Chapter 2

Metallic nanowires:

properties and devices

2.1 Introduction

A key component of the approaching nanotechnology revolution will require high aspect ratio nanomaterials for a variety of applications such as electrical interconnects, optical waveguides and mechanical resonators. Since the 1980's, a simple technique for making micron and sub-micron diameter wires has been known.[1] This technique makes use of porous membranes as a template in which to deposit the metal of choice. The pores restrict the size and shape of the material being deposited, with the diameter of the wires determined by the diameter of the pores. This technique can be applied to porous membranes of materials such as glass[2] and anodized alumina[3], as well as various polymers[4,5]. For the wires used in our experiments, metal was electrodeposited into a commercially available polycarbonate membrane (SPI Supplies, West Chester, PA), which is available in a variety of pore sizes. The nanowires that resulted from this process had diameters from 20 to 60 nm, though most were close to 40 nm with lengths from 1 to10 μm. We have created nanowires out of gold, platinum, nickel and silver and

made efforts to integrate them into a variety of devices described in the sections of this chapter. One type of device in particular, a mechanical resonator, is fully described in Chapter 3.

2.2 Fabrication

Nanomaterials offer novel challenges with respect to their fabrication and integration. Generally, nanowires, regardless of material, cannot be synthesized monolithically, i.e., in the exact location and orientation required on a substrate with preexisting structures. Alternative techniques must be utilized to fabricate useful devices from these "bottom-up" materials and integrate them with "top-down" processes, a theme which runs through this work. The next section will describe how we make the nanowires and the next explains our primary method of accessing them with top-down processing.

2.2.1 Nanowire synthesis

The process to create metallic nanowires, brought to Prof. Scherer's group by postdoc Mladen Barbic, starts with a commercially available polycarbonate membrane with nominal pore size of 20 nm. A layer of gold (thickness 100 nm) is thermally evaporated onto one side of the membrane. It is important that the gold layer completely blocks the pores. The opposite side of the membrane is placed into contact with a commercially available plating solution for the desired metal (Technic, Cranston, RI). Figure 2.1 depicts the plating setup. A current source drives the metal to plate onto the gold layer, through the pores, with a current of 1-100 μA (typically 10 μA). The plating

runs for several hours, depending on what length of wires is desired. Once plating is completed, the membrane is removed from the solution and carefully washed with water and isopropyl alcohol. Gentle sonication in isopropyl alcohol removes the evaporated gold coating from the membrane. Finally, to release the wires, the membrane is dissolved in chloroform, resulting in a suspension of metallic nanowires.

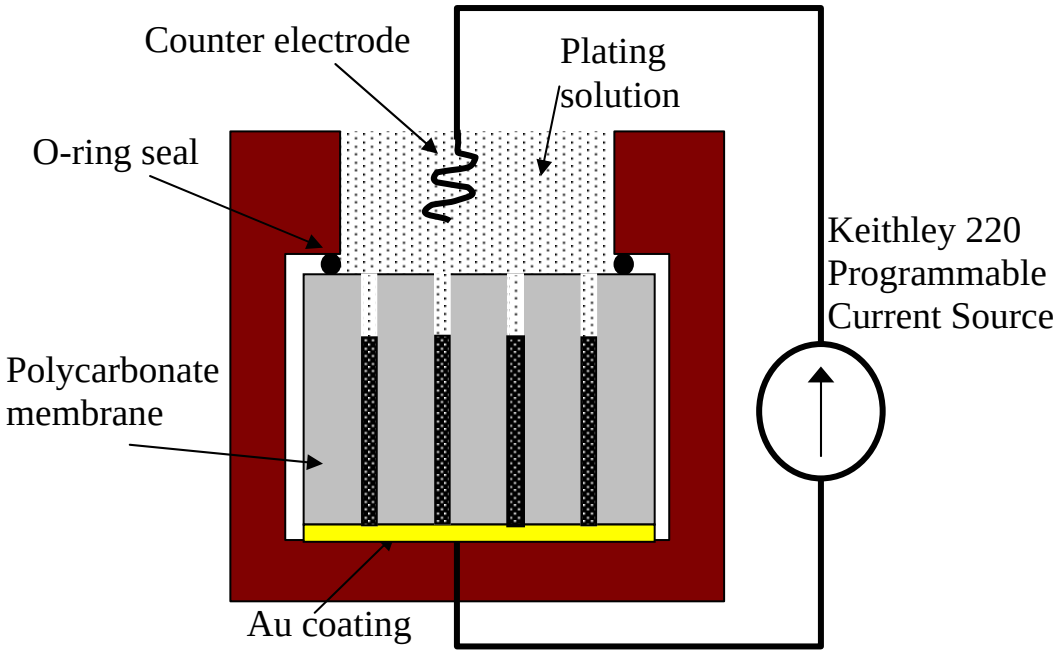


Figure 2.1: Diagram of process to synthesize metallic nanowires in porous membranes.

