2$ gas.

Nanowires were successfully electrodeposited in the pores of AAM if the size of the voids or the thickness of the cracks was less than 50 nm. A longer reverse-bias etching time results in larger voids and cracks forming between AAM and Ti layer. If the voids and cracks become large enough to connect to each other, it results in the liftoff of AAM from the substrate. Thus, the growth of nanowires becomes impossible. However, this technique was used to detach thick AAM anodized from the residual Al plate. Large free standing AAMs (more than 10 cm × 5 cm) with average pore diameters from 30 nm to sub-10 nm were routinely fabricated with this technique. Since, this process does not widen the pores, AAMs with the same anodization voltage as before results in smaller pore sizes.

### 3.1.2 Electrodeposition

Using templates such as described in the previous section, nanowires of various metals [34, 35], semiconductors [36] and conducting polymers [37] have been fabricated by many groups around the world. Also, these nanowires can be deposited into the pores by different techniques such as electrochemical deposition, chemical vapor deposition[38], electroless deposition[39], sol-gel chemistry [36]etc. Out of all available techniques, electrochemical deposition is the most widely used method to infiltrate conducting materials into the nanometer-size pores to form continuous nanowires with large aspect ratios. Because it is cheap, easy, reliable and high output fabrication process.

Electrochemical deposition, or commonly used term ”Electrodeposition”, is the process of reducing cations of a desired metal from a solution to coat a conductive object with a thin layer of the metal. In my research, electrodeposition was used
to fabricate Zn, Ni, Co, Au, Pb, AuSn nanowires within the nanopores of PCM and AAM.

Electrodeposition is carried out in a three-electrode electrochemical cell containing a working electrode, a counter electrode and a reference electrode. Figure 3.4 shows a schematic of the electrochemical cell used for the electrodeposition of nanowires.

![Schematic of an electrochemical cell used for fabrication of nanowires.](image)

**Figure 3.4.** Schematic of an electrochemical cell used for fabrication of nanowires.

In the current study, porous membranes serve as the working electrode, a platinum strip was used as counter electrode and a Ag/AgCl was used as the reference electrode. In some cases, it was not required to use reference electrode and electrodeposition was carried out in a 2-electrode cell.
Electrodeposition can be done only on a conductive object because current has to pass through the circuit. However, both the porous membranes are insulating in nature. So, a metallic film was evaporated on the backside of the membranes. This metallic layer will act as seed for the growth of nanowires. As the open side of the template is exposed to the electrolyte and the current is applied to the "seed" layer, positively charged ions in the electrolyte move towards the bottom of the pores. When the cations reach the bottom of the pores, they accept the electrons supplied from the applied current and get reduced to its metallic form. This is shown in equation 3.2 for metal "M" with "n" valency:

\[ M^{n+} + ne^- \Rightarrow M \]  \hspace{1cm} (3.2)

This technique is not limited to nanowires of pure elements. Nanowires of metal alloys can be fabricated with good control over stoichiometry. For ex: inter-metallic phases of AuSn were fabricated with electrodeposition [40]. It was also employed to fabricate axially modulated nanowires with multiple segments of superconductor (Pb) and ferromagnet (Ni) discussed in chapter 5 of this thesis.

3.2 Structural characterizations

Nanowires fabricated by electrodeposition are further characterized for their structural properties: crystal structures, growth orientations, physical dimensions, compositions etc. Preliminary characterization was done by X-ray diffraction whereas detailed studies of crystal structures, interface roughness and compositional analysis were done by Transmission Electron Microscopy.
3.2.1 X-Ray Diffraction (XRD)

XRD measurements were done in a Philips X’pert X-ray Diffractometer using Cu $K_{\alpha}$ X-ray of wavelength 1.54 Å. A piece (typically 3 cm $\times$ 3 cm) of porous membrane containing nanowires was used to characterize the crystallinity of nanowires. Sample for XRD is prepared by carefully removing backside seed metallic layer either by etching with nitric acid (for AAM) or wiping out in ethanol (for PCM). Porous membrane is now fixed on a zero-background holder and set for measurements inside the diffractometer. X-ray Diffraction spectra give information about the crystallinity of sample and whether there is any preferred growth direction. The peaks in the spectra correspond to the crystal plane of the sample. Knowledge of the diffraction spectra helps out in detailed analysis of individual nanowires in TEM. Figure 3.5 (a) shows the XRD spectra for an array of 70 nm AuSn NWs embedded in PCM. The peaks fit the standard powder XRD spectra of bulk AuSn showing all the peaks, thereby indicating there is no preferred growth orientation. Figure 3.5(b) shows the XRD spectra for an array of 40 nm Co NWs embedded in AAM. There is only one big peak corresponding to crystallographic orientation of [220] for a face-centered cubic (fcc) crystal. So, it is safe to conclude that 40 nm Co NWs are single crystal with a fcc structure and a strongly preferred growth orientation of [110]. Although being a powerful tool otherwise, use of XRD is limited for the case of our nanowires. It cannot be used to characterize the physical dimensions of nanowires, interface between different layers, amorphous phases etc.

3.2.2 Transmission Electron Microscopy

TEM imaging was done using Philips EM-420T microscope operating at 120 keV. High-resolution and Scanning TEM imaging was done with JEOL EM-2010F mi-
Figure 3.5. (a) X-Ray diffraction spectra of an array of 70 nm AuSn nanowires embedded in PCM (b) X-Ray diffraction spectra of an array of 40 nm Co nanowires embedded in AAM.
croscope equipped with a field emission gun, with a operating voltage of 200 keV.

Sample used for TEM should be electron transparent, i.e. it should allow electrons to transmit through it. Normally, a sample should not be thicker than 100 nm to be used for TEM imaging. This makes the sample preparation for nanowires very easy. Porous membrane containing nanowires is dissolved to obtain a suspension of nanowires. A few drops of suspension was dropped on a lacey carbon coated copper grid [41]. Grid was left to get dry and then loaded onto TEM sample holder for the characterizations. Figure 3.6 (a) shows a low magnification TEM image of 80 nm Co nanowires, fabricated in PCM. Figure 3.6(b) shows a high magnification image of 80 nm Co nanowire. Inset shows the selected-area electron diffraction (SAED) pattern from the middle of nanowire. These Co nanowires are fabricated with the same condition as the 40 nm Co NWs in figure 3.5(b). Co nanowire is observed to be very straight with little variation in diameter along the length. SAED pattern can be indexed to obtain the growth direction and crystal structure. From the inset of figure 3.6(b), it indicates a fcc crystal structure with a growth direction along [110]. These results exactly match with the interpretation of XRD data shown in 3.5(b).

Another powerful tool of TEM is the energy dispersive X-ray spectroscopy. It is an analytical technique used for the elemental analysis of a sample. It is based on a fundamental principle that each element has a unique atomic structure allowing x-rays that are characteristic of an element’s atomic structure, which can be identified uniquely from each other. X-rays are emitted by the interaction of sample with the high-energetic electron beam of TEM. This technique is used for the compositional analysis of nanowires. By mapping out the elemental composition across an interface, it is also used for determining the diffusion of elements into each other in the case of multi-segmented nanowires. EDX spectroscopy is
Figure 3.6. TEM images of 80 nm Co nanowires obtained by Philips EM-420T (a) Low magnification image of a bundle of nanowires (b) High magnification image of a single nanowire. Inset shows the SAED pattern for the nanowire.
available in both Philips and JEOL TEM.

In short, structural studies are an integral part of the characterizations of nanowires. Detailed structural analysis for specific cases will be discussed in the next chapters of this thesis.

3.3 Electrical transport measurements

Electrical transport measurement is one of the most common and effective approach to characterize the electronic properties of nanowires. Conventionally, transport measurements are performed using a four-probe configuration, as illustrated in Figure 3.7.

![Figure 3.7. Schematic of four-probe transport measurements on nanowire.](image)

An electrical current is passed through the outer electrodes and the voltage is measured between the inner ones. Since, there is negligible amount of current passing through the voltage electrodes, four-probe measurements does not include contributions from the contact resistances between electrodes and nanowire. In our case, it would be ideal to obtain isolated freestanding nanowires and connect
four electrodes for the transport measurements.

However, superconducting as well as magnetic nanowires used in the current study present a unique challenge for a successful transport measurement. Most of the nanowires discussed here are made up of elemental metals. Once released from the membrane, these nanowires are easily oxidized when exposed to atmosphere. Commonly, nanowires with single crystal morphology develop an oxide layer on their surface, for ex- Sn, Pb, In, Zn and Al. These oxide layers are self-limiting and stop growing after initial exposure with thickness on the order of few nanometers. This insulating oxide layers prevent good electrical contact between electrodes and nanowires. On the other hand, polycrystalline nanowires form oxide layers at the grain boundaries, which make the nanowires insulating. Hence, it is extremely difficult to perform a four-probe measurement on individual free-standing nanowire by using conventional techniques. One of the previous graduate student in our lab, James Kurtz, had tried to make electrical contacts on Sn nanowires using a combination of electro-fluidic alignment and e-beam lithography [42]. Successful conducting contacts were rarely achieved in this procedure. Even though the nanowires looked well connected to lithographically-patterned measurement probes, they always had large (> MΩ) resistances at room temperature.

To overcome this problem, one needs to satisfy either of the three conditions: (1) Fabricating nanowires which can withstand oxidation during the whole procedure of making contacts and performing transport measurements, or (2) Devise a procedure which does not expose nanowire for oxidation and still can provide reliable electrical measurements with zero contact resistances, or (3) Develop a method to get rid of the oxide layer effectively and efficiently to measure free-standing nanowires in four-probe configuration.

Superconducting alloys and inter-metallic compounds do not oxidize easily and
can be a good candidate for four-probe measurements on individual nanowires. They are also a subject of great interest in the past few decades due to their high transition temperatures, high critical fields and higher stability than elemental superconductors. However, the coherence lengths in these superconductors are usually low, $\sim 10$ nm. With our current fabrication capabilities, we can reliably make nanowires with diameter only in the range of $\geq 20$ nm. Nanowires with coherence lengths less than 20 nm will not be in the 1-D regime and hence may not show any quantum confinement signatures. Transport measurements on a superconducting inter-metallic compound AuSn will be discussed in the next chapter to illustrate this issue. Hence, this approach may not be the best option to observe 1-D effects in nanowires using four-probe configuration.

3.3.1 Solution I: Quasi four-probe measurements

Second option is to protect nanowires from oxidation. A useful technique to measure electrical properties of nanowires without releasing them out of the membranes is in practice for quite some time. In this technique, two-probe measurements were made on an array of nanowires embedded inside the membranes. A conducting silver paint was used to affix two measurement electrodes (typically gold wires) on the either side of the membrane contacting multiple number of nanowires [6, 7]. In other case, in-situ contacts were prepared by evaporating metallic film on membranes to contact an array of nanowires [43]. Although in some cases, even single nanowire was claimed to be measured in the above configuration. This technique was quite successful in measuring electrical properties of superconducting nanowires and revealing some interesting phenomena. However, there was no way one can avoid contact resistances in all those measurements. So, the measured
resistances may not be the true characteristics of the system under study. Also, a non-zero contact resistance connected in the series for all transport measurements may have eclipsed some quantum mechanical fluctuations.

To circumvent this problem, a novel technique was devised to use bulk superconductors (BulkS) as the electrodes for two-probe measurements. The schematics for this arrangement is shown in 3.8. A small piece of membrane containing nanowires is taken for the measurement. A Q-tip soaked in ethanol was used to wipe out any over-growth on the surface of membranes as well as the metallic seed layer on the backside. The cleaned membrane was fixed between two superconducting wires making an assembly of BulkS/NW/BulkS. High purity (99.999 %) superconducting wires of 0.5 mm diameter were used for the measurement electrodes. The whole assembly was put in between two brass blocks, machined and threaded to have two stainless steel screws going from the top block to the bottom one. Two small pieces of sapphire were used as the spacer between BulkS and brass blocks. Sapphire was used because it is a good thermal conductor as well as a good insulator; thereby preventing electrical short between brass blocks and electrodes and maintaining good thermal contact. Bottom brass block was fixed to the sample puck of the cryostat. Membrane was mechanically squeezed between BulkS by tightening the screws. The number of nanowires contacted between BulkS can be adjusted by careful tightening of the screws. From the standpoint of nanowires, this technique is similar to the one used before; it is still a two-probe measurement of nanowires. However, from a different perspective, the arrangement is a four-probe measurement on a BulkS/NW/BulkS system, as depicted in the right half of figure 3.8. The total measured resistance of the system includes contributions from BulkS (typically $< 1 \, \Omega$), NWs and interfaces BulkS/NWs.

So, the question now arises: What is the importance of superconducting elec-
Figure 3.8. Schematic of quasi four-probe transport measurements: Top image shows the experimental setup and bottom image shows the electrical configuration.

Below their superconducting transition temperature $T_c$, BulkS reached a zero-resistance state. Also, due to the proximity effect (discussed in section 2.3.1), it forces the interface BulkS/NW to go superconducting (i.e. zero resistance) as well. In essence, the answer to the above question is: Superconducting electrodes can get rid of contact resistances in a two-probe measurement configuration. So,
below $T_c$ (Bulk), the total resistance of system only includes resistance from the array of nanowires. Practically, behaving as a four-probe electrical transport measurement and hence, the name "Quasi four-probe measurement". This method was successfully employed to measure electrical properties of a variety of nanowires, for ex:– Sn, Zn, In, Pb, Ni, Co, Al, Bi, AuSn. Some of them will be discussed in the next two chapters of the thesis.

3.3.2 Solution II: Four-probe measurements on freestanding single nanowire.

Even though the quasi four-probe measurement discussed in previous section resulted in transport measurements without contact resistances, there were still some concerns about it. Firstly, measurements are done on an array of multiple nanowires in most of the cases. Secondly, since it required soft materials as electrodes, there is limitation on the use of different superconducting materials. So, an efficient and reliable process was needed to etch the oxide layer and fabricate four electrodes for electrical measurements.

3.3.2.1 Focused Ion Beam

Focused Ion Beam, commonly known as FIB, is a technique used for site-specific analysis, deposition and ablation of materials. Figure 3.9 shows a schematic of a dual beam FIB/SEM system. FIB instrument at Materials Characterization Laboratory, Penn State is a FEI Quanta 200 3D dual beam FIB/SEM system. Electron beam is used for imaging the sample, similar to a conventional SEM. FIB also uses a focused beam of highly energetic $Ga^+$ ions, accelerated to an energy of 5-30 keV, for the sputtering atoms from the surface of the sample. Because
of the sputtering capability, FIB is widely used as a micro/nano-machining tool, to modify or machine materials at very small scale. Our system is also equipped with a Gas Injection System (GIS). Using GIS, a FIB can also be used to deposit materials, fabricating conducting nanostructures via ion-beam induced deposition (IBID). A precursor gas such as tungsten carbonyl, W(CO)$_6$ is introduced into the vacuum chamber through GIS needle and allowed to chemisorbs onto the sample. A scanning ion beam decomposes the precursor gas into volatile and non-volatile components. Non-volatile component such as tungsten is left on the surface as deposition. By adjusting the ion beam scan, nanostructures with dimensions on the order of 100 nm can be deposited with IBID. FIB was used to deposit platinum and tungsten as the measurement electrodes on nanowires. Also, since the ion beam has inherent sputtering capability, the oxide layer can be sputtered away in the course of deposition. Before using Pt and W deposition for fabricating electrodes on nanowires, their electrical properties were also studied. Table 3.2 lists parameters for the FIB-assisted Pt and W deposition. Figure 3.10(a) shows
Table 3.2. Parameters for FIB-assisted Pt and W deposition.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Pt-deposition</th>
<th>W-deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Precursor Gas</td>
<td>$C_5H_5(PtCH_3)_3$</td>
<td>$W(CO)_6$</td>
</tr>
<tr>
<td>Temperature</td>
<td>30°C</td>
<td>55°C</td>
</tr>
<tr>
<td>Current density</td>
<td>2 - 10 pA/µm$^2$</td>
<td>50 pA/µm$^2$</td>
</tr>
</tbody>
</table>

a platinum strip fabricated by FIB-assisted deposition across Au electrodes, and (b) shows the Resistance vs. Temperature plots for Pt strip. It can be seen that temperature dependence of resistance is not metallic. This may be explained by the fact that deposited Pt strip is not a pure metal but an amorphous mixture of Pt, Ga and C. This is confirmed by the EDX measurements on a similar Pt strip in TEM shown in figure 3.10(c).

On the other hand, FIB-deposited W is known to be superconducting around 5 K [44]. Figure 3.11 (a) shows a SEM image of W strip across Au electrode and (b) shows R-T dependence showing a superconducting transition with $T_c$ at 4.8 K. Several groups have had success in making four-probe measurements on metallic nanowires using ion-beam induced Pt deposition [45, 46]. However, we were the first group to ever report the fabrication of superconducting W electrodes on the nanowires [47].

Thermally oxidized silicon wafers of 4” diameters were used as the base substrates. Low doped and highly resistive silicon was used to avoid any leakage current through the substrate, which can interfere with the nanowire measurements. Also, silicon wafers with [100] crystal orientation were used for ease of cleaving of the final wafer into smaller dies that could be tested independently.

Photolithography processing was done on the oxidized wafers. The mask used for photolithography was a Cr-coated, 4-inch glass plate with patterns defined by the software package L-Edit and written to the plates by mask manufacturer. It
Figure 3.10. Top: SEM image of FIB-deposited Pt-strip with Au measurement electrodes. EDX spectra of Pt-strip. Bottom: R-T plot at zero magnetic field for the above Pt-strip.
Figure 3.11. Top: SEM image of FIB-deposited W-strip with Au measurement electrodes. Bottom: R-T plot at zero magnetic field for the above W-strip.
was a positive mask and was used with a positive photoresist. So, the metal was ultimately deposited on the wafers only in the areas exposed to the light or where Cr coating was missing from the glass plate.

