The Electrical Properties of Electrochemically Fabricated Ni Nanowires

by

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A thesis submitted in conformity with the requirements for the degree of Master of Science
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0-612-50358-5
Abstract

Metallic Ni nanowires were deposited electrochemically into porous anodic alumina template. The technique produces arrays of parallel wires embedded in alumina, with a narrow distribution of pore diameters and lengths. Recently developed methods greatly improve the periodicity of the porous alumina arrays and truly make the templated fabrication of various nanostructures in AAO a viable alternative to the expensive lithographic techniques.

The ordered arrangement of nanowires has been utilized to measure the resistance of single wires with the Scanning Tunneling Microscope (STM). Measurements reveal high nanowire resistivity compared to the bulk Ni. It is thought to be due to the disorder of the electrodeposited material and possibly due to the quasi-1D effects.

The electrodeposited nanowires have been characterized with Scanning and Transmission Electron Microscopy (SEM and TEM), electron and X-ray diffraction and density measurements.
Acknowledgments

I would like to thank my adviser, Professor Martin Moskovits for his guidance, encouragement and friendship throughout the work on my thesis and beyond.

The expert direction of Dr. Jing Li with the alumina and nanowire fabrication proved invaluable. I am truly grateful to Dr. Dimitri Davydov for teaching me the how to use the Scanning Tunneling Microscopy, for his help and advice in many aspects of the project. I also wish to thank all members of Moskovits group, especially Dr. Tom Haslett.

Last but not least, I thank my husband for unending support in my endeavors.
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1.1. Introduction

Protective and decorative anodic coatings on Al surfaces have been commercially available since the early 1920's. The anodic layer provides better protection against corrosion than native, air-grown oxide, and as an added benefit, such coatings can be permanently coloured \(^{1,1}\). The oxide's striking porous structure and growth mechanism have since been elucidated, and what had started as an esthetically stained protective coating, has became a versatile templating method for nanotechnology.

A self-organizing mechanism gives rise to a regular honeycomb-like array of pores, where the hexagonal cell pattern extends over the single crystal domains in the original aluminum substrate. Each cell contains a cylindrical channel oriented perpendicular to the surface. A thin, electrically rectifying barrier layer lines the bottom of each pore.

Thanks to this regular void structure, the porous alumina matrices have been utilized as elegant templates in which metallic, semiconductive and alloyed nanowires \(^{1,2,1,3}\), multiwalled carbon nanotubes \(^{1,4}\) can be deposited or synthesized. The alumina has been reported to serve as an evaporation masks for nanodot arrays \(^{1,5}\) and as a sacrificial ion etching mask \(^{1,6}\) to produce arrays of indentations in a substrate material.

Nanoscale systems have generated tremendous interest in recent years. From carbon nanotubes \(^{1,7}\), to self assembling monolayers (SAM) \(^{1,8}\), all the way to nano-machines \(^{1,9,1,10}\) -- researchers have been fascinated with Lilliputian structures with dimensions on the order of a few atoms. Quantum effects due to individual defects, such as voids or impurity atoms, have enormous consequences on the properties of these materials. Low impurity and defect tolerance in nanoscale systems is further compounded by possible size and shape effects, which have an enormous consequence on the nanomaterial's properties, often strikingly dissimilar from the bulk material.
In this study we focus on the electrical properties of nanowires deposited electrochemically in anodic aluminum oxide (AAO) templates. These characteristics differ significantly from those in the bulk, even in the bulk nanocrystalline material. The morphology, density and crystallinity of the nanowires are characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), electron and X-ray diffraction, and by density measurements. The electrical resistance of a single nanowire is measured using a Scanning Tunneling Microscope (STM). The resistance is extracted from two types of measurements: Current vs. Bias (IV) and Current vs. Electrode Separation (IZ).

The cellular periodicity of the alumina template is discussed, together with most recent methods to improve the periodic order as monitored by a pair correlation function.
1.2.1. Anodic Oxide Films

Anodic oxide is formed by the electrochemical oxidation of metals such as aluminum, tantalum, zinc, tin, tungsten, hafnium, nubidium, uranium, silicon and titanium. Two types of anodic oxide films are formed: a compact barrier layer type and a porous type. For aluminum a nonporous, barrier oxide forms in electrolytes which do not dissolve the oxide, for example in ammonium borate, ammonium tartrate, neutral boric and citric acid aqueous solutions. Electrolytes such as sulphuric, oxalic, phosphoric and chromic acids in which the oxide is slightly soluble yield a porous anodic oxide.

1.2.2. Barrier Type Oxide

When Al is anodized in a neutral or slightly acidic electrolyte, pH > 5, a non-porous, insulating barrier oxide develops. This layer is electrically rectifying permitting current to flow only in one direction, from aluminum substrate to the electrolyte solution. A non-porous oxide grows to a thickness proportional to the applied voltage, at a rate of 10-15Å/V, depending on the electrolyte.