A variation on this process yields single-crystal silver wires.[6] In this variation, the electrical driving is unnecessary. A commercially available silver enhancement solution (Ted Pella, Redding CA) containing silver ions provides the material. This solution spontaneously deposits single crystal silver on any gold or silver surface. Silver enhancement has been commonly used to enhance the visibility of gold nanoparticles in the tagging of biological molecules. Silver is of particular interest for optical applications due to its property of low loss at the localized plasmon resonance frequency, which is

occurs at visible wavelengths. The resonance frequency is heavily influenced by the size of the particle at nanometer scales.[7] Due to the plasmon resonance, silver nanoparticles glow brightly when imaged by optical microscopy.[8]

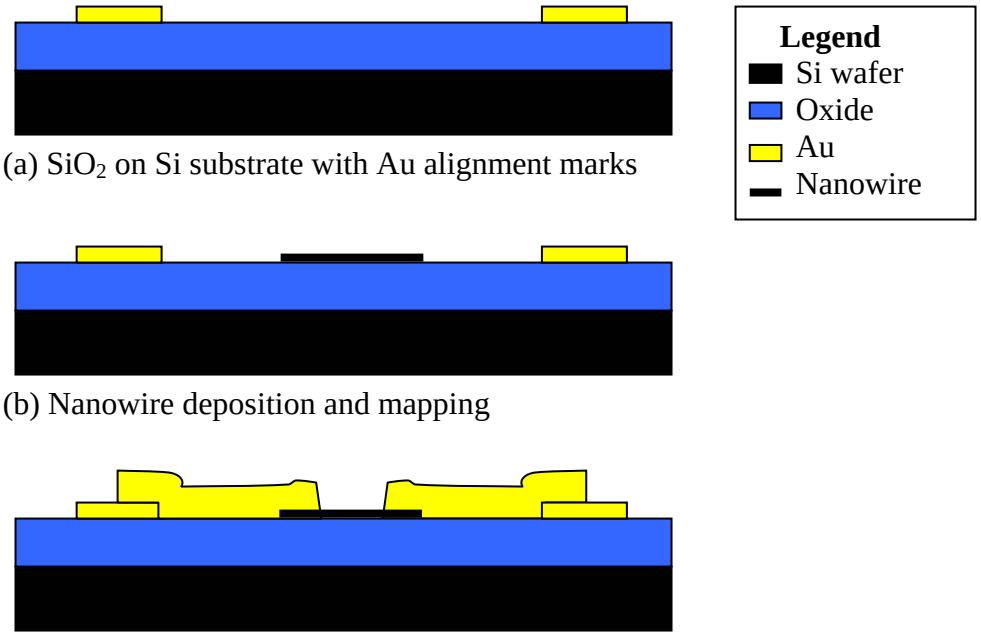
Variations and combinations of these processes have the potential to make more complex structures than homogeneous cylinders of metal. For example, by changing the plating solution after only partially filling the holes, one can grow heterowires, composed of more than one metal with a well defined boundary between them. One could imagine a making a nano-thermocouple with an appropriate junction.[9] By overplating, i.e., over filling the pores, mushroom shaped structures would result. The isotropic deposition of Ag can yield other interesting structures, an example of which will be described in Section 2.5 below.

2.2.2 Making electrical contact to nanowires

It is important for many potential applications of metallic nanowires to be able to carry out electrical measurements upon them. For example, it is well known that the resistance of carbon nanotubes changes depending on what gas is adsorbed on the surface. Electronics also offers fast signal transfer, high data rates and a large variety of components and devices that can be used to create measurement circuitry. Finally, future researchers will be able to integrate nanomaterials with on-chip electronics for signal processing or feedback.

We developed a process to fabricate electrical contacts to single, isolated nanowires, depicted schematically in Figure 2.2. A Si wafer with thermally grown

silicon dioxide (SiO_2) is pre-patterned with both large gold pads using photolithography and alignment marks using electron-beam lithography. The substrate was chosen to provide electrical isolation. In each of these steps, 5 nm/80 nm of Cr/Au is evaporated onto the patterned resist and then lift-off is performed by soaking in acetone, leaving the pattern in metal (Figure 2.2a). Next, a suspension of nanowires in chloroform is dried on the sample one drop at a time, depositing the nanowires randomly on the surface as in Figure 2.2b. The wires can be seen in an optical microscope due to their strong light scattering properties.[10] The nanowires are mapped relative to the alignment marks and then e-beam lithography, evaporation and lift-off complete the process leaving a nanowire with electrical contacts patterned on it (Figure 2.2c).



(a) SiO_2 on Si substrate with Au alignment marks

(b) Nanowire deposition and mapping

(c) E-beam lithography, evaporation and lift-off

Figure 2.2: Fabrication process to make electrical contact to nanowires.

We tried many different methods to make electrical contact to the silver wires, including depositing a variety of metals such as Cr/Au, Ti/Au and Pt, in-situ milling before evaporation, and post-annealing. Nearly every attempt measured as an open circuit across the wires. Unfortunately, electrical contacts were extremely difficult to make to the silver wires, possibly because of sulfides that form on the surface of the wires. The smog problems of the Los Angeles area are well known; this may have caused the wires to tarnish all the way through before they could be measured. Taking an Ag lattice spacing of ~.4 nm, the typical wire is only about 100 atoms across. Often, SEM pictures would show crumbled, broken pieces, as in Figure 2.3.