A single step photolithography was used. Since, there were no small features in this step, a multipurpose photoresist BPRS-100 was used for the photolithography [42]. A Karl-Suss aligner with a UV-light source was used for the photoresist exposure. Alignment was required to make sure that the line running between the cells was lined up with crystal axes. This was important only for cleaving of wafers in the final step. Exposed photoresist was developed in PL251 developer. Afterwards, wafers were cleaned with acetone, followed by IPA. Patterns were visually inspected for any damage by an optical microscope.

Wafers were loaded in a Thermionics thermal evaporator chamber to the metalization. A thin, adhesion layer of Ti followed by Au was deposited on the wafers. Lift-off was done in acetone to remove excess metal and photoresist in order to obtain the desired patterning. A whole wafer was cleaved into several small dies, each containing an array of cells. Fig. 3.12 (a) shows one of such die with a $4 \times 4$ array of cells. Fig. 3.12 (b) shows a SEM image of a cell containing four Au pads. These pre-pattern silicon substrates are now ready for making nanowire devices.

### 3.3.2.2 Electrodes on the nanowires

This section outlines the steps involved in the fabrication of electrodes on a single nanowire using FIB. A small piece (typically 2 mm across) of membrane containing nanowires was dissolved in 1 cc of appropriate solvent (dichloromethane, CH$_2$Cl$_2$ for PCM and NaOH for AAM). The resulting suspension was stored in a centrifuge tube and left for few hours to let the nanowires settle down at the bottom. After that, solution was decanted and nanowires were washed with DI water couple of
Figure 3.12. (a) SEM image of a die containing an array of cells (b) SEM image of an individual cell.
times. This was done to remove any unwanted residues from the dissolution of membranes. A new suspension was made in IPA and then further diluted by a factor of typically 100-1000. Since, AAM has higher density of nanowires, it requires more dilution than wires grown in PCM. Approximately 5 - 7 µL of the new suspension was then dropped on a pre-patterned die.

After IPA is evaporated, nanowires remained stick to the substrate by Van der Waals forces. The wire density on the substrate proved to be a critical factor in making good quality electrodes on nanowire. Too high a density results in lumps of nanowires, balled up like spaghetti, making it extremely difficult to locate an isolated nanowire for the device. Another critical factor is the length of nanowires. If the wires are too short, it becomes tough to pattern four electrodes on a single nanowire. Majority of nanowires deposited in PC1 membranes comes out relatively short. On the other hand, PC2 membranes, because of their larger thickness, are more suitable for producing long nanowires. Dispersed nanowires are inspected in a Dark Field optical microscope. Typically in each die, there are 2-3 cells with an isolated nanowire in the window area between the Au pads. Cells containing isolated nanowires were identified and the substrate will proceed to FIB for the fabrication of devices.

The substrate was transferred onto the sample stage of FIB vacuum chamber. Isolated nanowires in the previously identified cells were located with the help of SEM. Once an isolated nanowire was found, four electrodes (typically 5 - 10 µm in length) were digitally patterned on the nanowire in the FIB GUI software. The digital patterns define the scanning area for the ion beam during deposition. The sample stage is rotated at an angle of 52° to make sure it is perpendicular to the ion beam. A GIS needle was introduced close to the substrate. Deposition was carried out by flowing a jet of precursor gas through the needle along with the Ga+
ion beam. Deposition can be paused anytime to monitor the progress or quality of the deposited electrodes. After the completion, these electrodes were then joined to the larger Au pads using longer patterns. Fig. 3.13 show four Pt electrodes patterned on a 50 nm diameter Ni nanowire. Once all the patterns are deposited, device was ready to be mounted on the cryostat for the measurements.

Further connections to the sample stage were done by putting Indium contacts on the big Au pads. Ultra-thin Au wires were fixed to the Au pads by pressing tiny indium pieces with a pointed bamboo stick. While making contacts, a grounded wrist-strap was always worn to get rid of any static discharge. Extreme care was undertaken to safeguard the device from any damage due to the electrostatic discharges. The sample with Au wires was fixed with Ge varnish on the gold-plated platform of the sample holder (or puck). The sample was connected to the leads
of the puck by pressing Au wires with the indium pieces.

After all wiring was done; sample puck was inserted into the receptacle of the cryostat for the measurements. The next two chapters of this thesis will present the results of the electrical measurements done using above technique.
4.1 Why Zinc nanowires?

Bulk zinc (Zn) is a conventional type I BCS superconductor. It has a superconducting transition temperature, $T_c$ of 0.85 K and a critical magnetic field, $H_c$ of 50 Oe (at $T = 0$ K) [48]. Zn is an interesting material from the standpoint of observing dissipations due to the quantum fluctuations. The superconducting coherence length of bulk Zn in clean limit, $\xi_0(T = 0 \text{ K})$ was estimated to be in the range of 1.55 - 2.2 $\mu$m [49]. This is almost an order larger than those of the other widely studied superconducting materials, e.g. Sn, In, Pb, Nb, inter-metallics and alloys. As discussed in chapter 2, quantum mechanical fluctuations depend closely on the coherence length of superconducting nanowires. With such a large coherence length, Zn nanowires stand a better chance to show dissipative behavior or one-dimensional effects in comparison to other superconducting nanowires of the same diameter.
4.2 Synthesis of Zn Nanowires

Zn nanowires were fabricated by template-based electrochemical deposition as described in chapter 3. The electrolyte (or the plating solution) for the synthesis was prepared by dissolving 0.18 M of ZnCl$_2$ into 200 ml distilled water, and then mixed with 40 ml saturated KCl and 0.5 g gelatin. The additives, KCl and gelatin, aid in increasing electrical conductivity and wetability, respectively. Electrodeposition was carried out in a two-electrode assembly with a pure bulk Zn strip acting as the anode. Zn nanowires were plated inside the porous membrane under a constant DC potential -0.4 V at room temperature. Zn nanowires with diameters in the range of 40 - 100 nm and lengths from 2 - 6 µm were fabricated in PCM. For longer nanowires, I have used AAM with lengths up to 35 µm.

The computer-controlled electrodeposition was extended for a few minutes after the nanowires are completely filled in the membranes. This was done to ensure an overgrowth of bulk Zn layer on the top. This overgrown layer acts as a protective shield from oxidation for the nanowires inside the pores of membrane.

4.3 Structural Characterizations

The structural properties of Zn nanowires were determined by a JEOL-2010F TEM. Figure 4.1 shows a low magnification image of a bundle of 70 nm Zn nanowires released after dissolving the host membrane. TEM image indicate that the majority of the nanowires has polycrystalline structure with elongated single-crystal segments which ranges from several hundred nanometers to a few µm in length. Occasionally, crystallinity was found to extend throughout the entire length of the 6 µm long wires. Figure 4.2(a) shows the high-resolution TEM (HRTEM)
Figure 4.1. Low magnification TEM image of 70 nm Zn nanowires.

image of a single 70 nm ZNW. As can be seen, there is an oxide layer uniformly on the entire surface of the nanowire. Figure 4.2(b) shows the magnified image of the surface layer. The oxide layer of ZnO is observed to be highly crystalline with an epitaxial-like growth with respect to Zn nanowire. This is confirmed by the selected area electron diffraction (SAED) pattern shown in figure 4.2(c). The bright spots on the pattern represent the crystal planes of Zn and ZnO crystal. The spots from oxide layer as well as Zn nanowire follow the same symmetry and arrangement in the SAED pattern. This is a confirmation of epitaxial growth of ZnO layer on Zn nanowire; making a core-shell structure [50]. This native oxide layer, as will be explained later, is the biggest obstacle for four-probe measurements on freestanding individual Zn nanowires.

On the other hand, crystalline nature of Zn nanowires has an advantage over previous experiments where the nanowires were either amorphous or granular [2, 3, 4, 5]. A good quality crystalline nanowire avoid the contributions from inter-
Figure 4.2. HRTEM images of (a) single-crystal segment of a 70 nm ZNW and (b) Zn-ZnO surface layer. (c) SAED pattern from the surface layer shown in above figure.

grain interactions debated in granular nanowires as well as the variation of $T_c$ with physical dimensions seen in amorphous nanowires.

4.4 Electrical Transport Measurements

Electrical transport measurements were carried out with a commercial Physical Properties Measurement System (PPMS) (Quantum Design Inc.), equipped with a He-3 cryostat and a superconducting magnet. The base temperature of the cryostat is 0.45 K and it can generate a magnetic field of up to 9 T. The experimental arrangement is shown schematically in fig. 4.3. Details about the electrical transport measurements are described in previous chapter of this thesis. Bulk superconductors (BulkS) used for the electrical measurements are either Sn, In or Pb. Prior to the measurements, the pre-deposited Au film on the back side and
overgrowth Zn on the surface of PM was removed by wiping out with a Q-tip dipped in ethanol. BulkS were mechanically squeezed onto the two sides of the membrane making electrical contact to the nanowires embedded in the membrane forming a BulkS/ZNW/BulkS structure.

Since, the $T_c(s)$ of the BulkS (Sn, In and Pb) at 3.7 K, 3.4 K and 7.2 K, respectively were much higher than that of Zn at 0.85 K, any additional feature below the $T_c(s)$ of BulkS was attributed solely to the contributions from the Zn nanowires and the interfaces NWs/BulkS. Most of the transport measurements reported here are made with small dc excitation currents (usually 100 nA and well below the critical current of nanowires), unless stated otherwise. With this technique, 45 samples of different configurations were measured. Reproducible results were always found in the samples of similar configurations. Table 4.1 lists the details about the representative samples of each configuration, discussed in this thesis.
Table 4.1. List of the samples with different configurations.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Diameter</th>
<th>Length</th>
<th>BulkS</th>
<th>No. of nanowires contacted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1</td>
<td>100 nm</td>
<td>6 µm</td>
<td>In</td>
<td>1</td>
</tr>
<tr>
<td>Z2</td>
<td>70 nm</td>
<td>6 µm</td>
<td>Sn</td>
<td>11</td>
</tr>
<tr>
<td>Z3</td>
<td>40 nm</td>
<td>6 µm</td>
<td>Sn</td>
<td>4</td>
</tr>
<tr>
<td>Z4</td>
<td>40 nm</td>
<td>6 µm</td>
<td>In</td>
<td>6</td>
</tr>
<tr>
<td>Z5</td>
<td>40 nm</td>
<td>2 µm</td>
<td>In</td>
<td>1</td>
</tr>
<tr>
<td>Z6</td>
<td>40 nm</td>
<td>35 µm</td>
<td>In</td>
<td>55</td>
</tr>
<tr>
<td>Z7</td>
<td>40 nm</td>
<td>2 µm</td>
<td>Pb</td>
<td>5</td>
</tr>
<tr>
<td>Z8</td>
<td>40 nm</td>
<td>6 µm</td>
<td>Sn</td>
<td>5</td>
</tr>
<tr>
<td>Z9</td>
<td>40 nm</td>
<td>6 µm</td>
<td>Ag and Sn</td>
<td>13</td>
</tr>
<tr>
<td>Z10</td>
<td>40 nm</td>
<td>6 µm</td>
<td>Au</td>
<td>7</td>
</tr>
</tbody>
</table>

4.4.1 BulkS-SNW-BulkS

Fig. 4.4 shows the resistance (R) vs. temperature (T) plot of an array of 100 nm ZNWs attached to superconducting In electrodes. The resistance is normalized to the value at 4 K, which gives the residual resistance ratio, RRR= R(300K)/R(4K), of these ZNWs to be \( \sim 1.5 \). The R-T curve shows linear (i.e. metal-like) behavior from 300 K down to 4 K. This means that the contacts between BulkS and ZNWs are metallic in nature. The number of ZNWs connected in parallel in the measured array is estimated by using a resistivity of \( \rho_{Zn}(4K) = 18.2 \mu \Omega \text{ cm} \) at 4 K. The total resistance of ZNWs was considered to be the large resistance drop observed at their \( T_c \), when ZNWs are cooled from normal to the superconducting state. The estimate for multiple wires are correct to within 30% given the uncertainty in resistivity (20%) and the wire dimensions (10%).

In a previous study of single-crystal Zn, the product of the elastic electron mean free path, \( l_e \), and resistivity, \( \rho_{Zn} \), at 4.2 K was found to be \( 2.2 \times 10^{-11} \Omega \text{ cm}^2 \) [49]. Using this relation and the resistivity value of \( \rho_{Zn}(4K) = 18.2 \mu \Omega \text{ cm} \), mean free path \( l_e \) was estimated to be 12 nm.
Figure 4.4. Normalized resistance vs. temperature curve for 100 nm ZNWs with In electrodes at zero magnetic field.

According to Ginzburg-Landau theory, superconducting phase coherence length in the clean limit follows the relation

$$\xi(0) \sim (\xi_0 l_e)^{1/2}$$

(4.1)

where $\xi_0$ is the phase coherence length in the dirty limit and $l_e$ is the mean free path [51]. Using eq. 4.1, $\xi$ for our ZNWs was estimated to be 155 nm. As mentioned in the previous section, ZNWs are polycrystalline with grain sizes up to few $\mu$m in length. However, estimated mean free path ($l_e = 12$ nm) is much smaller than the grain size. One of the possible reasons maybe the presence of dislocations or other defects inside the ZNWs. Dislocations and defects can enhance the electronic
scattering leading to a smaller mean free path.

Electrical measurements of ZNWs with smaller diameters were performed in the similar fashion. Fig. 4.5(a) shows the R-T curves of a 70 nm Zn nanowire array with bulk Sn as the electrodes, measured at different magnetic fields (H) aligned perpendicular to the nanowires. The length of the Zn nanowires is 6 µm. At H=0 Oe, the resistance of the system shows a small drop at 3.7 K and then a much larger drop near 1.0 K, before decaying to zero resistance below 0.7 K. The two resistance drops at 3.7 K and 1.0 K are due to the superconducting transitions of bulk Sn and ZNWs, respectively. The total resistance of the system becomes zero below 0.7 K implying that the entire Sn/ZNWs/Sn system is superconducting at low temperatures. This is indeed expected of a BulkS/ZNW/BulkS system with Sn electrodes and Zn nanowires independently exhibiting superconductivity below their respective transition temperatures. The broadening (△T ∼ 0.2 K) of the superconducting transition below 1.0 K can be attributed to the thermally activated phase slip process, which has been investigated in various 1d superconducting system [24, 25, 52].

The superconductivity of the bulk Sn electrodes can be quenched by applying a magnetic field of 300 Oe. As a result, the system shows only one large resistance drop around 0.9 K due to the superconducting transition of the ZNWs. Even though the critical field of bulk Zn is only 50 Oe, the superconductivity in the ZNWs persists at 300 Oe. This is because the critical field of the ZNWs is enhanced to 1.2 kOe at 0.47 K due to their reduced diameter [51]. At low temperatures, the system showed a finite resistance of ∼ 5 Ω, roughly equal to the resistance drop observed near 3.7 K for zero magnetic field. So, at H = 300 Oe, the finite resistance is mainly due to the interfaces and the bulk Sn electrodes. The onset transition temperature thereafter decreases with increasing H and becomes
Figure 4.5. (a) Resistance vs. temperature curves for an array of 70 nm Zn nanowires with Sn electrodes at different magnetic fields. (b) Voltage - current characteristics at two magnetic fields.
lower than 0.47 K at a field of 1.2 kOe. Regardless of whether the bulk Sn electrodes are superconducting or normal, the ZNWs array always shows the expected superconductivity below 1.0 K. The zero resistance state also indicate that the interface and contact resistances below 0.7 K are negligibly small at zero magnetic field. Since, the actual resistance of bulk Sn wires is very small, drop at 3.7 K is most likely due to the contributions from both bulk Sn electrodes and the two Sn/ZNWs interfaces at the end of nanowires.

R-T curves are well supported by the V-I measurements shown in fig. 4.5(b). At \( H = 0.0 \text{ Oe} \) and \( T = 0.47 \text{ K} \), there is a well-defined critical current, \( I_c = 6.5 \mu\text{A} \), below which ZNWs are in superconducting state. A field of 0.6 kOe results in the appearance of finite resistance denoted by the linear slope in the V-I curve. The linear V-I dependence also suggests that the interface resistance is metallic or "Ohmic" in nature. In both the cases, irrespective of the state of bulk electrodes, ZNWs always show superconducting transition with well-defined critical currents. Similar behavior is also observed in 100 nm ZNWs array shown in Fig. 4.4. Since, the coherence length of ZNWs is estimated to be 155 nm, all of the nanowires with diameters 70 nm and 100 nm should show behavior similar to one-dimensional superconductors described in Chapter 2 of this thesis. To observe dissipative behavior, the zero field R-T dependences of 70 nm and 100 nm ZNWs arrays are plotted in log scale as shown in Fig. 4.6. As seen in the above figure, for \( d = 100 \text{ nm} \), ZNWs shows broadening of transition \( \Delta T \sim 0.25 \text{ K} \) around \( T_c \). On the other hand, 70 nm ZNWs also show similar broadening of transition but in addition a resistive tail appeared extending down to low temperatures. Broadening of transition and low temperature resistive tail are the two key signatures of dissipation in one-dimensional superconductors. The former is attributed to the thermally activated phase slips (TAPS) whereas the latter is due to the much debated quantum phase
Figure 4.6. Resistance vs. Temperature curves for 70 nm and 100 nm ZNWs arrays at zero magnetic field in log-log scale.

slips (QPS). The origin and significance of phase slips in studying one-dimensional superconductors are outlined in chapter 2 of this thesis. R-T dependence of 70 nm and 100 nm ZNWs are consistent with those obtained previously in different quasi 1D superconducting systems [2, 4, 5, 6, 8, 35]. Nanowires with progressively decreasing diameter show increasing dissipative behavior. If we assume similar behavior for ZNWs as was observed for Sn nanowires [8], then wires with diameter smaller than 70 nm will be expected to show strong dissipative transition. Next section describes the unusual dissipative behavior observed in the transport properties of 40 nm ZNWs.
4.4.2 Anti-Proximity Effect

Array of ZNWs with diameter 40 nm and length 6 µm were fabricated in PCM and measured in the similar configuration. Fig. 4.7(a) shows R-T plots for 40 nm ZNWs attached to bulk Sn electrodes measured at different magnetic fields. At \( H = 0 \) Oe, R-T curve shows the expected drop at 3.7 K, the \( T_c \) of Sn electrodes. However, in strong contrast to the data of 100 nm and 70 nm nanowires [figs. 4.4, 4.5], there is no sign of a resistance drop near 1.0 K, the expected \( T_c \) of ZNWs. Instead, there is a large finite resistance extending down to 0.47 K (the lowest temperature of measurement). One possible explanation to this strange behavior may be: *ZNWs of 40 nm diameter cannot sustain superconductivity.*

Similar to the case of 70 nm ZNWs, a field of 0.3 kOe is applied to drive Sn electrodes into normal state. Surprisingly, a prominent resistance drop is observed around 1.0 K indicative of a superconducting transition in ZNWs !! This strange behavior suggests that ZNWs are incapable of showing superconductivity when BulkS are in superconducting state. However, driving BulkS to normal state results in the recovery of superconductivity in ZNWs.

The results shown in figure 4.7(a) are well complemented by V-I measurements done at 0.47 K (fig. 4.7(b)). At \( H = 0 \) Oe, when BulkS is superconducting, the V-I curve of the system shows “Ohmic” behavior at all excitation currents. Under a field of 0.3 kOe, when BulkS is normal, the V-I curve shows a change in slope at a critical current of \( I_c = 0.6 \) µA. This corroborates the earlier conclusion that 40 nm ZNWs remain in a non-superconducting state when electrodes are in superconducting state. ZNWs recover their superconductivity when electrodes are driven into normal state, indicated by the observation of a well-defined critical current, \( I_c \).
Figure 4.7. (a) Resistance vs. temperature curves for an array of 40 nm Zn nanowires with Sn electrodes at two magnetic fields. (b) Voltage - current characteristics at same magnetic fields.
The phenomenon described above is very counterintuitive in the framework of classical proximity effect. Bulk superconducting electrodes can be considered as strong superconductors since they are not affected by the dissipative fluctuations usually associated with low-dimensional superconductors such as quasi 1D nanowires. On the other hand, superconductivity in nanowires can be termed as weak due to the quantum mechanical and thermal fluctuations in the form of phase slips. Based on the standard model of proximity effect, one would guess that a strong superconductor will either enhance the superconductivity of weaker one or at least show independent superconducting properties [51]. However, in our case the observed phenomenon suggests a conflicting interest between strong and weak superconductors. Due to this conflicting nature, we termed this unusual phenomenon as "Anti-Proximity Effect" or APE.

Since, APE is not observed in thicker wires with diameter $\geq 70$ nm, it is clear that this phenomenon is related to the quantum confinement effects. APE is observed to be strongly dependent on the superconducting properties of bulk electrodes. The next step in characterizing this phenomenon would be to change the bulk electrode material. Also, Proximity effect is well known to be dependent on the length of system. It maybe reasonable to assume APE also depends on the length of nanowires. So, another direction in characterizing APE would be to modulate the length of ZNWs.

4.4.2.1 Bulk In/ ZNWs/ Bulk In

This section describes the measurements made on three In/ZNWs/In samples. In this samples, the diameter of ZNWs was kept fixed at 40 nm but their lengths were varied from 2 $\mu$m to 35 $\mu$m. Fig. 4.8 describes the R-T dependences of sampleZ4 with 40 nm ZNWs (length = $6\mu$m) sandwiched between In electrodes.
Only difference between Z3 and Z4 is the BulkS, former has Sn while latter has In. Expect that, everything was kept similar in samples Z3 and Z4. However, in contrast to Z3, sample Z4 showed transition near 1.0 K at H = 0 Oe. But the transition was very broad with a high finite resistance of 100 Ω at 0.47 K. When bulk In electrodes are driven normal by a field of 0.3 kOe, a larger and sharper resistance drop is observed near 1.0 K. This result is well supported by the corresponding V-I plot shown in the inset of figure 4.8. A clear well-defined critical current, $I_c$, is only observed at H = 0.3 kOe; when electrodes are in normal state.

Fig. 4.9(a) shows the R-T plots of sample Z5 with 40 nm ZNWs with length of 2
μm between In electrodes. Based on the estimation of number of nanowires, sample

![Figure 4.9.](image)

**Figure 4.9.** Resistance vs. Temperature plots for 40 nm ZNWs array of length (a) 2 μm and (b) 35 μm sandwiched between In electrodes. Inset shows the respective V-I measurements at different magnetic fields.

Z5 contains a single ZNW. A similar but stronger suppression effect is observed in this case. The measured resistance at H = 0 Oe shows a smooth decrease from 3.4 K to 0.47 K with no big change in resistance. A magnetic field of 0.3 kOe, as in samples Z3 and Z4, results in a sharp resistance drop near 1.0 K. Qualitatively,
results of Z5 closely resemble that of Z3 (6 µm length with Sn as BulkS). In both the cases, there was no sign of transition near 1.0 K. Hence, these samples will be described as showing "complete suppression" of superconductivity in ZNWs.

These results indicate that tin(Sn) as BulkS is more effective than indium(In) in suppressing the superconductivity of ZNWs. Also, APE depends on the length of NWs connecting the two BulkS. Strength of APE increased when length of NWs are reduced from 6 µm to 2 µm.

When the length of ZNWs is increased to 35 µm, no obvious sign of APE was observed, as shown for sample Z6 in figure 4.9(b). There was no suppression of superconductivity as seen in R-T curves, whether BulkS is superconducting or normal. However, subtle sign of APE was observed in the V-I curves measured at two different magnetic fields (Inset of figure 4.9(b)). The critical current, $I_c$, was found to increase from 1.6 µA to 2.0 µA as the magnetic field is increased from 0 Oe to 0.3 kOe. APE was not evident in R-T curves but the V-I curves show that ZNWs in sample Z6 show a slightly stronger superconductivity (indicated by larger $I_c$) when BulkS is normal rather than superconducting.

So, it can be clearly concluded that APE is closely related to the electronic states of BulkS. To get more details about the role of BulkS, R-H scans were measured at different temperatures. Since Z5 shows complete suppression of superconductivity, it’ll be easier to decipher the role of BulkS from the R-H measurements of this sample. Fig. 4.10 shows the R-H scans at four different temperatures; 1.2 K (above $T_c$ of ZNWs) and 0.47 K, 0.65 K & 0.75 K (below $T_c$ of ZNWs). At 1.2 K, ZNWs are in the normal state whereas bulk In electrodes are superconducting ($T_c$(In) = 3.4 K). The discontinuous rise in R at 0.245±0.01 kOe with increasing H pinpoints the critical field of bulk In electrode, $H_{c1}^{In}$. Scans at 0.47 K, 0.65 K and 0.75 K, show sharp drops in R as H is increased above 0.27±0.01 kOe, the
Figure 4.10. Resistance vs. Magnetic field plots at different temperatures above and below $T_c$ of ZNWs for Sample Z5.

$H_{c1}^{ln}$ at these temperatures. So, it can be clearly seen that the abrupt switching of ZNWs from a non-superconducting to superconducting state (and vice versa) is completely opposite to the electronic states, namely superconducting and normal, of the BulkS. Since, this was the case of complete suppression, it would be worth studying the cases of incomplete or partial suppression. Next section deals with the APE in ZNWs with Pb electrodes and details the role of BulkS in this interesting phenomenon.

4.4.2.2 Bulk Pb/ZNWs/Bulk Pb

Compared to bulk Sn and In, bulk Pb has higher $T_c$ (7.2 K) and critical field $H_c$ ($\sim 803$ Oe) [48], along with a shorter coherence length $\xi(0) \sim 83$ nm. The Pb induced APE is found to be even weaker than that using In or Sn as electrodes.
Fig. 4.11(a) shows the R-T measurement of a 40 nm ZNWs array (length = 2 µm) in contact with Pb electrodes (sample Z7), measured at an excitation current of 0.01 µA under different H.

The ZNWs at H=0 Oe show a sharp superconducting transition near 0.9 K with a very small finite residual resistance (∼ 1 Ω) at 0.47 K. The critical field, $H_c(Pb)$ of Pb electrodes in this sample was observed to be higher than the reported bulk value. This enhancement maybe due to the strains induced in the Pb electrodes by squeezing. At H = 1.2 kOe, Pb electrodes are completely driven into normal state and the R-T curve shows only one drop near 0.85 K due to the superconducting transition of ZNWs. The slight reduction of $T_c$ from 0.9 K(at 0 Oe) to 0.85 K (at 1.2 kOe) is due to the influence of magnetic field on the superconducting energy gap of ZNWs. R-T curve also shift up and shows a finite resistance due to the normal Pb electrodes and Pb/ZNWs interfaces. The onset temperature thereafter decreases with increasing magnetic field and becomes lower then 0.47 K at a field of 3.0 kOe. These R-T curves qualitatively resemble those shown in fig. 4.5(a) of 70 nm ZNWs sandwiched between bulk Sn electrodes, exhibiting no suppression of superconductivity at all fields. There is no sign of APE in these R-T scans measured at 0.01 µA.

In sharp contrast, R-T curve measured at an excitation current of 2.5 µA, under H = 0 Oe and 0.7 kOe, do not show any resistance drop near 0.9 K(Fig. 4.11(b)). When a magnetic field of 1.2 kOe is applied, a sharp resistance drop appears near 0.85 K. These R-T curves show APE and resemble the results obtained for 40 nm ZNWs with bulk Sn and In electrodes. However, the dependence of APE on the excitation current was not seen before with Sn and In as BulkS. These interesting results can be understood with the help of V-I measurements done at low temperatures under different magnetic fields.
Figure 4.11. Resistance vs. Temperature plots for Sample Z7 at an excitation current of (a) 0.01 $\mu$A, and (b) 2.5 $\mu$A at different magnetic fields.
Systematic V-I measurements at 0.47 K reveal different properties at magnetic fields below [Fig. 4.12(a-b)] and above [Fig. 4.12(c-d)] the critical field of Pb electrodes, $H_{c}^{Pb} = 0.97$ kOe. There are two critical currents observed in these measurements, $I_{c1}$ and $I_{c2}$, defined as the lower and upper critical current, respectively. Below $I_{c1}$, nanowires are in “superconducting” states with a small finite resistances whereas above $I_{c2}$ the nanowires are completely in the normal state. The V-I curves below $I_{c1}$ are found to be linear in the log-log plot of figure 4.12(b) and parallel to the curves in normal state above $I_{c2}$. This indicates that the small finite resistance below $I_{c1}$ is “ohmic” over the excitation current range from $I_{c1}$ down to 10 nA. The origin of this resistance will become clearer later in this section. Between $I_{c1}$ and $I_{c2}$, ZNWs are in the intermediate region between the superconducting and normal state where the resistance is strongly dependent on the excitation current. When H<600 Oe, the V-I curves are almost insensitive to the applied magnetic field with the two critical currents, $I_{c1} =1.6$ µA and $I_{c2} = 2.2$ µA, denoted by the arrows. Between $I_{c1}$ and $I_{c2}$, the measured voltage shows a particularly steep dependence on I. Under a magnetic field between 600 Oe<H<900 Oe, when Pb electrodes are still superconducting, both $I_{c1}$ and $I_{c2}$, increase with increasing magnetic field. This is contrary to the behavior of a standard superconductor which under increasing magnetic field always show a decrease in critical current. For H>900 Oe, above the $H_{c}^{Pb}$ of Pb, both $I_{c1}$ and $I_{c2}$ show the expected decrease with increasing magnetic fields. The critical field of ZNWs was observed to be about 3 kOe at $T = 0.47$ K. The higher finite resistance ($\sim 10 \ \Omega$) below $I_{c1}$, indicated by the dashed line in figs. 4.12(c) and (d), is due to the normal Pb electrodes combined with contact resistance. These results clearly indicate that the neighboring bulk Pb superconducting electrodes weaken the superconductivity of ZNWs.

Both critical currents, $I_{c1}$ and $I_{c2}$, estimated from figure 4.12 are plotted as a
Figure 4.12. Voltage vs. excitation currents plots of sample Z7 at magnetic fields (a)-(b) below $H_c^{Pb}$ and (c)-(d) above $H_c^{Pb}$. 
function of applied magnetic field in figure 4.13. In a magnetic field range between 0.6 kOe and 0.9 kOe, a sharp increase can be seen in $I_{c1}(I_{c2})$ from 1.6 $\mu$A (2.2 $\mu$A) to 3.8 $\mu$A (4.8 $\mu$A). The puzzling result of R-T curves shown in fig. 4.11 can be understand by this unconventional dependence of critical current on the magnetic field. In fig. 4.11(b), there was no superconducting transition below 0.7 kOe because the used excitation current of 2.5 $\mu$A is larger than the upper critical current, $I_{c2}$, in this magnetic field region. Also, the recovery of superconductivity at a higher magnetic field, $H >> 1.2$ kOe is because the same excitation current...
of 2.5 $\mu$A falls below $I_{c2}$ in that magnetic field range. Similarly, if an excitation current less than $I_{c1} = 1.6 \mu$A at 0.47 K is used, as it is the case for the results in fig. 4.11(a), then the sample shows superconducting behavior irrespective of whether the Pb electrodes are superconducting or normal. As it’ll be discussed in more detail later, the suppression of critical current by the bulk electrodes turned out to be another manifestation of APE along with the results shown in figs. 4.7, 4.8 and 4.9.

In order to explore the role of BulkS, resistance was measured as a function of magnetic field at 0.47 K using four different excitation currents as shown in fig. 4.14. At an excitation current of 11 $\mu$A, higher than $I_{c2(\text{max})} = 4.8 \mu$A (fig. 4.13), ZNWs are always in normal state at all fields. A resistance jump between 0.94 and 1.0 kOe pinpoints the superconducting to normal transition of Pb electrodes. The onset field of 0.94 kOe was defined as the critical field, $H_{Pb}^{c}$, of Pb electrodes. This is the value of critical field used in all the analysis. Next two R-H curves measured at 3.0 and 4.0 $\mu$A are important as these values are less than for all $H < H_{Pb}^{c}$. These curves show a sharp resistance drop from about 55 $\Omega$ down to about 1 $\Omega$. These drops start at $H^{d} = 0.65$ kOe for the 3.0 $\mu$A curve and 0.75 kOe for 4.0 $\mu$A curve. The resistance remains at these low values until the field is increased to $H_{Pb}^{c} = 0.94$ kOe. Fig. 4.14(b) with R plotted in log-scale over a narrower range in H showcases the results in low resistance region. Four additional R-H curves are added to this plot for I = .01, 0.5, 1.0 and 1.9 $\mu$A. These curves are generated by estimating the resistance at specific magnetic field values from the V-I curves shown in fig. 4.12. The R-H curve at 1.9 $\mu$A looks similar to the ones at 3.0 and 4.0 $\mu$A, except that the resistance in the low magnetic fields for $H < H^{d}$ ($\sim 0.6$ kOe) is lower. This is because 1.9 $\mu$A lies between $I_{c1}$ and $I_{c2}$ below 0.6 kOe [fig. 4.13].
Figure 4.14. (a) Resistance vs. magnetic field at different excitation currents. (b) Resistance vs. magnetic field in log scale.
The R-H curves measured at excitation currents lower than \( I_{c1}(H=0 \text{ Oe}) = 1.6 \mu\text{A} \) display one of the most interesting behavior. Fig. 4.14(b) shows that R-H curves measured at .01, 0.1, 0.5 and 1.0 \( \mu\text{A} \) collapse on each other for magnetic fields between 0 and 0.6 kOe. This indicates that the resistance is independent of current and hence “ohmic” with a value of 1 \( \Omega \). However, when the field is increased further, the resistance begins to drop reaching a minimum of 0.35 \( \Omega \) before showing a steep increase at the \( H^\text{Pb}_c \). This behavior is similar to the R-H curves measured at higher currents of 1.9, 3.0 and 4.0 \( \mu\text{A} \). The fact that a minimum in R is found over the same magnetic field range at such a low excitation current proves that \( H^d \), the field value at which R begins to drop, is an important characteristic field related to APE.

More interestingly, even though the R-T scans at low excitation current of 0.1 \( \mu\text{A} \) doesn’t show any signs of APE [fig. 4.11(b)], there are subtle signs of APE in ZNWs with Pb electrodes captured by V-I and R-H scans. However, the APE is very weak as the R changes only from 1 to 0.35 \( \Omega \) when Pb electrodes goes from superconducting to normal state. This is very small in value when compared to the huge change in resistances observed for Sn and In electrodes. A qualitative model of APE based solely on experimental observations will indicate its origin in the coupling of the superconducting order parameters of the bulk electrodes and the ZNWs. The \( H^d \) observed in the Pb/ZNWs/Pb system can be considered as a critical decoupling field. Above \( H^d \), the coupling between Pb electrodes and ZNWs becomes significantly weakened and the ZNWs become a more robust superconductor resulting in an enhanced \( I_c \) and lower resistance. So, Is \( H^d \) a universal feature of APE or just a special case for Pb/ZNWs/Pb system?