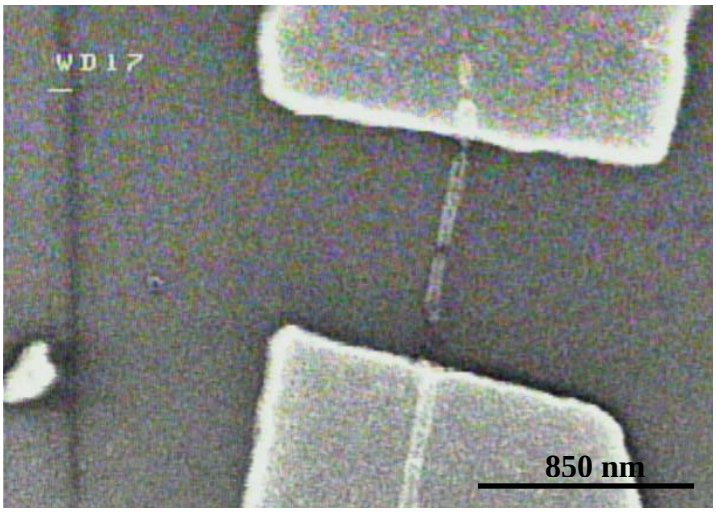


Figure 2.3: SEM image of broken silver wire.

It should be noted that the nanowires we worked with were very sensitive to electrostatic discharge. Often, in the absence of rigorous controls, the wires would act as nano-fuses, melting and severing the circuit, as shown in Figure 2.4. To protect the wires when they were initially characterized, personnel wore grounding wristbands and

employed a make-before-break switch sequence when lowering probes onto the chip. These precautions eliminated destruction of gold and platinum wires on the probe station. However, nickel wires were particularly hard to protect and would break unexpectedly and inexplicably. Nickel, possibly due to oxides, also had very high contact resistance, hindering experiments in many samples.

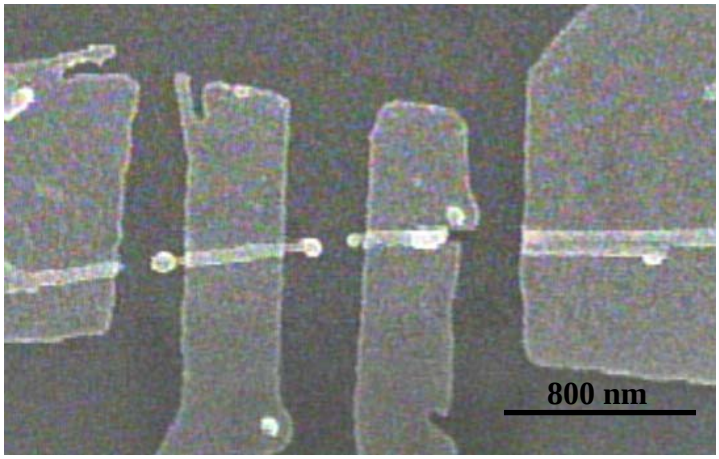


Figure 2.4: SEM picture of platinum nanowire broken by electrostatic discharge.

2.3 R vs. T measurements of nanowires

As an initial experiment, and to characterize the wires, leads were attached to the nanowires in a four probe configuration. Four-probe electrical measurement allows us to measure the resistance of the wires free of contact and lead resistance. Figure 2.5 shows a schematic of four probe electrical measurement. A current source is connected to the outer two electrodes. The flow of current produces a voltage drop through the wire, which is measured with a voltmeter at the inner two electrodes. In this way the effects of contact resistance and lead resistance are excluded from the measurement of the voltage

drop. To create a simple current source, a 10 MΩ resistor was placed in series with the nanowire. As long as the two probe resistance of the wire is much less than10 MΩ, this is a valid circuit to deliver a known current to the nanowire. All the samples for which data is shown had a two probe resistance, which includes the contact resistance, less than 10 kΩ. The digital lock-in amplifier used put out periodic voltage spikes for calibration so low pass filters, each with cut-off frequency of 1 kHz, at the input and output were included. For the measurements presented here, a 13Hz AC current of 100 nA (V_{out} = 1 V) was applied by the lock-in amplifier.

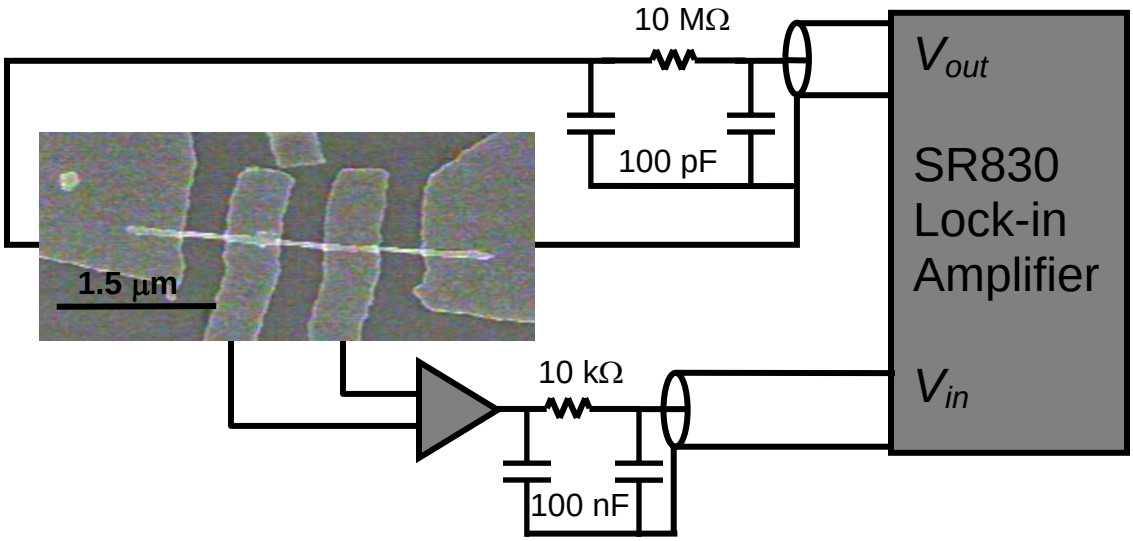


Figure 2.5: Four-probe electrical resistance measurement setup for nanowires with bias resistor and preamplifier.

The samples were loaded into a cryostat, pumped out to about 1 x 10^{-5} torr, which included a heater and temperature sensor. The cryostat was cooled using liquid helium, and allowed to stabilize at 4K. Then the resistance of the wires was measured, as a function of temperature. Figure 2.6 displays the results for gold, platinum, and nickel.

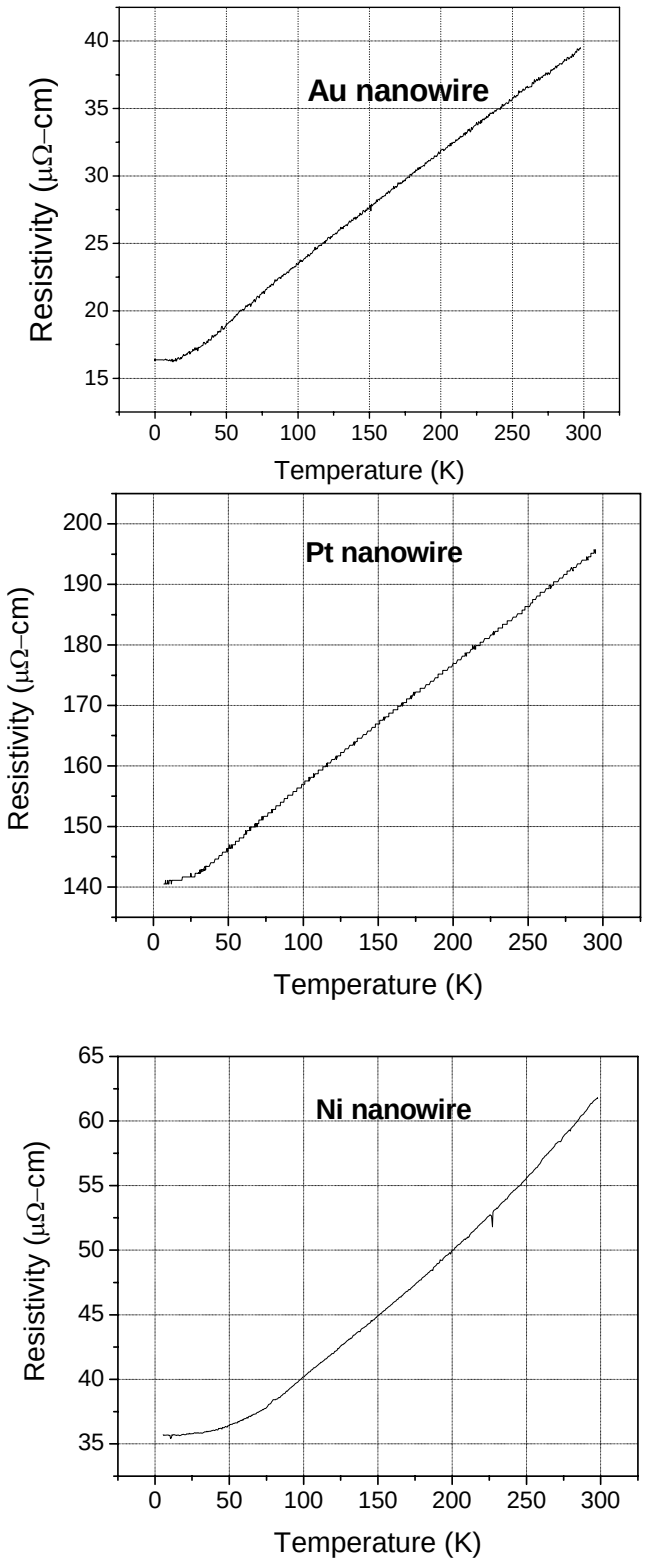


Figure 2.6: Resistivity vs. temperature for Au, Pt and Ni nanowires.