Additional measurements and analysis were done to resolve this issue about the decoupling field, \( H^d \). Some of the earlier measurements were re-analyzed to
look for $H^d$. For ex:- In sample Z5 with 2 $\mu$m long, 40 nm diameter ZNWs, complete suppression of superconductivity of ZNWs was observed. From fig. 4.10, R-H curves show an abrupt switching of R from suppressed state to superconducting state precisely, i.e. within 5 Oe, at the critical field of In electrodes without any evidence of a decoupling field, $H^d$. However, the evidence of a $H^d$ was found in sample Z4 with 6 $\mu$m long ZNWs exhibiting partial suppression of superconductivity. R-H curves measured with low excitation current of 10 nA at different temperatures are shown in fig. 4.15(a). An enlarged portion of R-H curves highlighting a narrower magnetic field region is shown in fig. 4.15(b). For $T < 0.7$ K, R-H scans of fig. 4.15 show a minimum just below the critical field of Indium at 0.27 kOe. Resistance begins to drop at a magnetic field of 0.25 kOe. If $H^d$ is assigned to be 0.25 kOe, then the magnetic field range corresponding to minimum in R in sample Z4 is many times narrower than that shown in fig. 4.14 for sample Z7. So, it is reasonable to speculate that every system exhibiting APE will have a magnetic field region between $H^d$ and $H_c$ where R will be minimum. In the particular case of complete suppression of superconductivity [figs. 4.7, 4.9], this region maybe so narrow that it cannot be detected with the limited resolution of our measurement system. The smallest step to change the magnetic field is 5 Oe. So, in the current measurement setup, it is not possible to measure a decoupling field region smaller than 5 Oe !!

4.4.3 Control Experiments

It should be noted that all the key experimental results reported in previous sections have been checked with multiple samples for reproducibility. However, there are still some concerns whether the observed Anti-Proximity effect is a real phe-
Figure 4.15. (a) Resistance vs. magnetic field at different excitation currents for sample Z4. (b) Magnified lower magnetic field region of plot (a).
nomenon related to the intrinsic behavior of dissipative low dimensional superconductors or an artifact of the experiments.

4.4.3.1 Interface resistances and Bulk electrodes

Since the phenomenon we are studying is the effect of the bulk electrodes on the ZNWs, there are always two BulkS/ZNW interfaces involved in all of the transport measurements. However, it is extremely unlikely that the interface resistances are responsible for the observed phenomenon. This is because in all the different experimental configurations with different bulkS described above, the interfaces resistances are considerably smaller than the actual finite resistance of the system at $H=0$ Oe, when BulkS are in superconducting state. Also, as seen in the case of 70 nm ZNWs with Sn electrodes [fig. 4.5], interface resistances between BulkS and ZNWs becomes negligible below the $T_c$ of BulkS.

To investigate the effect of interface resistances, an array of 40 nm ZNWs were measured with Sn electrodes (Sample Z8). In this case, after growing ZNWs into the PCM, membrane was left in air for 10-15 minutes. This is to allow the tip of ZNWs inside the PCM to get oxidized. Fig. 4.16 shows the $R$ vs. $T$ curves of sample Z8. As expected, the presence of oxide layer between ZNWs and BulkS resulted in higher interface resistance. Sample Z8 has a similar configuration as Z3 except a considerably higher interface resistance. There is no clear signature of APE in R-T curves, as was observed for sample Z3. But below 0.75 K, the resistance is slightly lower at 0.3 kOe as compared to that at zero field. This is probably the only evidence of APE in the R-T curves. However, the critical current, $I_c$, at 0.3 kOe is found to be higher than that at zero field; a weak signature similar to the one observed for sample Z7 with Pb electrodes. This implies that the APE becomes weaker with the high interface resistance between BulkS and ZNWs. This is in
agreement with the observation of Sample Z7 that there is coupling between BulkS and ZNWs. Coupling can be reduced either by applying external magnetic field or increasing interface resistance, BulkS/ZNWs.

In another control experiment, transport measurements have been made with different bulk electrodes on the two sides of membrane. Sample Z9 has a configuration of Ag/ZNWs/Sn were Ag and Sn were used as bulk electrodes. There is no obvious evidence of APE in the R-T curves as shown in fig. 4.17(a). But a clear signature of the effect, as in the cases of sample Z6 and Z7, was found in the V-I
Figure 4.17. Resistance vs. temperature of (a) Sample Z9 with bulk Ag and Sn electrodes (numbers indicate the magnetic field in kOe), and (b) Sample Z10 with Au electrodes (Arrow indicates the $T_c$ of ZNWs). Inset of (a) shows the V-I curves for sample Z9 at 0.47 K.
characteristics shown in the inset of fig. 4.17(a). The critical current, $I_c$, at $H = 0.3$ kOe, with Sn electrodes in normal state is higher than that at zero magnetic field. This shows that APE is present even when one of the electrodes is normal metal, however it becomes considerably weak. So, a logical next step would be to perform measurements on ZNWs attached to both normal electrodes. Fig. 4.17(b) shows the $R$ vs. $T$ dependence of sample Z10 containing 40 nm ZNWs attached to bulk Au electrodes. As expected, ZNWs always show superconducting transition with $T_c \sim 0.78$ K. The slightly lower $T_c$ than bulk Zn is due to the inverse proximity effect by normal Au electrodes on superconducting ZNWs.

All of the control experiments discussed above corroborate the observations from previous section that the BulkS are responsible for the suppression of superconductivity in 40 nm ZNWs. Also, the suppression effect, or APE, becomes weaker with decreasing coupling between BulkS and ZNWs.

4.4.3.2 Electrical Noise

Noises generated from electromagnetic environments are always a concern for electrical transport measurement of nanoscale systems. Superconducting nanowires are found to be extremely sensitive to their electromagnetic environments. Dissipations in superconducting nanowires can be altered by electromagnetic noises by influencing the phase-slips processes. Therefore, it is necessary to use low-noise measurement techniques equipped with sufficient filtering.

In our case, twisted-pair cables were used on all of the measurement leads coming out from PPMS sample chamber. Low-noise co-axial connectors and electrical leads were used. All electrical leads going through the measurement bridge were made to pass through room-temperature pi filters (purchased from www.newark.com). To estimate the impact of electrical noises on the transport
data, electrical measurements were done with and without the filters. Fig. 4.18

![Resistance vs. temperature of 40 nm ZNWs (length = 6 μm) with and without electrical filters.](image)

**Figure 4.18.** Resistance vs. temperature of 40 nm ZNWs (length = 6 μm) with and without electrical filters.

shows the R vs. T dependence of an array of ZNWs attached to Sn electrodes at two magnetic fields (blue and red symbols represent measurements done with and without filters, respectively). At H = 0 kOe, measurement without any filters shows a complete suppression of superconductivity in ZNWs whereas the one with filters show a very small and broad resistance drop around 1.0 K. Similarly, at H = 0.3 kOe, when electrodes are in normal state, measurements without filters shows a smaller resistance drop than with filters. Interestingly, in both the cases, there is suppression of superconductivity (or APE) in ZNWs. Also, the resistance drop
of ZNWs without superconducting electrodes (at 0.47 K) is bigger in case of filters indicating that APE is stronger when measurements are done with pi filters.

In conclusion, electrical noises do have some effects on measurements but they are not the reason behind the observation of APE.

4.5 Relevant Theoretical Models

Electrical transport measurements discussed above give a complete experimental picture of the Anti-Proximity effect observed in Zinc nanowires. However, an exact theoretical model elucidating the microscopic origin of APE is required to fully understand this novel phenomenon. In the following paragraphs, I'll discuss some theoretical models, which maybe relevant in understanding APE.

Buchler et al.[53] investigated the conductance and quantum fluctuations in a thin superconducting nanowire of finite length coupled to the environment through appropriate boundary conditions. The coupling between nanowire and the environment imposed a drastic change in the phase-slip dynamics while modifying the wire’s low energy physics. They found that the environment plays a crucial role on the conductance of the finite-size nanowire and modifies the phase diagram of the system at $T = 0$ K.

In this case, the disappearance of the superconductor to insulator quantum phase transition and its resurrection due to the wires coupling to its environment is characterized through the dimensionless shunt conductance $K = R_Q/R_P$, where $R_Q = 6.5$ kΩ is the quantum resistance in 1-dimensional system and $R_P$ is the shunt resistance which characterizes coupling of the environment to the nanowire. When $K < 1$ (i.e. $R_Q < R_P$), a nanowire of both, finite or infinite length, is in insulating/metallic state due to the proliferation of phase slips. In the case of $K > 1$, a
well conducting shunt relaxes the strain on nanowire leading to a superconducting state. In this case, quasi-long-range order and stiffness of superconducting order parameter survives at $T = 0$ K. In our system, the shunting resistance is always smaller than the quantum resistance which falls under the category of $K > 1$. This is because the resistance of an individual ZNW ($\sim 250 \, \Omega$), electrodes and the interfaces ($< 20 \, \Omega$) is small enough when compared with $R_Q$. So, even though this model highlights an important issue regarding the effect of environment on finite length nanowire, the observed APE cannot be explained using this approach.

Martin-Rodero et al.\cite{54, 55} developed a self-consistent theory consisting of a narrow superconducting channel coupled to two wider superconducting electrodes. In their model, wires of different lengths ($L$) were considered as a superconducting mesoscopic weak-link. Our system resembles the theoretical case of $L \gg \xi_0$. In this limit, the theory predicts the existence of a well-defined core region of length $\xi_0$ at the center of the channel between the electrodes where the superconducting order parameter is nearly zero at $T = 0$ K and the phase shows an abrupt change. In other words, there would be a phase-slip center at zero bias voltage. This phase slip center would lead to a very low value of critical current and a finite resistance at the core region. This model seems to be relevant to our observations in Pb/ZNWs/Pb system. However, there is no scope of complete destruction of superconductivity in the 1D channel within this model, similar to the ones observed in the Sn/ZNWs/Sn and In/ZNWs/In systems. The channel material in the model is same as the wider electrodes and the amplitude of the order parameter in the constriction was considered to be the same as its bulk value of the electrodes. It would be interesting to extend this model to a system where the narrow channel is made of a different material from the electrodes. This extended model may shed some light on the mystery of APE.
Recently, two theoretical groups have developed microscopic models based on our experimental data to explain some of the aspects of Anti-Proximity effect. I’ll discuss both of them in details in the next section.

4.5.1 Fu et al model

Fu et al. [56] developed a theory representing a superconducting nanowire coupled to various environments. This theory considered the boundary effect and phase-slip interactions in the presence of dissipative environment and suggested that the APE is due to the dissipation at the boundary between the ZNWs and the bulk electrodes.

When the nanowire of finite length is placed in a dissipation free environment, the ends of the wire can be mapped onto two parallel boundary lines that can screen the vortex-antivortex interaction of the superconducting order parameter and destroys the superconducting phase even at T = 0 K. When the ends of the wire are coupled to a dissipative environment (such as normal metal electrodes in our experiments), the screening becomes incomplete. As a result, for sufficiently large dissipation the superconducting phase of the wire is stabilized and the superconductivity is recovered. Because a quantum wire can undergo depairing when the phase fluctuation is severe, Fu et als model did not require the normal state resistance of a quantum wire exceeding the quantum resistance. This theory is qualitatively consistent with a number of the experimental observations. However, this model does not address the observation that the strength of APE is dependent on the materials of the bulk superconducting electrode.
4.5.2 Vodolazov model

This model is based on the argument that the phase-slips processes in quasi 1D superconducting nanowire analogous to the thermal fluctuations in a point-like Josephson junction with a finite capacitance [57]. It is known that an increase in the intrinsic dissipation $W$ in Josephson junctions ($W = V^2/R$) suppresses both quantum and thermal fluctuations. The author argued that magnetic field can enhance the critical currents of the phase slips processes in nanowires and intensifies the intrinsic dissipation. Similar to the case of Josephson junctions, it would lead to a suppression of rate of fluctuations and a decrease in the fluctuated resistance.

Time-dependent Ginzburg-Landau (TDGL) equation was used to describe the dynamics of absolute value of order parameter, $|\Delta|$ and the phase gradient of order parameter, $\nabla \phi$, in the phase slip center. These dynamics resulted in the estimation of critical currents, $I_{c1}$ and $I_{c2}$, in short nanowires with length $L \ll \lambda_Q$, where $\lambda_Q$ is the charge imbalance length. As discussed in chapter 2, there is a charge imbalance in phase slip center due to the generation of quasi-particles. The author discussed that an external magnetic field influences the critical currents by suppressing the order parameter in the bulk electrodes. Based on the experimental arrangement, the theoretical model assumed that the normal metal-superconductor (NS) boundary forms far from the ends of nanowire for $H \leq H_c^{bulk}$. On the other hand, NS boundary approaches the ends of nanowire for $H \geq H_c^{bulk}$, when bulk electrodes become normal.

So, for $H \geq H_c^{bulk}$, the conversion of normal current into supercurrent at the NS boundary leads to an additional charge imbalance, $Q_0$, at the ends of nanowire. This results in an increase of $I_{c1}$ with increasing $H$ because $Q_0$ changes from zero
to the maximum value when the NS boundary touches the ends of the nanowire. This can be understood from the relation of critical current of a nanowire of length $L$ to the charge imbalance given by eq. 4.2

\[
\frac{I_{c_1}(H, L)}{I_{c_1}(H = 0, L = \infty)} = \frac{-Q_0/Q_c + \cosh(L/2\lambda_Q)}{\sinh(L/2\lambda_Q)}
\] (4.2)

where $Q_c$ is the charge imbalance in phase slip center and $I_{c_1}(H = 0, L = \infty)$ is the critical current for an infinite length nanowire.

In essence, the characteristic length for the proposed mechanism is the decay length of charge imbalance, $\lambda_Q$. It means that the APE should exist only in condition of short nanowires with length $L \leq \lambda_Q$. For our ZNWs, $\lambda_Q$ is estimated to be 22 $\mu$m. This will explain why APE was observed to be weaker in sample Z6 with $L > 30$ $\mu$m. In a separate case, $\lambda_Q$ in Sn nanowires used in ref. [8] was estimated to be 750 nm. Since, lengths of the Sn nanowires were in the range 6-30 $\mu$m, it is not surprising that APE was not seen in those nanowires.

Also, another condition to be fulfilled is the diameter of the nanowire. Critical field for a wider nanowire, $H_c \sim 1/(\xi d)$ and a bulk superconductor, $H_c^{bulk}$ can become close to each other. This would lead to a strong suppression of $|\Delta|$ in the nanowire itself, and hence decrease in critical currents, $I_c$. This may explain why APE is observed in ZNWs with $d = 40$ nm $\sim \xi/4$ and not in wires with $d \geq 70$ nm $\sim \xi/2$ (The estimated coherence length for our ZNWs is 155 nm [58]). Also, in the proposed model, author assumed that the time relaxation of order parameter, $\tau_\delta$ and charge imbalance length, $\lambda_Q$, are independent of magnetic fields. This assumptions will be valid only for $H \ll H_c^{NW}$.

Vodolozov’s model has successfully addressed some of the most salient features of Anti-proximity effect observed in our experiments. However, the role of the
bulk superconducting electrodes is still unclear. It is worth mentioning that the ratio of the superconducting gap \(2\Delta\) to the transition temperature \(T_c\), \(2\Delta/kT_c\), of ZNWs is about 3.2. One interesting correlation regarding the materials of the electrodes and the strength of APE is that the value of \(2\Delta/kT_c\) is about 3.5 for Sn, 3.6 for In, and 4.3 for Pb. According to BCS theory [51], ratio, \(2\Delta/kT_c\), is related to the electron-phonon coupling in a superconductor. Thus, the strength of the APE qualitatively varies “inversely” with the strength of the electron-phonon interaction. As if now, there is no explanation for such a correlation.

4.6 Additional experiments

Till now, APE is only observed in 40 nm Zn nanowires. Due to the unavailability of suitable membranes with smaller pore diameters and length, we are not able to make measurements on smaller diameter ZNW with appropriate length. Also, one of the biggest concerns with the above results is that the measurements are done only in array of ZNWs inside the membranes. It would be good to repeat those measurements on individual freestanding nanowires. This is not possible in the current configuration since ZNW oxidize quickly, making these measurements almost impossible. So, we focused our attention on superconducting materials that do not oxidize easily and can be fabricated as crystalline nanowires. A natural candidate would be a superconducting inter-metallic compound.

Superconductivity of alloys and inter-metallic compounds is a subject of great interest due to their high critical fields and higher stability than elemental superconductors [59, 60]. We chose AuSn as the inter-metallic compound of interest because we can fabricate nanowires with good crystalline quality containing a single AuSn phase using our electrodeposition technique. Transport measurements
were done on array of NWs inside the membrane as well as four-probe measurements on a single NW [40]. At H = 0 Oe, system shows a small resistance drop at 7.2 K due to the superconducting transition of Pb electrodes. Resistance continue to decrease slowly as the temperature is lowered before exhibiting a much larger resistance drop at 1.5 K due to the transition of AuSn NWs and by 0.85 K the resistance is zero within the resolution of measurement. Increasing the applied magnetic field leads to a decrease in $T_c$ and becomes lower than 0.45 K at H = 6 kOe. The superconducting transition temperatures for the two stable phases of Au-Sn, AuSn and AuSn$_4$, were reported earlier to be around, 1.25 K and 2.4 K, respectively. Since, R-T curves showed only one resistance drop and the observed $T_c$ was closed to the value reported in literature, it is reasonable to assume that our nanowires contain single AuSn phase. Also, there was no sign of dissipation in these nanowires. It might be possible that these wires are too big in comparison to their coherence length.

To determine coherence length, R-H curves were measured at different temperatures as shown in fig. 4.19(b). At T = 0.47 K, the first small step around H = 0.98 kOe is due to the transition of Pb electrodes from superconducting to normal state. The resistance continue to increase with increasing magnetic field before saturating at around 6 kOe, the critical field, $H_c$ of the nanowires at 0.47 K. As expected, critical field decreases with increasing temperature. Fig. 4.19(a) shows the R-T curves of a 70 nm AuSn NWs array attached to Pb electrodes. Superconducting phase diagram for AuSn NWs was obtained by plotting the critical field values as a function of temperature, shown in the inset of figure 4.19(b). Using the empirical relation,

$$H_c(T) = H_c(0)[1 - \left(\frac{T}{T_c}\right)^2]$$

(4.3)
Figure 4.19. Transport measurements of a 70 nm AuSn NW array with Pb electrodes, (a) R vs. T at different magnetic fields, and (b) R vs. H at different temperatures. Inset shows (a) schematic of transport measurement, and (b) Critical field, $H_c$, as a function of temperature, solid line is a fit to eq. 4.3.
a good fit to the experimental data was obtained, as shown by the solid red line in the inset of fig. 4.19(b). Using Ginzburg-Landau theory and \( \frac{dH_c}{dT} = -0.63 \, T \, K^{-1} \) (for \( T \sim T_c \)), the superconducting coherence length, \( \xi \), was estimated to be 7.8 nm [51].

For comparison, four-probe measurement was done on individual AuSn NW. Four Pt-electrodes were made on a single, freestanding 70 nm AuSn NW using FIB technique described in section 3.3.2 of previous chapter. The SEM image of the nanowire with electrodes is shown in fig. 4.20(a).

The distance between two inner voltage probes was set to be 1.09 \( \mu \)m. R-T curve at zero magnetic field is shown in fig. 4.20(b). Extra care was taken for the measurement of single nanowires. To avoid any self-heating or damage to the nanowires, a very small excitation current of 10 nA was used for all measurements. The resistance shows a drop at 1.5 K before going to zero resistance around 0.6 K. This is in close agreement with the results of array of NWs, showing similar transition temperature of \( T_c \). Also, the critical field (inset of fig. 4.20(b)) is close to the value obtained in array measurements.

Since, diameter, \( d = 70 \) nm of AuSn NWs is bigger than estimated \( \xi \), it is not surprising that we did not observe any dissipative behavior. So, to observe any dissipation or a probable APE in these NWs, one needs to fabricate NWs with diameter less than 7.8 nm. This is not possible with our current method of fabrication. Even though the study of AuSn NWs didn’t solve the original purpose of observing APE, it proved to be the first comparison between the two prominent methods of performing electrical measurements in our lab. It also provides credibility to the process of making electrical contacts using FIB. As observed, the electrical transport measurements of superconducting NWs remain unchanged when going through the processing steps of FIB. After this study, numerous NWs
Figure 4.20. (a) SEM image of a 70 nm free-standing AuSn nanowires with four Pt electrodes, and (b) R vs. T at zero magnetic field. Inset shows R vs. H curve at T = 0.47 K

comprising of superconducting, metallic and magnetic, are routinely measured using the above four-probe configurations in our lab.
Hybrid Superconductor-Ferromagnet nanostructures

5.1 Introduction

This chapter will describe our efforts on the study of hybrid superconductor-ferromagnet (S-F) nanostructures. It includes fabrication, structural and magnetic characterizations and transport measurements on different S-F systems.

We observed magnetoresistance peaks in the transport measurements of ferromagnetic Ni nanowires attached to superconducting electrodes. A long-range proximity effect and resistance peak around $T_c$ was observed for Co and Ni nanowires in contact with a disordered superconductor, W, fabricated by FIB-assisted deposition. We have also successfully fabricated and measured transport properties of axially modulated nanowires containing alternate S and F segments.
5.2 Ferromagnetic nanowires attached to superconducting electrodes

5.2.1 Fabrication of magnetic nanowires

Nickel (Ni) and Cobalt (Co) were used as the ferromagnetic nanowires in our experiments. Nanowires are fabricated by electrodepositing Ni and Co inside the nano-sized channels of porous PCM and AAM. For Ni, electrolyte is an aqueous solution of 100 g/L NiSO$_4$, 30 g/L NiCl$_2$ and 40 g/L H$_3$BO$_3$ with pH=2.5 adjusted by 1M H$_2$SO$_4$ [61]. For Co, the electrolyte was made by adding 200 g/L CoSO$_4$, 40 g/L H$_3$BO$_3$ with pH=1.0 adjusted by 1M H$_2$SO$_4$ [62].

The nanowires were deposited using potentiostat PAR263A in a three-electrode assembly, with Pt as the counter electrode and Ag/AgCl as the reference electrode. Ni nanowires were deposited at a potential of $V = -1.0$ vs. Ag/AgCl, where Co nanowires were deposited at an higher potential of $V = -1.45$ V vs. Ag/AgCl.

5.2.2 Structural and Magnetic Characterizations

The growth orientation of Ni nanowires was characterized by X-Ray diffraction. Array of Ni nanowires embedded in PCM were used as samples for XRD measurements. Arrays with different diameter NWs were measured to observe diameter dependence of crystal structure. Fig. 5.1 shows the XRD spectra for arrays of 40 nm, 70 nm and 100 nm Ni NWs. Nanowires with different diameters and fabricated with same electrodeposition parameters show identical XRD spectra. [111] crystallographic axis was observed to be the preferred orientation for growth of Ni nanowires. XRD spectra for an array of 40 nm Co nanowires were already shown in fig. 3.4(b) and will not be reproduced here.
In comparison to Ni, Co nanowires show good single crystal structure with a strongly preferred growth orientation along the axis [110], indicated by a single large peak at 76°.

The morphologies of nanowires were studied with JEOL 2010F Field Emission Transmission Electron Microscope. Fig. 5.2(a) shows the low magnification TEM image of 40 nm Ni nanowires obtained by JEOL 2010F. Majority of nanowires were observed to be long and straight throughout their length. Figure 5.2(b) shows the magnified TEM image of 40 nm Ni nanowires. The image shows the Ni nanowires to be polycrystalline with little or no inhomogeneity in the diameter along the wire’s
Figure 5.2. TEM image of 40 nm Ni nanowires.
axis. Magnetization measurements were made with a Quantum Design SQUID on an array of 40 nm Ni nanowires embedded inside the polycarbonate membrane. The magnetic field direction is perpendicular to the axis of nanowires. Ni nanowires were observed to be ferromagnetic with a coercive field, $H_c=1.3$ kOe at $T=2.0$ K. The easy axis of magnetization is aligned along the axis of nanowires as a consequence of the magnetic shape anisotropy. The banana-shaped M-H loop, instead of a square one, is a common feature observed in the previous measurements of ferromagnetic nanowires with magnetic fields perpendicular to easy axis [63].

5.2.3 BulkS-FNW-BulkS

As described in previous chapter, we successfully used the quasi 4-probe measurements technique to investigate the influence of bulk superconductors on the superconducting properties of nanowires. This gave us an opportunity to study the spin-polarized transport in ferromagnetic nanowires in the presence of bulk superconductors. The main objective of experiments described in this section was to measure the electrical transport in 40 nm Ni nanowires attached to superconducting Sn electrodes. These measurements were carried out in a Physical Property Measurement System (Quantum Design Inc.) equipped with a dilution refrigerator option with a base temperature of 50 mK and a 9 T superconducting magnet. The schematic arrangement of the electrical transport measurements is similar to those used for superconducting nanowires. Specifically, an array of 40 nm Ni nanowire embedded inside the PCM was mechanically squeezed between bulk Sn wires (0.5 mm diameter, 99.99 % purity supplied by Alfa Aesar, Inc.). Bulk Sn wires act as the superconducting measurement electrodes. Since, BulkS were squeezed on to the both sides of PCM, the resulting interface BulkS/NW is parallel to the
NW’s axis. Also, due to their small diameter (40 nm), junctions formed by these nanowires can be considered as point contact junctions having cross-sectional area same as the NWs. This is better illustrated in the inset of figure 5.3(a). So, one channel of measurement consists of a Ni NW connected in series with two S-F point contact junctions and the overall measurement is done on multiple such channels connected in parallel. Here, we assumed that resistance contributions from bulk electrodes will be negligible \(\sim 0.4\Omega\).

Figure 5.3(b) shows the Resistance (R) Vs Temperature (T) plots for sample S1 consisting of an array of five 40 nm Ni nanowires sandwiched between bulk Sn electrodes [13]. R-T plots are measured at different excitation currents at two magnetic fields of 0.0 kOe and 0.3 kOe. At \(H=0.3\) kOe and \(I = 0.1\) \(\mu\)A, Sn electrodes are in normal state and sample resistance, \(R_N=272\) \(\Omega\) is found to be independent of temperature. At zero magnetic field with same excitation current, as the temperature is decreased, the sample resistance shows a drop near 3.7 K corresponding to the superconducting transition of Sn electrodes. The resistance decreases by nearly 27 \(\Omega\) out of the normal state resistance, \(R_N=272\) \(\Omega\). As, temperature keeps on decreasing, resistance reaches a minimum around 3.0 K, before increasing with further decrease in temperature. Since, the resistance of bulk Sn electrodes is less than an ohm, the 27 \(\Omega\) drop in R must have contributions from BulkS/Ni interfaces and possibly some parts of Ni nanowires due to the superconducting proximity effect. At a higher excitation current of 5 \(\mu\)A, the upturn in resistance is suppressed and the resistance becomes flat after the sharp drop at 3.7 K.

The observed behavior can be understood in the framework of ”Proximity Effect” due to Andreev Reflection and the so called ”Re-entrant Proximity Effect” [64]. The initial drop at the \(T_c\) of Sn electrodes and the subsequent decrease in
Figure 5.3. (a) Resistance vs. temperature plot of an array of 40 nm Ni NWs with Sn electrodes. Inset shows the schematic of Bulk Sn-Ni NW- Bulk Sn system. (b) R-T plot at lower temperatures.
resistance till 2.85 K can be explained by proximity effect due to superconducting Sn electrodes on the Ni NWs and the interfaces between them. The increase in resistance below 2.85 K is opposite to the normal behavior of proximity effect. However, similar behavior has been predicted and observed in S-N and S-F systems [13, 65].

Further analysis was done by performing V-I measurements. In figure 5.4, normalized differential conductance is plotted against voltage at different temperatures. Differential conductance values are obtained by taking numerical derivative,

\[ \frac{dI}{dV} \]

using software Origin 7.0. All the plots are normalized to the conductance

\[ G_n \]

Figure 5.4. Normalized conductance as a function of voltage for sample S1 at different temperatures.
value measured at $T = 4.0$ K (above $T_c$ of Sn), “normal state conductance”. At $T = .17$ K, the normalized conductance increases with increasing voltage, showed a peak around 0.7 mV and approaches normal state value 1 with the further increment in potential. As the temperature is increased, conductance peak becomes smaller and broader and eventually at $T = 3.5$ K, close to the $T_c$ of Sn electrodes, it becomes almost flat with no visible peak. Similar kind of behavior is observed before in numerous experiments utilizing point contact Andreev Reflection to estimate spin polarization of ferromagnetic thin films [20, 21]. In those experiments, conductance peak was observed exactly at the energy gap of the superconductor forming the S-F point contact. In our case, energy gap of Sn electrodes, $E_g$(Sn) = 0.55 meV whereas the peaks are observed at 0.7 mV.

This can be explained by the fact that our measurements always have a huge resistance of the Ni nanowire connected in series with the Sn-Ni point contact junctions. So, the total voltage drop is distributed between Sn-Ni junctions and Ni nanowires. Presence of a series resistance were observed to smear out the conductance peaks making it broader and shifting it to voltages higher than the energy gap of the superconductor [21]. These results suggest that in our experimental setup, we actually have point- contact junctions between bulk Sn electrodes and Ni nanowires. However, due to the presence of large series resistance of Ni nanowires, this cannot be used effectively for PCAR spectroscopy. If the length of the nanowires can be reduced, then this technique can prove to be a simple and effective method to measure spin polarization in ferromagnetic nanowires.

Figure 5.5(a) shows magnetoresistance (MR) measurements of the sample S1 at different temperatures at an excitation current of 5 $\mu$A. For the sake of clarity, MR measurements are only shown for three temperatures; 0.2 K, 3.0 K and 3.8 K. Prior to the MR measurements, a high magnetic field of -1.0 T was applied along the
Figure 5.5. (a) Resistance vs. magnetic field plot of sample S1 at different temperatures. (b) Magnified R-H plot at different temperatures and excitation currents.
axis of nanowires to saturate their magnetization. To account for the possible hysteretic behavior of magnetic Ni nanowires, all MR measurements were done by sweeping magnetic field from negative to positive, followed by positive to negative.

At T=0.2 K, the sharp jumps at +170 Oe and -180 Oe are due to the superconductor to normal transition of Sn electrodes when magnetic field is swept from negative to positive direction. In the field range where Sn electrodes are superconducting, we observe peaks in the resistance around 100 Oe as the magnetic field was swept in both the directions. The mismatch in the peak positions for the different direction of magnetic field is probably due to the magnetic hysteresis of Ni nanowires. The peak height is around 0.2-0.3 Ω which is very small. However, this is the effective resistance of 5 nanowires connected in parallel and thus the peak height for individual nanowire will be 1.0-1.5 Ω which is 3.7-5.5 % of the total resistance drop at $T_c$ of Sn. At a higher temperature, $T$=3.0 K, $H_c$ of Sn electrodes is reduced and hence peaks are observed at smaller values of magnetic field. Similar peaks are also observed when measurements are done at other excitation currents. Figure 5.5(b) shows the MR behavior measured at different excitation currents of 5 $\mu$A and 8 $\mu$A. Peaks height and position are observed to be similar for both excitation currents.

In contrast, no peaks were observed in measurements done at $T$=3.8 K, above the $T_c$ of Sn electrodes. Since, the direction of magnetic field is parallel to the axis of nanowire; magnetoresistance change due to AMR will be almost negligible [14]. This is the reason why there is no evident resistance change in resistance due to AMR at T=3.8 K. Since, the peaks are observed only when BulkS are superconducting, it is most likely that the phenomenon is due to the S/F junctions formed by bulk Sn electrodes and Ni nanowires.

In order to exclude the possibility that the observed phenomenon may be due
to collective behavior of multiple nanowires, measurements were carried out on a single Ni nanowire attached to superconducting electrodes. We used a dual-beam FEI Quanta 200 3D Focused Ion Beam (FIB)/Scanning Electron Microscope (SEM) system to make electrical contacts to individual Ni nanowire. Ion-beam induced deposition (IBID) in FIB was used to deposit superconducting strips of tungsten with $T_c = 5.0$ K [17]. Deposited tungsten is an amorphous compound containing W, C and Ga. Details about the process of making contacts with FIB is explained in chapter 3 of this thesis. Following the deposition parameters from reference [17], we fabricated superconducting W contacts on nanowires by IBID according to the schematic shown in figure 5.6(a). For the purpose of studying the S/F interface, a thick W strip (width=300 nm, length=3 µm, thickness=100 nm) was deposited on one end of the Ni nanowire to form a overlapping Ni/W interface. Four measurement electrodes allowing 4-probe measurement on Ni/W interface were fabricated. These 4 electrodes were then joined to the larger Au pads to make further connection to the sample stage. The SEM image of the actual device is shown in figure 5.6 (b). Since, IBID uses ion-beam for deposition; it etches out any oxide layer from the surface of nanowire resulting in a good ohmic contact.

Figure 5.6(c) shows the R vs. T plots for a single 40 nm Ni nanowire connected to superconducting W strip, at different magnetic fields. At $H=0.0$ kOe, a sharp drop in resistance is observed near $T = 4.6$ K marking the $T_c$ for the W strip. This drop is followed by a slow decrease in R extending down to 1.8 K. With increasing magnetic field, $T_c$ is pushed to lower values. Since the W strip deposited by FIB is not pure tungsten and is in the form of a thin film, its critical field, $H_c = 6$ T is observed to be much higher than that of pure bulk W ($H_c$ (bulk W) = 1 Oe). In contrast to measurements on array of nanowires, there was no re-entrant proximity
Figure 5.6. (a) Schematic of measurements on individual Ni nanowire. (b) SEM image of a single 40 nm Ni nanowire attached to W electrodes. (c) Resistance vs. temperature plots of Ni-W system at different magnetic fields.
effect observed down to 1.8 K. It is not surprising since the re-entrant proximity effect closely depends upon the interface resistance. Ion beam etching in the case of single wire measurement may lead to different interface resistances than that of array measurements. The temperature dependence for sample S2 was similar to the one observed for a four-probe measurement of a W-strip deposited under similar conditions with identical geometry.

Figure 5.7 shows the MR measurements at different temperatures of sample S2. The applied magnetic field is perpendicular to the nanowire. The top-most plot is measured at T=6.0 K, above the superconducting transition of W strip. It shows the typical anisotropic magnetoresistance (AMR) expected for Ni nanowire [14]. A negative MR is observed as the magnetic field is scanned in both directions. Since magnetic field is perpendicular to the wire, there is a clear AMR contribution indicated by the negative magnetoresistance. AMR % can be determined by the following equation:

\[
AMR \% = \frac{R_{\text{max}} - R_{\text{min}}}{R_{\text{min}}} \times 100
\]  

(5.1)

where, \(R_{\text{max}}\) is the maximum resistance at zero magnetic field and \(R_{\text{min}}\) is the minimum resistance at the saturation magnetic field. Using eq. 5.1, AMR is 0.25 % as compared to parallel field case of multi-wire measurements in figure 5.5(a). However, this value of AMR % is inaccurate because Ni nanowire is always measured in series with a highly resistive W strip. So, the actual AMR % of these Ni nanowires should be much higher than the above estimated value.