The bulk resistivities at room temperature of Au, Pt, and Ni are 2.4, 10.6 and 8.7 μΩ-cm.[11] Each sample tested displayed a resistivity about an order of magnitude larger than the bulk values. There are several possible reasons for this discrepancy. The plating process creates polycrystalline wires, which would increase the resistivity. Additionally, impurities arising from the plating solution would have the same effect. The small size of the wires may also come into play, with increased resistance from surface states, relative to the bulk conduction.

In metals, at room temperature lattice vibrations, or phonons, are the dominant scattering mechanism for electron transport.[12] At low temperature, phonon states are unpopulated and scattering is dominated by grain boundaries and impurities. For all the metals tested, the resistivity saturated at low temperature once the phonons had frozen out, as expected for metals. As described in Section 2.1, we were not able to produce results for silver due to problems creating contacts to the silver nanowires, possibly due to the development of sulfides.

2.4 Magnetoresistance and crossed magnetic nanowires

Nanomagnetic materials have application in data storage media and spintronics. Hard drives and other magnetic storage technologies are a $100 billion/yr industry, based upon the alignment and detection of nanomagnets to store and retrieve information.[13] Magnetic nanoparticles have been used for data storage since the time of tape drives. However, only recently have researchers been able to probe single nanomagnetic particles through the magneto-optical Kerr effect, magnetic force microscopy and other

techniques. In this work, electrical transport acts as a probe of the magnetization of nanoparticles.

Research into spin transport, as well as new magnetic materials, has spawned spintronics, a new field analogous to electronics, but where charge is replaced by the spin of the electrons. Also, manipulation of spins is currently recognized as a plausible method of scaling up quantum computing to a large number of bits.[14] A large amount of research is being done in magnetic semiconductors[15], magnetic junctions[16], and spin injection for devices such as spin-valve transistors.[17] Research into magnetic tunnel junctions has led to innovations such as a magnetic random access memory (MRAM) by IBM, which has a very low power consumption compared to electronic circuits, as well as a very short boot-up time.

To realize such future technology, nanoscale anisotropic magnetic effects must be understood to improve data storage densities and advance the field of spintronics. Ferromagnetic materials can serve as a source of spin-polarized electrons.[18] Nanowires of nickel, which is ferromagnetic, are an ideal structure to study nanoscale physics and to fabricate and measure simple devices. Wires of multiple metals, lithographic contacts and other junctions can be used to study interactions of spin, magnetization, and electron transport.

Magnetization and magnetic fields interact with electron transport in a number of ways, many of which can be placed under the heading of magnetoresistance, several types of which are relevant to this work. Anisotropic magnetoresistance (AMR) is an effect where the resistance of a magnetic material is related to the relative directions of the magnetization, M, and the current, J. The resistance is lower if M is perpendicular to

J, and higher if *M* is parallel to *J*. Tunneling magnetoresistance (TMR) can be measured in structures where the current tunnels from a magnetic metal through an insulating material to another magnetic metal. The resistance is dependent upon the relative orientation of the magnetizations. So called ballistic magnetoresistance (BMR) may play a part in the structures presented here. BMR occurs at nano- or atomic-scale point contacts between ferromagnetic electrodes. It is not clear if ballistic transport actually takes place, though this effect can change conductance by several orders of magnitude.[19]

Shape and size play an important part in the magnetic properties of nickel nanowires. Due to their small size, nickel nanowires of the dimensions we fabricated are single domain magnets, uniformly magnetized along the wire, or easy, axis, with two possible stable magnetizations in the absence of an applied field. This property is referred to as shape anisotropy.

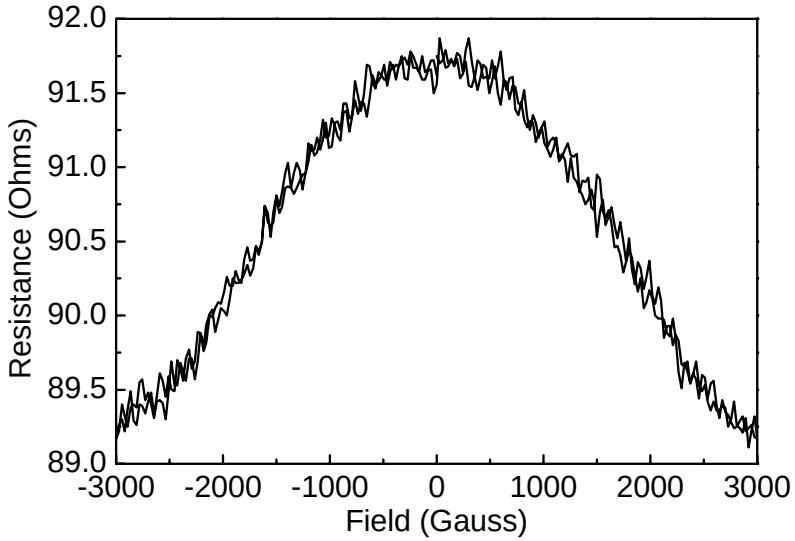


Figure 2.7: Resistance of nickel nanowire vs. magnetic field perpendicular to wire axis.