The bottom three plots are measured at temperatures when W strip is in superconducting state. At T=1.8 K, MR measurements showed peaks when magnetic field is scanned in both the directions. These peaks are qualitatively similar to the ones observed for the multi-wire measurements except that the peaks are observed
Figure 5.7. (a) Schematic of measurements on individual Ni nanowire. (b) Resistance vs. temperature plots of Ni-W system at different magnetic fields.
at different magnetic field values. In this case, peaks are observed around ±1.4 kOe. Similarly, at T=2.5 K peaks can be observed but at a slightly lower field value of ±1.1 kOe. At T=3.0 K, there are no clear peaks as the data is very noisy at these temperature at a lower excitation current of 0.1 µA. Magnetoresistance measurements were done at a number of other temperatures between 1.8 K and 6.0 K. For the sake of clarity, all of the data are not shown in this plot. However, a progressive reduction in the peak heights was observed with increasing temperature and the peaks disappeared in the noise around T=3.0 K, which is in contrast to multi-wire measurements. However, small negative magnetoresistance due to AMR is visible at T > 3.0 K.

Also, it is interesting to note that the peak in resistance due to AMR at H = 0.0 kOe and T= 6.0 K seems to develop into a dip as the temperature is decreased below the superconducting transition of W strip. In other words, the magnetoresistance in the low field region (±3 kOe) changes sign from negative to positive as the temperature is decreased from 6.0 K to 1.8 K. Giroud et al. [13] observed contrasting MR behavior in Co wire attached to Al wire. They observed AMR (i.e. a peak in resistance at zero magnetic field) in Co wire only when neighboring Al wire was superconducting. And there was no MR behavior above the $T_c$ of Al wire. However in our case, we do not see the typical MR behavior when W strip is in superconducting state.

From the above measurements, it appears that the observed peaks in the MR measurements of 40 nm Ni nanowires are influenced by the superconducting electrodes. The positions of MR peaks depend on the nature of superconducting electrodes rather than the intrinsic magnetic properties of Ni nanowires. For the multi-wire case, $H_c$ of Sn electrodes is 270 Oe and the peaks are observed around 100 Oe whereas in the single wire case, $H_c$ of W strip is 6 T with peaks observed
at 1.4 kOe. There is no obvious relationship between the critical field values and the positions of peaks.

Since, we used superconducting electrodes for the single nanowire measurements; there can be some concern about its influence on the properties of Ni/W interface. But, the separation between the voltage and current electrodes fabricated on Ni nanowire is around 2.25 µm. It is not possible for any superconducting correlations to penetrate for such a long distance in a ferromagnet like Ni. So, influences from the current carrying electrodes are unlikely to have an effect on the MR of the Ni/W interface.

We are not sure of the exact mechanism for the observation of MR peaks in Ni nanowires. However, it is very clear that the re-entrant proximity effect which shows strong excitation current dependent and observed only in Sn/Ni/Sn multi-junction array, is not related to the intrinsic nature of the S/F junction but the details of the interfaces (such as the interface quality or barrier height etc.). Recently, long-range proximity effects have been seen in strong ferromagnets e.g. Ni, Co [3, 4]. This has been attributed to the presence of long-range triplet component (LRTC) of superconducting order parameter along with usual singlet component [1]. It might be possible that the observed peaks are related to the competition between the LRTC and usual singlet components on the junction in the presence of externally applied magnetic field.

From the above results, it is clear that the MR peaks are a result of superconducting influence on the ferromagnetic nanowires. It would be interesting to study the proximity effect between ferromagnetic nanowire and FIB-deposited superconducting W.
5.2.4 Disordered Superconductor-Ferromagnetic NW

We have successfully used FIB deposited Pt and W to make electrical contacts to AuSn and Ni nanowires. In the results presented ahead, we have used FIB-deposited disordered superconductor W to make electrical contacts on Co and Ni nanowires. Four-probe measurements were done to exclude the contribution from the interfaces and to reveal the true nature of proximity effect, if any, in ferromagnetic nanowires.

5.2.4.1 Sample C1 with diameter = 80 nm and length = 1.5 µm

We used W strips as electrical contacts on ferromagnetic Co nanowires to measure electrical transport in a four-probe measurement. Fig. 5.8(a) shows the SEM image of sample C1 in which a free standing 80 nm Co nanowire is connected to four W electrodes. One point to note is that the all measurement electrodes are superconductors instead of normal metals used in conventional four-probe measurements. The distance between the inner two voltage electrodes is 1.5 µm. As mentioned in previous chapter, four probe measurements result in true electronic properties of nanowires without contributions from contact resistances. In this case, below $T_c(W)$ we can measure the proximity induced electrical properties of Co nanowire due to the superconducting W electrodes. Fig. 5.8(b) shows the R-T plots for the corresponding sample at different magnetic fields. At $H = 0$ T, as the temperature is lowered, a huge peak in resistance appeared around 5.2 K, the onset $T_c$ of W electrodes. The peak height is almost equal to the normal state resistance of 30 Ω with maximum value around $T_{max} = 4.4$ K. Below $T_{min} = 4.2$ K, resistance started to decrease gradually with decreasing temperature and reached a minimum of 15 Ω at 1.8 K, the lowest measured temperature. At higher magnetic fields, the $T_c(W)$
Figure 5.8. (a) SEM image of sample C1 with an individual Co nanowire connected to four W electrodes. (b) Resistance vs. temperature plots for sample C1 at different magnetic fields.
is pushed to lower temperatures and so does the peak position. Interestingly, peak heights get reduced with increasing magnetic field accompanied by considerable broadening. At $H = 7$ T, the onset $T_c$ is around 2.5 K but the peak has broadened beyond 1.8 K and hence not observed completely. This magnetic field values are similar to the magnetic field dependence of isolated W-strips measured separately in four-probe configuration.

There are two important aspects of the observed electrical properties of sample C1. First, resistance of Co nanowire decreased from a normal state value of 30 Ω to $\sim$15 Ω at 1.8 K; a drop of almost 50 % !!! Second, a huge resistance peak near the onset $T_c$ of superconducting W electrodes.

The large resistance drop below $T_{\text{min}}$ can only be understood in terms of long-range proximity effect between superconducting W electrodes and ferromagnetic Co nanowires. Long range proximity effect in S/F structures were observed previously in Ni/Al and Co/Al systems [66]. Origin of the resistance peak will be discussed later in the chapter.

To further explore the origin of resistance peak, magnetoresistance measurements were done at different temperatures. Magnetic field direction was perpendicular to the nanowire’s axis. Fig. 5.9 shows the R-H plots for sample C1 at different temperatures lower than the onset $T_c$ of W electrodes. At $T = 4.6$ K, R-H plot shows the usual AMR behavior expected for ferromagnetic Co nanowire in a perpendicular magnetic field. There is a negative magnetoresistance extending to the saturation field of around 2 T. Using eq. 5.1, AMR % was estimated to be 16 %. This value is considerably higher than the AMR values (typically $\sim$ 1 %) reported previously for Ni nanowires fabricated under similar conditions [66]. On the other hand, at $T_{\text{max}} = 4.4$ K, sample shows a huge negative MR contribution. The estimated AMR at this temperature is a huge value of 94 % !!!!! This unprece-
Figure 5.9. Magnetoresistance measurements for sample C1 at temperatures (a) below and (b) above the onset $T_c$ of W electrodes.
dented AMR values can be understood from fig. 5.8(b). Onset $T_c$ of W electrodes or in other words, the onset $T_c$ of induced superconducting correlations inside Co nanowire is around 5.2 K. So, true AMR contributions can only be estimated by MR measurements above 5.2 K. Fig. 5.9(b) shows the MR measurements done at 5.8 K. Magnetic field is scanned in both directions. AMR % at this temperature is estimated to be 0.8 %, which is a reasonable value expected for ferromagnetic nanowires.

Surprisingly, in fig. 5.9(a), for $T < T_{\text{min}} (= 4.2$ K), the single huge peak in MR measurements develops into two peaks on either side of magnetic field scan. With decreasing temperatures, peaks decrease in height, become wider and occur at higher magnetic field values. For the sake of clarity, we have only shown MR measurements at few temperatures. The evolution of single peak into double peaks was observed to be a smooth transition with temperature. Also, the low magnetic field regions at lower temperatures appear to be very different from higher temperature measurements. A magnified version of fig. 5.9(a), highlighting the low magnetic field regions is shown in fig. 5.10. The y-axis is broken into 2 parts to clearly show the difference between MR behaviors at higher and lower temperatures. The peak in MR at zero magnetic fields develops into a "dip" at lower temperatures. This behavior is similar to the one observed in the case of Ni nanowires attached to W electrodes (fig. 5.7(a)). A small positive magnetoresistance in the low field region is a common observation for a superconductor/non-superconductor systems. It has been observed in a similar geometry by J. Wang et al. [67] for Au nanowires connected to W electrodes.
5.2.4.2 Sample C2 with diameter = 45 nm and length = 750 nm

As discussed in previous sections, it has become clear that long-range proximity effect is possible in a ferromagnetic nanowire, contrary to the classical theory of proximity effect. So, the question arises is: *What is the nature of induced superconductivity in a ferromagnetic Co nanowire and where does it fit in the picture of classical proximity effect?* Sample C1 showed a 50% drop in resistance when cooled below the $T_c$ of W electrodes. The measurement was done on the Co nanowire with length 1.5 $\mu$m between the two voltage electrodes. To investigate the length dependence and to see whether we can achieve superconductivity in whole Co nanowire, we reduced the distance between the voltage electrodes.

We have made measurements on an individual 45 nm diameter Co nanowire.
Fig. 5.11(a) shows the SEM image of single Co nanowire with four W electrodes. In this case, the distance between voltage electrodes was reduced to 750 nm. Fig. 5.11(b) shows the R-T plots for sample C2 at different magnetic fields. The direction of magnetic field is perpendicular to the wire’s axis. R-T curves look very similar to the transport measurements done on superconducting nanowires described in chapter 4. In particular, at $H = 0$ T, sample C2 shows a big resistance drop near 4.2 K before going to zero at 3.5 K. At higher magnetic fields, $T_c$ is pushed to higher values. This is the usual characteristic of four-probe measurements on a superconducting nanowire.

Induced superconductivity in Co nanowire is further characterized by magnetoresistance measurements. Fig. 5.12(a) shows the R-H plots at different temperatures. The numbers indicate the temperature values for the corresponding curves. R-H plots of sample C2 resemble magnetic field dependence of superconducting nanowires. We can define two critical fields, upper ($H_{c2}$) and lower ($H_{c1}$) similar to the case of superconducting nanowires. Upper critical fields at lower temperatures are too large to measure in our case. So, we’ll concentrate on the lower critical fields, $H_{c1}$. For $T < 3.5$ K, transition from superconducting to normal state occurs at $H_{c1}$. Below $H_{c1}$, system is in zero-resistance state or “superconducting state”.

Fig. 5.12(b) shows the magnified version of R-H plots highlighting the lower resistance regions. It is interesting to note that below $H_{c1}$, there is a small magnetic field region in which system shows negative resistance. This is only observed for MR curves measured at 1.8 K, 2.3 K and 2.8 K. It is quite possible that at higher temperatures $H_{c1}$ is so small that there cannot exist a negative resistance region, similar to the ones at lower temperatures. A negative magnetoresistance leading to a “negative resistance state” below $H_{c1}$ was also observed in another samples.

R-T and R-H plots of sample C2 shows behavior qualitatively similar to the
Figure 5.11. (a) SEM image of sample C2 with 45 nm Co nanowire connected to four W electrodes. (b) Resistance vs. temperature plots for sample C2 at different perpendicular magnetic fields.
Figure 5.12. (a) Magnetoresistance measurements of sample C2 at different temperatures. Numbers indicate the temperature values for the corresponding curves. (b) Resistance vs. Magnetic field plots for sample C2 at different perpendicular magnetic fields.
ones usually observed for superconducting nanowires. Using data from fig. 5.12(a), lower critical field $H_{c1}$ is plotted against the temperature in fig. 5.13(a). Solid line is a fit to the empirical relation given by eq. 4.3. Lower critical field values for both parallel and perpendicular directions of magnetic field are plotted. As expected for the case of a superconducting nanowire, $H_{c1}$ for parallel field is almost double of the perpendicular field value. This is due to the demagnetization factor for the case of a long cylindrical geometry of nanowires [51].

Long range proximity effect observed in sample C1 is successfully reproduced in sample C2. Reducing the distance between the two voltage electrodes results in a zero-resistance state in sample C2. A ferromagnetic Co nanowire with a diameter = 45 nm and length of 750 nm acquired superconducting properties due to the proximity from neighboring superconducting W electrodes.

However, the most intriguing part of this result is the appearance of “negative resistance” states. Magnetoresistance measurements were also done for this sample as shown in fig. ??(b). At T=6 K, above the $T_c$ of W electrodes, sample shows only AMR from the Co nanowire. Using eq. 5.1, AMR ratio is estimated to be 1.3 %. For $T < T_c(W)$, sample shows zero resistance in the low magnetic field region, below corresponding $H_{c1}$. However, as magnetic field is increased, MR decreases showing a “dip” into negative resistance state. With increasing temperatures, dip occurs at lower magnetic field values.

5.2.5 Control Experiments

This section deals with the control experiments done in order to establish the exciting and interesting phenomena such as long-range proximity effect, resistance
Figure 5.13. (a) $H_{c1}$ vs. temperature plot for magnetic fields parallel and perpendicular to wire’s axis. (b) Voltage-Current plots for sample C2 at different perpendicular magnetic fields.
peak near $T_c$ and negative resistance state.

### 5.2.5.1 45 nm Co NW with Pt voltage electrodes

In the previous sections, we have shown electrical measurements done on single Co nanowire attached to superconducting electrodes. All four electrodes, including 2 current and 2 voltage, were fabricated by FIB-deposited superconducting W strip. There is always concern about using superconductors as the voltage probes. One of the reason is the possible contribution from the charge imbalance effects of the superconducting probe influencing the transport properties of nanowire [68]. So, we decided to measure the electrical properties of our Co nanowires using FIB-deposited Pt as the voltage probes. Fig. 5.14(a) shows the SEM image of sample C3 involving a 45 nm Co nanowire with inner Pt electrodes as voltage probes and outer W electrodes as current probes. The distance between voltage electrodes is 2.34 $\mu$m. Everything else is kept same as in the previous samples. Sample C3 displayed good metallic behavior from room temperature down to 20 K, i.e. resistance decreases linearly with temperature.

Fig. 5.14(b) shows the R-T plots of sample C3 at different magnetic fields applied perpendicular to nanowire’s axis. Temperature is plotted in log scale for the sake of clarity. At $H = 0$ T, resistance decreases very slowly with temperature. Around 4.2 K, a small resistance peak appeared looking similar to the resistance peaks at the onset $T_c$ of W electrodes observed in previous samples. The resistance started to decline gradually as the temperature is lowered further. There is a small enhancement in resistance around 2.4 K. Qualitatively similar behavior is observed at higher magnetic fields. However, as the magnetic field is increased, the resistance peak decreased in height and occurred at lower temperatures.

Current carrying superconducting W electrodes are 5.85 $\mu$m apart and there is
Figure 5.14. (a) SEM image of sample C3 with a 45 nm Co nanowire attached to Pt and W electrodes. (b) R-T plots for sample C3 at different perpendicular magnetic fields.
more than 1 µm distance between adjacent current and voltage probes. Also, it is not a coincidence that the resistance peaks appeared at the temperatures closely related to the $T_c$ of superconducting W electrodes. This suggests the influence of W electrodes on electrical properties of Co nanowire. The change in resistance due to induced-superconductivity is very small because the superconducting electrodes are very far from the measured section of Co nanowire. Also, our measurement structure is not symmetric i.e. electrodes are not fabricated symmetrically on Co nanowire. The top W electrode is much closer to the adjacent voltage electrode than the lower one. So, it may be possible that the small proximity effect observed in this sample originate solely from the top current carrying W electrode. The small enhancement in resistance at low temperatures may be due to the weak-localization effects in thin ferromagnetic Co nanowire [12].

The proximity effect is expected to enhance by adding extra superconducting reservoir close to the nanowire. So, we took the same sample C3 and fabricated an additional W strip on Co nanowire in between the voltage electrodes. Fig. 5.15(a) shows the R-T plots for the modified sample C3* at different perpendicular magnetic fields. When compared with the original sample C3 shown in fig. 5.14, there is a considerable proximity effect observed in the modified sample C3*. At $H= 0$ T, resistance shows an enhancement around 5 K which develops into a broad peak before a gradual decrease down to 1.8 K. The R-T behavior at zero magnetic field is qualitatively similar to the ones observed for sample C1. However, the resistance peak for sample C3* is very broad. The sample showed a resistance drop from a normal state value of 180 Ω to 117 Ω at 1.8 K. As expected, proximity effect is enhanced with the addition of an extra superconducting W strip. In addition, the resistance peak at the onset $T_c$ (W) also increased in height but becomes broader.
Figure 5.15. (a) R-T plots for modified sample C3* with a 45 nm Co nanowire attached to Pt and W electrodes. (b) R-H plots for modified sample C3* at different temperatures.
R-H measurements for the modified sample C3* at different temperatures is shown in fig. 5.15(b). Similar to the magnetoresistance measurements of sample C1, we observed MR peaks in both direction of magnetic field. As the temperature is increased, the peaks became smaller in height and occurred at lower magnetic fields. These results suggest that the observed resistance peak at the onset $T_c(W)$ and the long-range proximity effect may be related. Next section deals with a similar geometry with 50 nm Ni nanowire.

5.2.5.2 75 nm Ni NW with Pt and W electrodes

Another aspect to consider for the above results is the nature of superconducting W electrodes. Since, W strips are fabricated by FIB-assisted deposition, there is always some concerns regarding the exposure to the ion-beam or $Ga^+$ ion implantation. Another consideration would be to determine the true nature of proximity effect and if it can also be seen in other ferromagnetic nanowires. This can be done by using four non-superconducting strips as the measurement electrodes and one non-measurement W strip as the proximity source. In this way, proximity effect can only by induced by the middle W strip and hence will be easier to account for.