We measured the (AMR) of a single nickel nanowire. Using an electrical setup identical to Figure 2.5 above, with four contacts to the wire, the sample was placed in an electromagnet with the field oriented perpendicular to the axis of the wire. The resistance of the wire was recorded as the magnetic field was swept. Figure 2.7 plots the data. For a magnetic field orthogonal to current flow, the resistance of the wire decreases for increasing field, as has been reported previously.[20] The AMR can be explained briefly as follows. The magnetization *M* of the wire in the absence of a magnetic field is along the axis of the wire. As the field is increased, *M* tilts toward the field direction until the magnetization is aligned with the field. As *M* rotates, the resistance decreases until *M* is perpendicular to *J*, at which point the conductance saturates. The AMR is predicted to follow a cos^2B dependence for the magneto-resistance of a uniformly magnetized ferromagnet with respect to the applied field, and our measurements confirm this type of field dependence. In addition, an AMR value of ~2.5% is typical for nickel, and also matches well our measurement. Such a measurement therefore confirms that our nickel nanowire structure is a single domain magnet and behaves as expected when subject to an external magnetic field.

Crossed nickel nanowires give the possibility of creating a TMR spin-transport device where the relative magnetizations of the two wires can be varied continuously. Figure 2.8 shows the expected component of magnetization parallel to the magnetic field, $M_{||}$, vs. external field *B* for wires oriented parallel and perpendicular to *B*. A nickel nanowire cross could create a junction where spin polarized electrons travel from one magnetic domain to another through a possible tunnel junction due to oxidation of the wires. Ironically, oxidation may be to blame for the low yield in contacting nickel

nanowires. The resistance of the junction should decrease as the magnetization of the wires is aligned. In contrast to thin film techniques, template sythesized nanowires are cylinders. Laying one nanowire on top of another should create a very small contact area, introducing the possibility of observing BMR effects.

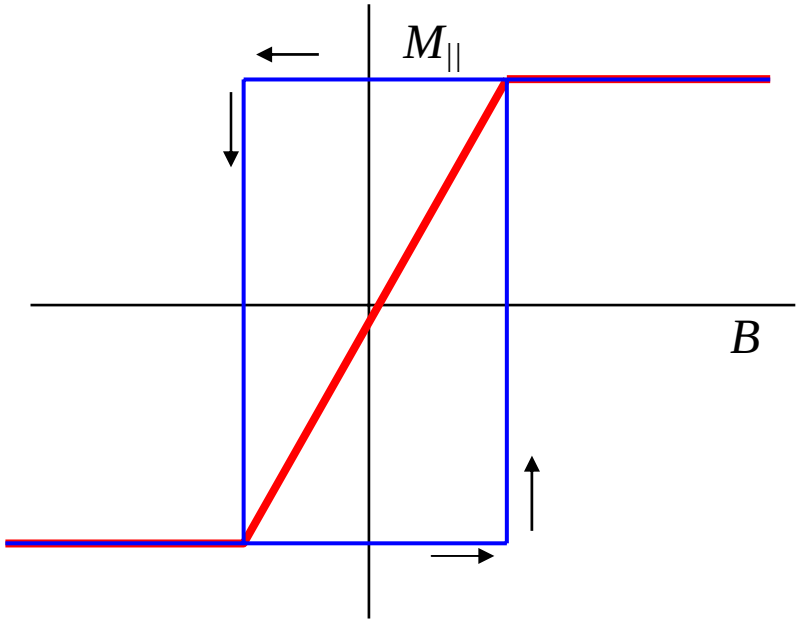


Figure 2.8: Theoretical parallel magnetization vs. magnetic field for nanowire oriented parallel (blue) and perpendicular (red) to magnetic field.

To create crossed nanowires, we begin with a suspension of nickel nanowires in chloroform. The suspension is gently washed over a thermal SiO2 on Si substrate in a magnetic field oriented parallel to the flow direction. This leaves Ni nanowires oriented parallel to the magnetic field deposited on the surface. The chip is turned by 90 degrees and the process is repeated. The result is as depicted in Figure 2.9, with Ni nanowires oriented in two perpendicular directions. Occasionally two nanowires will cross with enough overlap to place up to four contacts onto each wire.

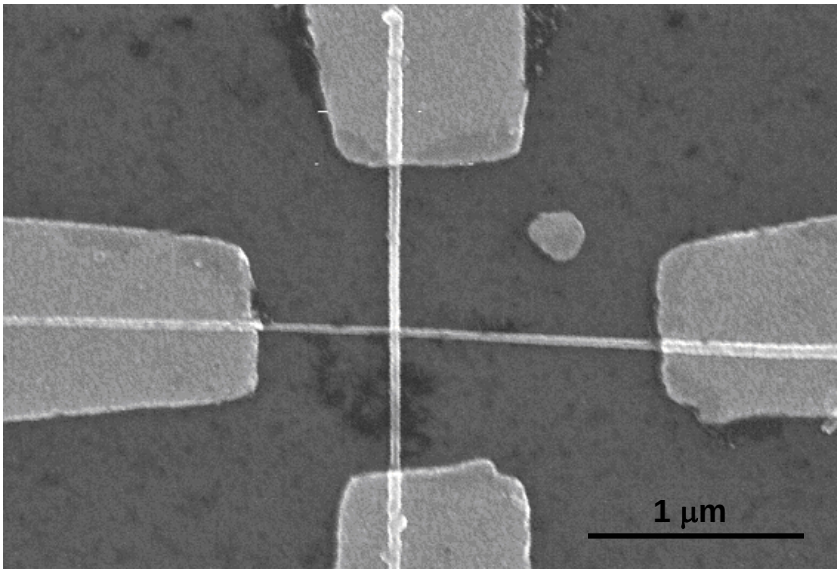


Figure 2.9: Crossed magnetic nanowires with microfabricated electrical contacts.

Very few devices had sufficiently low contact resistances for measurement. The yield was considerably reduced in the course of basic characterization and sample mounting. Of the devices that we measured in the cross configuration, we did not see any magnetoresistive effects at all. There is currently an ongoing controversy on the subject of atomic scale magnetic point contact with some groups observing dramatic effects, while others observing none. Our measurements fall into the second group.[21]

2.5 Magnetic nanowire resonator with plasmonic reflector

Motivation for nanoresonators is covered in depth in Chapter 3. Nanoresonator research often features structures that are actuated magnetomotively or capacitatively.

Here is described a proposal for a resonator fabricated using the methods described above that can be driven magnetically and detected optically.

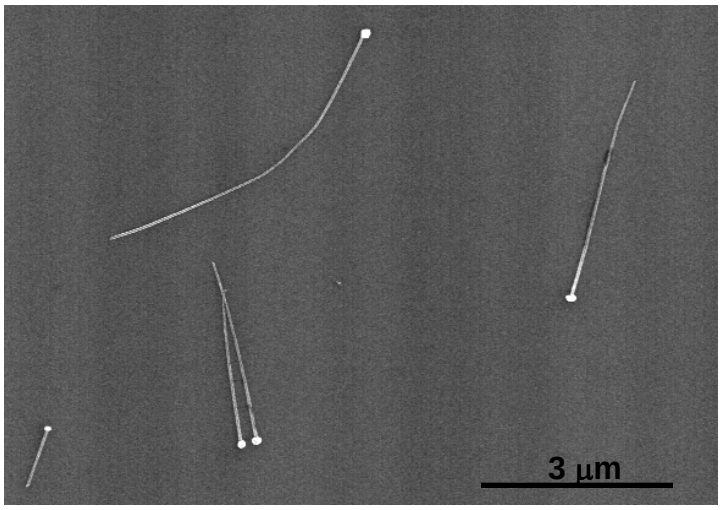
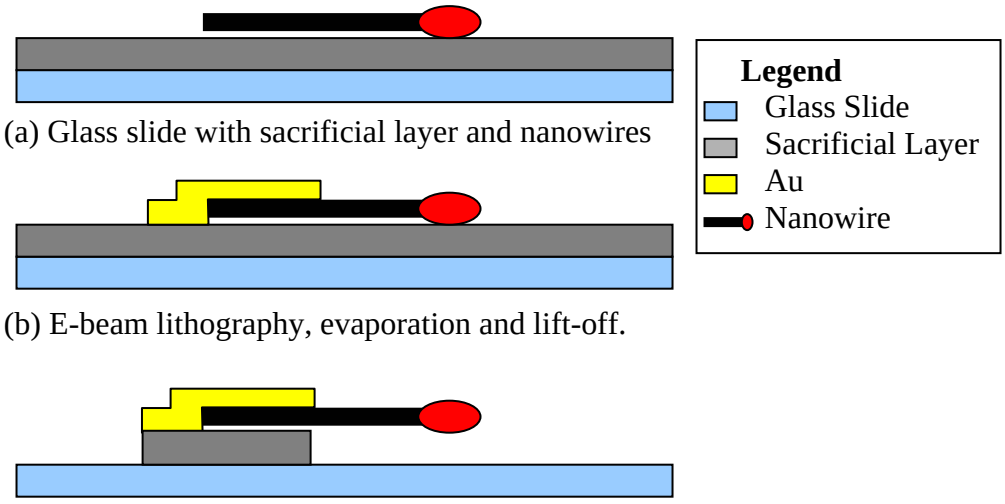


Figure 2.10: SEM picture of nickel nanowires with silver plasmonic reflectors

Beginning with the plating method described above, nickel wires were synthesized, taking care not to overplate the pores. Next, change the plating solution to Au, and plate it for a shorter time, to tip the wires in gold. Release the wires in chloroform and deposit them onto a substrate by gentle washing with the chloroform suspension. Place the substrate, with nanowires, into the Ag enhancement solution. The silver will deposit isotropically onto the gold tips forming a ball with very strong light scattering properties due to the plasmon resonance of silver. These have been fabricated here at Caltech, as shown in Figure 2.10.[8]



(a) Glass slide with sacrificial layer and nanowires

(b) E-beam lithography, evaporation and lift-off.

(c) Etch away sacrificial layer

Figure 2.11: Fabrication process for nickel nanowire resonator with plasmonic reflector.