Fig. 5.16(a) shows the SEM image of a 75 nm Ni nanowire contacted by Pt electrodes in a 4-probe geometry. An additional W-strip was deposited in between the inner voltage electrodes. Fig. 5.16(b) shows the R-T curves for sample C4 at different perpendicular magnetic fields. The resistance shows a big drop at $T_c = 5$ K, denoted by the arrow. The resistance gradually decreased as the temperature is lowered and becomes flat below 2.5 K. At higher magnetic fields, similar behavior is observed along with the reduction of $T_c$. There is a total drop of 35 Ω out of the normal state value of 80 Ω. So, the long-range proximity effect observed in Co nanowires was also reproduced similarly in Ni nanowires. The surprising fact is
Figure 5.16. (a) SEM image of sample C4 with a 75 nm Ni nanowire attached to four Pt electrodes and a middle W strip. (b) R-T plots for sample C4 at different perpendicular magnetic fields.
that there was no resistance peak at the onset $T_c(W)$ in the case of Ni nanowires.

Since, there was no resistance peak, it would be interesting to see how MR measurements will look different from the case of Co nanowires. Fig. 5.17 shows

![Figure 5.17. R-T plots at different magnetic fields for sample C4.](image)

the R-H plots for sample C4 at different temperatures. At $T = 6.0$ K, above the $T_c$ (W), there is no proximity effect. Hence, R-H measurements show the expected AMR effect in perpendicular magnetic field. This was very similar to the R-H measurements on Ni-W system shown in fig. 5.7. At lower temperatures, there are still contributions from the AMR effect. However, due to the absence of resistance peak at onset $T_c(W)$, there are no peaks in the MR measurements. AMR contributions from Ni nanowire changed below the superconducting transition of W strip. We do not have a clear explanation for that behavior. However, there is a clear long-range proximity effect in Ni nanowires but no resistance peak on the
onset $T_c(W)$.

5.2.5.3 S/F cross junctions

Interface resistances are always important in the study of hybrid systems. It becomes even more important at the nanoscale and can play a crucial role in determining the electronic properties of nanostructures. In this section, I’ll describe the measurements done exclusively on the interface between Ni nanowire and W strip. Deposition conditions for W-strip were kept same as that used for making electrodes on nanowires in samples C1-C4.

Fig. 5.18(a) shows the schematics for the transport measurements of Ni-W interface. W-strip is denoted by “ab” and Ni nanowire is denoted by “cd”. Electrical current is passed through the segment “ad” and voltage is measured between “cb”. In the path “cb”, current is flowed only through the Ni-W interface. So, the voltage drop across “cb” gives the true voltage across the interface. Fig. 5.18(b) shows the SEM image of sample C5 showing the cross junction geometry between a 75 nm Ni nanowire and a 200 nm wide W strip. Since, the nanowire and W strip are not exactly perpendicular to each other, the interface is not rectangular. Fig. 5.18(c) shows the R-T plots for the cross-junction at different perpendicular magnetic fields. The resistance measured in this manner is the total resistance of the Ni-W interface. At $H = 0$ T, the resistance showed a small enhancement around 5 K which looks more like a hump. At 3.7 K, resistance showed a big drop and reached a negative resistance of -1.1 $\Omega$. As the temperature is lowered, resistance started to increase at 3.4 K and reached a value of -0.5 $\Omega$ at 1.9 K. This enhancement looks very similar to the re-entrant proximity effect observed for Ni nanowires attached to superconducting Sn electrodes in fig. ref:40ni. At higher magnetic fields, $T_c$ is pushed to lower values and becomes lower than 1.9 K at a
Figure 5.18. (a) Schematic of the transport measurements of Ni-W interface. (b) SEM image of sample C5 with a 75 nm Ni nanowire forming a cross junction with a 200 nm wide W-strip. (c) R-T plots for cross-junction sample C5 at different perpendicular magnetic fields.
magnetic field of 4 T. The small resistance jump between 2.5 - 3.0 K at \( H = 0.25 \) T curve cannot be explained by previously observed phenomenon.

Fig. 5.19(a) shows the magnified plot near the onset \( T_c \) of W strip. The resistance peaks showed similar behavior as the previous samples C1-C4. However, the peak height increased with the increase in magnetic field, which is in contrast to the previous measurements. Magnetoresistance measurements is shown in fig. 5.19(b). Above the \( T_c \) of W strip, Ni nanowire show the expected AMR effect and is not shown in the figure here. Inset shows the R-H plot at \( T = 1.9 \) K. It shows the superconducting to normal transition of W strip with a lower critical field, \( H_{c1} = 0.75 \) T and a upper critical field, \( H_{c2} \sim 3 \) T. MR measurements showed symmetric peaks in the lower magnetic field region (± 1 T). Peaks were observed in both direction of magnetic field and were reproducible after repeated magnetic field scans. There was no obvious periodicity of the observed peaks. Negative MR contributions from AMR effect can be still seen as the bigger envelope to the peaks. Other interesting point is that all the peaks are observed in the negative resistance region. The observed negative resistance may have the same origin as the negative resistances observed in previous sample C2.

### 5.2.5.4 W electrodes on Co and Ni nanowire

One of the biggest concern regarding FIB-assisted deposition of nanostructures is the spread or diffusion of W (or Pt) on the nanowire during fabrication process [69]. We characterized this diffusion using analytical techniques of STEM and EDX spectroscopy. TEM samples were prepared by dispersing nanowires on a TEM grid. The usual TEM grid with lacey-carbon coating gets damaged by the high energetic ion beam (30 keV) of FIB. A special grid, SPI Supplies Brand Silicon Nitride membrane window grids for TEM, was used for this process [41]. Fig.
Figure 5.19. (a) Magnified R-T plots of sample C5 (b) R-H plots for cross-junction sample C5. Inset shows R-H measurements for a broader range of magnetic field.
Figure 5.20. (a) SEM image of a Si$_3$N$_4$ membrane TEM grid, (b) STEM image of a W strip across a 75 nm Ni nanowire. (c) EDX spectrum from a section of Ni nanowire close to W strip and marked with a red circle. (d) Line-profile measurements of W diffusion on Ni nanowire.
5.20(a) shows the SEM image of TEM grid with membrane window thickness of 100 nm $\text{Si}_3\text{N}_4$ and surrounding silicon support of 200 $\mu$m. Nanowires are dispersed on TEM grid with same process used for FIB processing discussed in chapter 3. Nanowires are located with SEM in FIB and a W strip was fabricated across it.

Fig. 5.20(b) shows the STEM image of Ni nanowire with a W strip in a cross geometry. A small section on Ni nanowire close to W strip is marked with a red circle. Fig. 5.20(c) shows the elemental composition obtained using EDX spectrum from the section of Ni nanowire denoted by red circle. EDX spectrum clearly shows that there is no W present in the Ni nanowire. A line-profile elemental composition was measured across the Ni nanowire along the red line depicted in fig. 5.20(b). Line profile is shown in fig. 5.20(d) mapping out the elemental profile of Ni and W. The line profile of W can be approximated to be a Gaussian curve. The total spread of W can be estimated to be 400 nm. So, it can be safely assumed that W spreads 200 nm on either sides of the nanowire. However, even though the W can spread 200 nm into the nanowires, it may not be conducting all the way. So, actual influence of W on the electrical properties of nanowires may turn out be smaller than 200 nm.

5.3 Axially modulated S-F nanowires

Previous sections described some very interesting and novel phenomenon in the case of ferromagnetic nanowires attached to superconducting electrodes. However, in all of the previous experiments the contacts between superconductor and ferromagnet were fabricated after the synthesis of nanowires. This was done by either mechanically squeezing bulk superconducting electrodes or fabricating FIB-assisted W strips.
It may be interesting to develop a method for fabricating in-situ superconducting contacts on our ferromagnetic nanowires. One of the promising methods is to fabricate axially modulated nanowires with alternating segments of superconductor and ferromagnet. There have been numerous studies on the multilayer structures involving superconductors, ferromagnets and normal metals. Electrochemical deposition has been used successfully to fabricate multilayered nanowires of alternating Superconductor-Normal metal \cite{7} and Ferromagnet-Normal metal \cite{70, 71, 72, 73} nanowires. With our current fabrication scheme, electrochemical deposition is the obvious choice.

However, the constituent metals should not diffuse a lot into each other. If the diffusion is strong, it may lead to the formation of alloys at the interface and can drastically alter the electrical properties of the nanostructure. For ex- Tin (Sn) is not a good candidate because it can easily diffuse into neighboring metal resulting in alloy formation. Tian et al \cite{74} carefully studied the diffusion of Sn into Au and the formation of AuSn alloys at the interfaces. This potential problem limits the choice of the superconductor and ferromagnet, which can be used for fabricating axially modulated nanowires.

In our lab, we have successfully fabricated superconducting nanowires of Sn, In, Zn and Pb. The available ferromagnetic materials are Ni and Co. Among the available superconductors, Sn and In are easy to diffuse and readily form alloys with other materials. Zn is a good choice but it has a lower $T_c$ of 0.9 K which makes the measurement possible only in a 3-He cryostat or a dilution refrigerator. Pb has the advantage of having a higher $T_c = 7.2$ K and a higher $H_c$ of around 1 T (for nanowires with diameter = 70 nm). This critical field is comparable to the saturation magnetic field for ferromagnetic nanowires like Ni and Co. Also, we can reliably fabricate good quality single crystal Pb nanowires. So, the possible
candidates for axially modulated nanowires are either Pb-Ni or Pb-Co. We chose Pb-Ni for our experiments.

5.3.1 Fabrication

There are two main methods to achieve multi-layered structures using electrochemistry. First method uses a single electrolyte containing salts of both constituent metals. Since, every metal has a different standard electrode potential, it can be reduced selectively at the corresponding potential. One of the main advantages of this method is that it can used to fabricate multilayers with thicknesses of individual layer as small as a few nm. This method requires constituent metals to have electrode potentials far apart in the electrode potential series to achieve sharp interfaces between adjacent layers. In our case, standard electrode potentials for Pb and Ni are respectively -0.13 V and -0.25 V relative to the standard hydrogen electrode. Since the electrode potentials of Pb and Ni are very close to each other, it’ll be difficult to achieve good interfaces between individual layers using the single electrolyte method. So, we have used the second method for fabricating the axially modulated nanowires.

The second method utilizes two separate electrolytes or bath for each constituent metal. The individual layers are deposited by corresponding electrolyte. After one layer is done, electrolyte is replaced with another one for the second layer deposition. In between the exchange of electrolytes, electrochemical cell was thoroughly cleaned with de-ionized water. Since, this method requires the physical exchange of electrolytes along with through cleaning, it is a very slow process. Hence, dual-bath technique is not suitable for making axially modulated nanowires with large number of segments. However, it can serve our purpose of studying S-F
and S-F-S junctions, as it requires only 2-3 segments.

Electrolyte for Pb deposition was prepared by mixing 10mM Pb(NO\textsubscript{3})\textsubscript{2} and 0.1M H\textsubscript{3}BO\textsubscript{3} with water. The pH of the solution was adjusted to 2 by using 1M H\textsubscript{2}SO\textsubscript{4}. Ni is deposited by an aqueous solution containing 0.4 M Ni(SO\textsubscript{3}NH\textsubscript{2})\textsubscript{2} and 0.1 M H\textsubscript{3}BO\textsubscript{3}. Electrodeposition potential for Pb was -0.7 V vs. Ag/AgCl reference electrode whereas Ni was electrodeposited at -1.0 V vs. Ag/AgCl. Fig. 5.21 shows the current-time plot measured during the electrochemical deposition of 75 nm axially modulated nanowires containing alternating segments of Pb and Ni. There are 3 segments of Pb and 2 segments of Ni in this sample.

According to Faraday’s Law of Electrolysis, the mass of a substance deposited at an electrode during electrochemical reaction is directly proportional to the amount of electricity or electrical charge transferred to that electrode [75]. Mathematically, it can be represented as

\[ m = \frac{QM}{nF} = \frac{M}{nF} \int I dt \]

where \( m \) = mass of the substance deposited at the electrode, \( Q \) = the total electric charge passed through the electrode, \( I \) = electrical current, \( F = 96485\ \text{C mol}^{-1} \) is the Faraday’s constant, \( M \) = molar mass of the substance and \( n \) = no. of electrons exchange or the valence no. of ions.

Since, the cross-sectional area of individual pores and the density of depositing metal are fixed, length of the deposited nanowire will be directly proportional to its mass. Using eq. 5.2, amount of charge transferred will be proportional to the length of the deposited nanowire. So, by monitoring the electrical charge during deposition we can control the length of each segment in a axially modulated nanowire. The electrical charge transferred can be calculated by integrating electric current over the period of time. For ex:- in fig. 5.21, for the first Pb segment, charge
transferred, $Q_{Pb} = 302 \text{ mC}$. Also, the charge transferred for Ni deposition, $Q_{Ni} = 280 \text{ mC}$.

In most of the electrodeposition, efficiency of current is not 100%. This means that the amount of mass actually deposited for a particular amount of charge may not be equal to the theoretical value. The actual length of each segments by determined by structural characterizations with TEM. The current efficiency of the process was determined by comparing the actual length determined from TEM and theoretical value estimated from eq. 5.2. This helped in calibrating the
process and determining the approximate length for the nanowires.

5.3.2 Structural and Magnetic Characterizations

Conventional TEM is a very powerful technique, which can offer nm-scale spatial resolution. However, with relatively better image contrast and a sharp electron probe scanning the sample pixel by pixel, Scanning TEM or STEM offers a unique advantage to study nanoscale multilayer systems. Most of the current TEM are equipped with a scanning unit. Besides an imaging of the nanostructure by different contrast techniques, emitted X-rays are also used as analytical signals. By means of an EDX spectrometer, elemental distributions of sample can be obtained.

In an Annular dark field- STEM or ADF-STEM technique, the central beam and all electrons scattered up to a certain semi-angle are excluded from imaging an annular objective aperture [76]. In this manner, the traditional high-resolution TEM image contrast is suppressed and a mass-thickness contrast is generated that depends exponentially on the sample thickness. Also, ADF-STEM is a chemically sensitive technique because of a Z-contrast. A heavier material (one with larger atomic number or Z) appears with higher intensity compared to a lighter material.

Fig. 5.22 shows the ADF-STEM image of a 75 nm axially modulated Ni-Pb nanowire. The different segments appear with different intensity and one can clearly see the four segments in the nanowire. Since, Pb has a larger atomic number (Z) than Ni, it appears brighter in the image. The two Pb-Ni interface is marked as “1” and “2” in the figure. Each length segments has different length because they are deposited for different electrical charge.

Energy dispersive X-ray (EDX) spectrometry was used to investigate the diffusion of elements across the interface. Fig. 5.23 shows the EDX spectra from the
Figure 5.22. (a) Annular Dark field STEM image of a 75 nm axially modulated Ni-Pb nanowire.

areas close to either side of interface “1” from fig. 5.22. Fig. 5.23(a) shows the spectra from the top of the interface in the Ni-rich region. As can be seen, most of the peaks correspond to Ni. Additional peaks related to C and Cu originated from the lacey-carbon coated copper TEM grid. Similarly, fig. 5.23(b) shows the corresponding EDX spectra from Pb-rich region. From both spectra, it is clear that there is not much diffusion of one element into another across the interface. Also, the dual-bath technique for electrodeposition doesn’t result in contamination of individual layers with other element.
Figure 5.23. Energy Dispersive X-ray spectra from (a) Ni segment and (b) Pb segment of axially modulated 75 nm Ni-Pb nanowire.
To further characterize the interface, a scanning electron probe was used to scan across the interface “2” shown in fig. 5.22. Fig. 5.24(a) shows the magnified ADF-STEM image of interface “2”. There is an oxide layer on the surface of Pb segment. Also, the Pb segment looks a little thicker (∼3-5 nm) than the Ni one. However, the interface looks sharp from the image. Scanning was performed along the red line across the interface “2”. The blue arrow defined interface. Fig. 5.24(b) shows the line-profile measurements of the interface “2”. Total scanned length is around 120 nm across the interface. Blue arrow indicates the interface position. The intensity of the emitted X-ray is proportional to the elemental composition. However, it is not a quantitative result. On the left hand side of arrow, there is a Ni-rich region, denoted by the intensity of Ni-K X-ray. Right hand side is predominantly Pb., denoted by the intensity of Pb-L X-ray. The region from 50 nm to 80 nm has some mixed composition. So, the interface is not so sharp as it looked from the image shown in fig. 5.24. The inter-diffusion region can be considered as 30 nm.

Similar, to the pure ferromagnetic nanowires discussed in section 5.2.2, magnetization measurements on axially modulated nanowires were done with Quantum Design MPMS. Fig. 5.25(a) shows the magnetization vs. temperature plot for an array of 75 nm axially modulated Ni-Pb nanowires. Each nanowire consists of alternating segments of Pb (L = 500 nm) and Ni (L = 250 nm) with total length of 20 µm. At T= 7.2 K, there is a drop in magnetization due to the superconducting transition of Pb segments. Due to the Meissner effect, superconducting Pb shows diamagnetic behavior. Magnetic field is applied parallel to wire’s axis. The M-T plot was measured during field cooling with a field of 100 Oe. This shows the superconducting characteristics of the nanowires.