Standard microfabrication techniques such as lithography, evaporation and etching can be employed to suspend the nanowire in a cantilever configuration with the silver sphere on the free end of the beam as shown in Figure 2.11. First the nanowires are deposited onto a glass slide which has had a 100 nm sacrificial layer deposited on the surface as in Figure 2.11a. The sacrificial layer could be Si, SiO_2 or even Si_2N_3. Electron beam lithography, evaporation and lift-off leave the wire clamped by one end on to the surface (Figure 2.11b). Finally the sacrificial layer is etched away leaving the nanowire cantilever (Figure 2.11c). Preliminary attempts to release it by isotropic dry plasma etching of a sputtered Si sacrificial layer were unsuccessful, as shown in Figure 2.12. An alternative method would be to use SiO_2 as the sacrificial layer and then perform a wet etch in hydrofluoric acid followed by critical point drying. Critical point drying evades surface tension effects that can damage a delicate suspended structure.

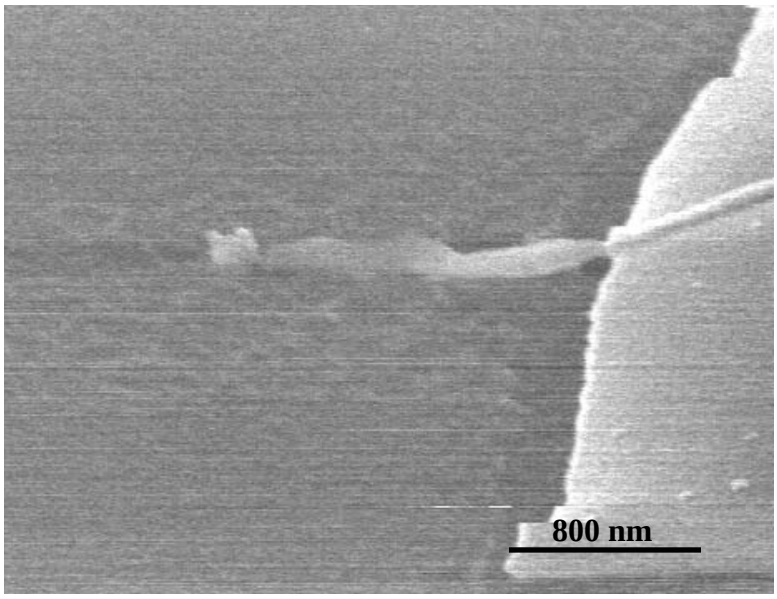


Figure 2.12: SEM picture of nanowire stuck to surface after isotropic dry etching in an attempt to create a cantilever device.

The silver nanosphere adds very little mass to the cantilever, yet presents a significantly increased scattering cross section due to its plasmon resonance when illuminated with visible light. Such a nanoparticle can serve as an efficient reflector for sensitive optical measurements. Because the Ni beam is a single-domain magnet, it can be actuated with a nearby electromagnet. To detect the oscillation, a laser would be reflected off the plasmonic silver ball. Figure 2.13 shows a possible experimental setup. The interface between the glass slide and vacuum provides a reflection that can be used with the reflection off the Ag ball to make a very sensitive interferometric measurement. An oil immersion lens prevents reflection from the first glass interface.[22]

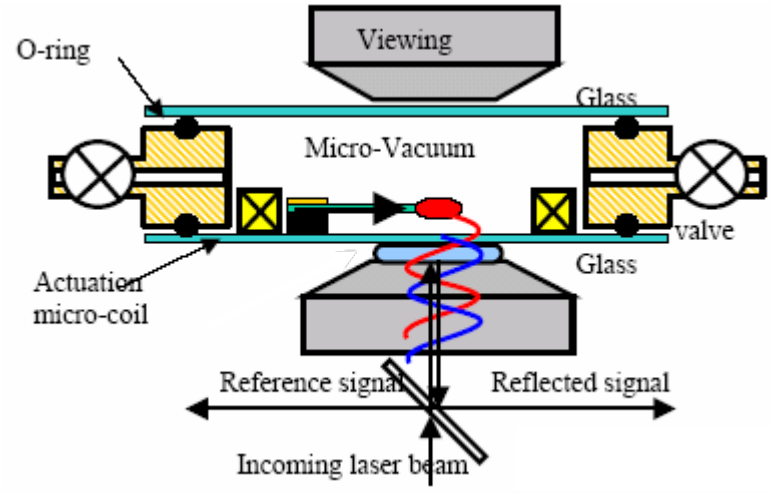


Figure 2.13: Schematic of proposed measurement setup for magnetic resonator.

2.6 Summary

Metallic nanowires are a useful and versatile bottom-up material for the development of interesting and novel devices. We have synthesized and measured the resistivity as a function of temperature of metal nanowires of gold, nickel and platinum. Though all the nanowires had resistivities larger than the bulk value for its metal, the temperature dependence was consistent with that observed in bulk metals.

Magnetic nanowire devices have been explored and the AMR of a single nanowire was measured. A crossed nickel nanowire device has been fabricated, though magnetoresistance effects were not observed. A novel nickel nanowire cantilevered resonator has been proposed. Further work is required to realize this device.

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