Fig. 5.25(b) shows the M-H loop for the array of nanowires below and above the
Figure 5.24. (a) Magnified ADF-STEM image of interface “2” from fig. 5.22. (b) Line-profile measurement of Ni-Pb interface showing the elemental composition of Ni and Pb.
Figure 5.25. (a) Magnetization- Temperature plot of an array of 75 nm axially modulated Ni-Pb nanowires in field cooling with 100 Oe. (b) M-H loop for the array. Magnetic field is applied parallel to nanowire’s axis.
$T_c$ of Pb. The curves measured at 1.8 K and 8.0 K collapse on each other in the low magnetic field region. Only difference is in the high magnetic field region which is due to the diamagnetic behavior of Pb segments in superconducting state at $T = 1.8$ K. The coercive field, $H_c$(Ni-Pb) was measured to be 860 Oe. In a separate measurement, an array of pure Ni nanowire with similar physical characteristics (diameter = 75 nm and length = 20 $\mu$m) was measured for magnetization. The coercive field for pure Ni nanowire, $H_c$(Ni) was found to be 740 Oe. It seems that the presence of Pb segments doesn’t affect the magnetic properties of Ni segments. This may not be surprising because the individual segments are very long ( $> 100$ nm) in our case and hence are very robust. Nevertheless, magnetization measurements confirm that our axially modulated Ni-Pb nanowires have superconducting properties of Pb and ferromagnetic properties of Ni. Hence, they are promising hybrid superconductor-ferromagnet nanostructures to study the interaction between competing spin orderings.

### 5.3.3 Electrical Measurements

Electrical measurements were done on array of nanowires with the quasi 4-probe technique described in chapter 3. However, in some cases bulk normal-metal wire like silver (Ag) were also used as the measurement electrodes instead of superconductors.

#### 5.3.3.1 Array of SFS junction with normal-metal electrode

Fig. 5.26(a) shows the R-T plots of an array of 70 nm Pb-Ni-Pb nanowires sandwiched Ag electrodes. In this sample, a 100 ($\pm$ 20) nm long Ni segment was deposited between Pb segments making a Pb-Ni-Pb junction of total length 6 $\mu$m.
Figure 5.26. (a) R-T plots of 70 nm Pb-Ni-Pb with bulk Ag electrodes at zero magnetic field. (b) Critical current vs. magnetic field plot measured at $T = 1.8$ K.
The junction is, however, not symmetric as one Pb part may be longer than the other. R-T plot was measured at zero magnetic field. The resistance showed a big drop at T = 7.2 K due to the superconducting transition of Pb segments of nanowires. Since, we are using Ag electrodes, there is always contact resistances measured in the series. Hence, there is a large finite resistance even at the lowest temperature of 1.8 K. Since, there is only one resistance drop, it can be concluded there is no separate superconducting transition due to the S-F-S junction in our system.

There is a slight enhancement in resistance in the low temperature region with a minima around T = 3.84 K. This may be due to the spin-polarized Andreev Reflection at the Pb/Ni interfaces. Similar enhancement was seen in the case of Ni nanowires sandwiched between bulk Sn electrodes. Magnetoresistance measurements showed the obvious AMR contributions from Ni nanowires and magnetic field dependence of superconducting Pb. However, interesting properties were observed in the V-I measurements.

Fig. 5.26(b) shows I_c-H plot for the S-F-S junction. Magnetic field is applied parallel to the wire’s axis. The critical current, I_c, values are estimated from the V-I characteristics at different magnetic fields. The jump in voltage from superconducting to normal state is defined as the critical current. I_c-H shows behavior qualitatively similar to the ones observed for Josephson junctions in magnetic fields. Ideally, for a circular Josephson junction critical current shows oscillation in the form of Airy diffraction pattern. This is analogous to the diffraction of light passing through a circular aperture. Oscillation of critical current with magnetic field observed in fig. 5.26(b) is usually an indicator of a good quality junction. The observed dependence is not a good fit to the Airy pattern. One possible reason may be the non-ideal interfaces between Pb and Ni segments.
We do not observe any oscillation of critical current with temperature, a signature of $\pi$ junctions observed in previously in mesoscopic S-F-S junctions. This can be easily explained from the fact that our junctions are far too big. For hard ferromagnetic materials like Ni, the junction width should be on the order of few nm. However, it is promising that we can achieve a decent quality SFS junction with our simple fabrication process.

5.3.3.2 Array of SFS junctions with BulkS electrodes

In this section, I’ll describe the measurements on a similar geometry SFS junctions as shown in fig. 5.26. However, in this case, bulk superconducting Pb electrodes were used as the measurement electrodes. So, in this sample, array of Pb-Ni-Pb junctions were attached to Pb electrodes forming a BulkPb-Pb-Ni-Pb-BulkPb system. This configuration is similar to the one employed for the measurements of Zn nanowires (Chapter 4) and Ni nanowires (current chapter). BulkS should get rid of the contact resistances from the electrical measurements as before. Fig. 5.27 shows the R-T plots of an array of 70 nm Pb-Ni(100 nm)-Pb junctions sandwiched between Pb electrodes at different magnetic fields. Magnetic field is applied parallel to the wire’s axis. At $H = 0$ kOe, system shows a large resistance drop at $T = 7.2$ K. This will include the superconducting transition of bulk Pb, Pb nanowires and the interfaces between them. Resistance dropped from a normal state value of 270 $\Omega$ to a low temperature value of $\sim 12$ $\Omega$. Even though we used superconducting electrodes, system did not reach the zero-resistance state. Since, this technique of quasi-4 probe measurement always result in zero contact resistance, it might be possible that Ni nanowire between the Pb segments is not completely superconducting. A magnetic field of 1 kOe was applied to drive the bulk electrodes into normal state. However, due to the shape anisotropy Pb nanowires has
Figure 5.27. R-T plots of an array of 70 nm Pb-Ni-Pb nanowires with bulk Pb electrodes.

much larger critical field. Resistance drop at $T = 7.1$ K can only be attributed to the superconducting transition of Pb segments in the nanowires. The system shows a low temperature finite resistance of 45 $\Omega$. This resistance mostly has contributions from bulk Pb electrodes, BulkPb/PbNW interfaces and possible Ni segment. With increasing magnetic field, $T_c$ of Pb nanowires is pushed to lower temperatures. Fig. 5.28(a) and (b) represents the R-H measurements of sample Pb-Ni(100nm)-Pb at temperatures below (1.8 K and 3.0 K) and above (10 K) the $T_c$ of Pb, respectively. For the sake of clarity, measurements are shown only for three temperatures. At 1.8 K, the small resistance jumps below 1 kOe are due to the superconducting to normal transition of bulk Pb electrodes and the interfaces BulkPb/PbNW. There is magnetic hysteresis easily visible when magnetic field is scanned from one direction to another. The total resistance jump at 1 kOe is
Figure 5.28. (a) R-H measurements for an array of 70 nm Pb-Ni(100 nm)-Pb junctions at $T = 1.8$ K (bottom curve) and 3.0 K (top curve), and (b) R-H measurements at 10 K.
equal to the finite resistance observed in the R-T measurements at \( H = 1 \) kOe as shown in fig. 5.27. Pb segments reach normal state at a much higher magnetic field around 1 T and not shown in the figure. Similar behavior is observed at \( T = 3.0 \) K curve. At this higher temperature, the critical field for bulk Pb has reduced to 450 Oe and there is one resistance jump to normal state. Magnetic hysteresis is still present and is due to the presence of Ni segments.

At \( T = 10 \) K, well above the \( T_c \) of both Pb electrodes and Pb nanowires, we observed a small magnetoresistance behavior. Since, magnetic field is parallel to the wire’s axis, there will be very small AMR contribution as observed. Above results suggest that there are both Ni and Pb components in our SFS nanowires. Both segments are showing their individual properties; Pb being superconducting and Ni being ferromagnetic. In both R-T and R-H measurements, there is no clear indication of any influence of Ni on the superconductivity of Pb nanowires. Also, there is no evidence of SFS junction behavior.

V-I measurements for the Pb-Ni(100 nm)-Pb nanowires at different magnetic fields are shown in fig. 5.29(a). There are voltage jumps observed in the V-I curves. Voltage jumps in V-I measurements are staple features of dissipation in one-dimensional superconductors. However, in the present case, Pb nanowires are not in one-dimensional regime. These voltage jumps may also occur due to inhomogeneity in the nanowire. At \( H = 0 \) T, there is a sharp voltage jump at 44 \( \mu \)A, defined as the critical current, \( I_c \) at this magnetic field. At higher magnetic field \( H = 0.1 \) T, as expected, critical current is reduced to 34 \( \mu \)A. Critical current gets progressively reduced with the increasing magnetic field.

Fig. 5.29(b) shows the magnified V-I curves measured at \( H = 0 \) and 0.1 T. The straight lines are the guides to eye showing the finite resistance slope. As is very clearly seen, there is a very small gradual step around 32 \( \mu \)A. This step is so small
Figure 5.29. (a) V-I characteristics of an array of 70 nm Pb-Ni-Pb nanowires measured with bulk Pb electrodes. (b) Magnified V-I characteristics showing lower current region.
that it was not visible previously. Similarly, at $H = 0.1$ T, there is a small step at $27 \, \mu A$. From this analysis, it seems that each critical current, $I_c$, defined in fig. 5.29(a) is preceded by a very small critical current, $I_c^*$. Since the smaller critical current, $I_c^*$, is responsible for a small change in resistance, it may be related to the S-F-S junction. However, we do not observe any oscillation of $I_c^*$ with the applied magnetic field. Since, the system doesn’t show zero resistance below $T_c$ of Pb, there is definitely no supercurrent flowing through the SFS junction. The observed critical current, $I_c^*$, must be related to the induced superconductivity in Ni section due to the proximity effect from the neighboring Pb segments. And since the resistance change is very small above $I_c^*$, proximity effect has to be very weak.

5.4 Discussion

We have observed quite a few interesting phenomena in the transport measurements of hybrid superconductor-ferromagnet nanoscale systems. Spin polarized transport was measured in Ni nanowires attached to superconducting electrodes. The most striking feature of these measurements was the observation of magnetoresistance peaks. MR properties of Ni nanowires were found to be strongly influenced by the superconducting electrodes. We are not sure of the exact mechanism for the MR peaks. However, this is not an interface phenomenon as we observed similar behavior in two different geometries; 2-probe measurements with bulk Sn electrodes as well as 4-probe measurements with FIB-deposited W electrodes.

Long-range proximity effect was observed in ferromagnetic Co and Ni nanowires electrically connected to superconducting W electrodes. In addition, a prominent resistance peak was observed near the onset $T_c$ of W electrodes in most of the
samples. The peak height, however, varied from sample to sample. In sample C1, the system showed a resistance drop of 50% of the normal state value. Since, the distance between the voltage electrodes was 1.5 µm, it suggests the proximity effect at a length scale of 750 nm. We have to take into account the spread of W on the nanowire and the fact that superconductivity is induced from both sides of nanowire. A conservative estimate of length scale of proximity effect is determined to be 275 nm. This value is more than an order larger than the length scale calculated from available theoretical models based on the singlet component of superconductivity.

The resistance peak near the onset $T_c$ is also a remarkable feature of our results. Similar resistance peaks have been observed before in the experiments done on superconducting aluminum [15]. In those cases, peak was attributed to the charge-imbalance effect in superconducting islands of aluminum. In contrast, we are measuring the resistance of a non-superconducting Co nanowire. One possibility may be that the superconducting correlations induced in Co nanowires due to W electrodes may have charge-imbalance effect leading to the observed resistance peaks. We have separately measured the electrical properties of a W strip, fabricated with similar conditions as the W electrodes in sample C1. R-T plot of that W-strip is shown in fig. 3.10 (b). There is no resistance peak near $T_c$ observed in this strip. Resistance showed a sharp drop near 4.8 K before going to zero resistance state around 4.5 K. So, the observed peaks in R-T plots of fig. 5.8(b) must have origin different from charge-imbalance effect in superconducting W electrodes. Charge imbalance, however, can still be the reason for the resistance but with origin inside the ferromagnetic nanowire itself.

As discussed in Chapter 2 of this thesis, a conversion of normal current (carried by quasiparticles) into supercurrent (carried by Cooper pairs) can lead to a charge
imbalance in the superconductor. This effect is characterized by a length scale called charge imbalance which is the distance required by quasiparticles to relax (or get paired) to be a part of the superconducting condensate.

In our case, some part of the Co nanowire acquires superconducting properties due to proximity effect, mostly on the two ends of the wire. The middle section of wire, however, is still in normal state. A S-F interface is formed inside the wire resulting in conversion of normal current to supercurrent. This can lead to the observed resistance peak around the onset $T_c$ of W electrodes. Once the temperature is sufficiently low, the system relaxes and the peak disappears. This can also explain why we do not see resistance peak in sample C2. The simple explanation may be that in C2, the wire is completely superconducting (zero resistance state) and hence there are no S-F interfaces. We still do not understand the absence of resistance peak in sample C4 where a 75 nm Ni nanowire was contacted with four Pt electrodes and one W strip in the middle.

Another important puzzling results is the “negative resistance” observed in sample C2 and C5. Since, other samples do not show complete superconductivity, it’ll not be possible to observe negative resistance in those cases. There are few reports of “negative resistance” in the literature. Herzog et al. [77] observed the negative resistance in the magnetoresistance measurements of granular Sn wires. They observed that “negative resistance” was observable in low magnetic field regime only in the case of thinner wires with smaller voltage probes. They attributed it to be an artifact caused by the screening currents in the narrow voltage probes distorting the current path. Negative resistance was also observed in transport measurements of 150 nm V/Au and V/Fe nanowires [78]. It was proposed that a particular arrangement of the electrical contacts together with the superconducting proximity effect can induce negative resistance below $T_c$. In those
experiments, negative resistance was avoided by doing measurements in a contact geometry where the current and voltage electrodes are arranged along a straight line, resulting in a single well-defined current path.

In our measurement structure, FIB-deposited W is not a very homogenous conductor. In addition, due to the diffusion of W, width of the contacts is more than the width of fabricated W strip. All this can lead to multiple current paths and redistribution of currents during measurements. This could possibly be the cause of the observed “negative resistance”.

We have also get some promising results from the study of axially modulated nanowires. Nanowires in the form of SFS junctions were fabricated by electrochemical deposition. A good interface was found between superconducting Pb and ferromagnetic Ni in the axially modulated nanowires. The diffusion of metals into each other was not found to be very serious. One of the limitations of our result is that electrical measurements were only done on array of nanowires embedded in membranes. However, we observed oscillation of critical current with magnetic field; a sign for good S-F-S junction. We are hopeful that future work on these structures will reveal novel physics about the one-dimensional SFS systems.
6

Summary and Future Work

6.1 Summary

In summary, we have observed very novel and interesting phenomena related to the superconductivity in one-dimensional systems. We have also observed exciting results in hybrid superconductor-ferromagnet nanostructures.

Anti-proximity effect was observed for superconducting 40 nm Zn nanowires sandwiched between bulk superconducting electrodes. Contrary to the existing theories, superconductivity in Zn nanowires was found to be suppressed by the neighboring bulk superconductors. This was later explained by the dissipative behavior of Zn nanowires. It was proposed that bulk superconductor increases the dissipation in Zn nanowires and hence destroy their superconductivity. On the other hand, a normal electrode stabilizes the dissipation in nanowires and help them retain superconducting characteristics.

Spin polarized transport was studied in Ni nanowires attached to superconducting electrodes. Ni nanowires connected to bulk Sn electrodes as well as superconducting W thin film showed unusual magnetoresistance properties. We have
also made successful four-probe measurements on individual nanowires using FIB-assisted Pt and W deposition. Magnetoresistance peaks were observed in both array measurements with Sn electrodes and single-wire measurements with W electrodes.

Long-range proximity effect was observed for Ni and Co nanowires in electrical contact with superconducting W electrodes. Proximity effect extended to long distances (∼ 400 - 500 nm) in ferromagnetic nanowires. In addition, a resistance peak was also observed near the onset $T_c$ of W electrodes. In some cases, “negative resistance” was observed below the superconducting transition of W electrodes. We do not have a complete theoretical model to understand our experimental observations. However, resistance peak may be assigned to the charge imbalance effect in Superconductor-Ferromagnet interfaces.

We have successfully used electrochemical deposition to fabricate quasi one-dimensional axially modulated nanowires consisting of alternating superconductor (Pb) and Ferromagnet (Ni) segments. Structural characterizations with TEM showed good interface quality. Electrical measurements were done on nanowires in the form of SFS Josephson junctions.

### 6.2 Future Work

Future work will be described along the two themes explored in this thesis.

First path will be in the direction of understanding one-dimensional superconductors and their interaction with the environment. It’ll be interesting to investigate APE in other superconducting systems. The next best candidate will be Aluminum because of large coherence length. Also, the exact microscopic mechanism governing APE should be developed.
Second path will lead to more understanding of the electrical properties of hybrid superconductor/ferromagnet nanostructures. Since, we have the capability of making superconducting contacts using FIB-assisted W deposition, it should be explored further to fabricate and study new hybrid systems. A more detailed investigation of long range proximity effect can be done by using other superconducting materials. E-beam lithography can be used to realize other hybrid systems of interest. Four-probe measurements on multi-segmented nanowires can be used to investigate properties of SFS, SNS Josephson junctions in one-dimension, FSF spin valves and spin switch etc.
References


[41] Purchased from SPI Supplies Inc. www.2spi.com


[53] Büchler, H. P., Geshkenbein, V. B., and Blatter, G., *Phys Rev Lett*, vol. 92, no. 6, p. 067007, Feb 2004


Vita
Nitesh Kumar

Nitesh Kumar was born and raised in Patna, India. He received his bachelors degree in Engineering Physics from Indian Institute of Technology Bombay, India in 2002. He came to US for graduate studies in Physics at Pennsylvania State University where he joined the research group of Moses Chan. He graduated from Penn State with a Doctor of Philosophy degree in Physics in 2009. After graduation, he is going to work as process engineer for Intel Corporation, Hillsboro, OR.