- Barrier layer oxides have been found to have a poorly developed cellular structure. The cells are delineated by a differential crystallinity and composition of the alumina. The material in the central portion of the cell is the most amorphous and soluble -- the site of a potential pore nucleation.

1.2.2. Oxide Growth

Both the barrier and porous oxides have a similar growth mechanism with a net oxidation reaction given by:
This is composed of the two half-reactions:

at the anode:

oxidation of Al (at Al/oxide interface) \[ 2\text{Al}^3+ + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{H}^+ \]  
field-aided dissolution \[ \text{Al}_2\text{O}_3 + 6\text{H}^+ \rightarrow 2\text{Al}^{3+} + 3\text{H}_2\text{O} \] and chemical dissolution of oxide (at oxide/electrolyte interface)

at the cathode:

hydrogen evolution \[ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \]

Gas evolution at the anode occurs only on bare metal spots exposed in cracks or pits in the oxide. During oxalic acid anodization CO\(_2\) may additionally be evolved \(^{(1,11)}\).

The oxygen, rather than the aluminum, is believed to be the mobile ion. This is indicated by the behaviour of random inclusions \(^{(1,13)}\) and specific “markers” \(^{(1,14)}\) which become buried progressively deeper in the oxide. If aluminum were the mobile ion, it would lead to oxide formation at the oxide/electrolyte interface and eventually obstruct the pores. Mobile oxygen produces oxide at the metal/oxide interface \(^{(1,15)}\). This process does not block the pores, but rather continuously thickens the barrier layer.

The oxide is a complex mixture of \(\gamma\)-Al\(_2\)O\(_3\), \(\gamma^\prime\)-Al\(_2\)O\(_3\), \(\alpha\)-Al\(_2\)O\(_3\), and amorphous Al\(_2\)O\(_3\); water of hydration, free water and acid anions are also incorporated in the oxide from the electrolyte. The composition and crystallinity depend strongly on the original aluminum and anodizing conditions.
Since the growth mechanism for both porous and barrier type anodic alumina films is the same, it is the solubility of the new-formed alumina in the electrolyte that determines whether the oxide will develop pores.

1.2.4 Structure of Porous Oxide

Porous anodic aluminum oxide consists of a highly ordered array of close-packed, hexagonal cells, parallel to each other and normal to the surface of aluminum (fig. 1). Each cell contains one

![Diagram of the hexagonal structure of AAO](image)

**Figure 1a.** Schematic drawing of the hexagonal structure of AAO, b. SEM micrograph of the AAO section, c. definition of angle \( \theta \).
cylindrical pore in its center, open at the surface and bound by a thin barrier layer oxide at the bottom. The cell size (C), pore diameter (P) and barrier layer thickness (d) are proportional to the formation voltage (V)

\[ P = C - 2(0.71d) = 1.29 \text{ V} \quad (1.16, 1.17) \]  

Porous anodic alumina is a brittle and hard oxide. The material was originally developed as a protective coating since it is macroscopically very robust, however the microscopic structure is more delicate. Our AAO films are a mixture of several crystalline/amorphous phases; the barrier layer properties being especially important in this study.
1.3.1 Oxide Growth-Dissolution Cycle

In an acidic electrolyte oxide growth continues by the mechanism described for the barrier oxide, however it must now compete with field-assisted dissolution at the most soluble spots in the oxide/electrolyte interface. Pore nucleation begins at impurities and defects in the native aluminum oxide, usually most abundant at the grain boundaries, where the activation energy for the solubilization of alumina is lowest\(^{(1.16)}\).

Since the pore and cell diameters and the barrier layer thickness are proportional to the formation voltage, they must obey constant geometrical ratios at the pore base and propagate this geometry into the new-formed oxide:

\[
\theta = \cos^{-1}\left(\frac{r}{b}\right) = \cos^{-1}\left(\frac{w}{W}\right) \quad (1.16)
\]

where \(r\) is the pore radius, \(b\) is the radius of curvature at the pore base, \(w\) is the cell-wall thickness and \(W\) is the thickness of the barrier-layer. The definition of angle \(\theta\) is given in fig. 1c \((1.16)\).

1.3.2 Pore shape

This direct relationship between the cell-wall and barrier-layer thicknesses (eqn. 1-1) and the constant radius of the curvature at the bottom of the pore, \(\theta\) (eqn. 1-2), limits the lateral spread of each pore and ensures close packing of neighbouring pores. Consider the schematic geometry of the pore base (fig.2). Both the dissolution and growth are controlled to maintain a specific balance between parallel and perpendicular electric field components, and thus a constant curvature at the pore base. As the pore base deepens (fig. 2a) and the radius of curvature increases, the perpendicular component of field, \(E_{\perp}\), increases causing the oxide growth rate to
increase because the barrier layer is thinner and the ion current is greater. As the oxide grows thicker it becomes more resistive and ion countermigration slows, in turn slowing down the rate of new oxide growth at the metal/oxide interface. Eventually, the barrier-layer dissolution rate becomes equal to the new-oxide growth rate (in a given solution and at a constant temperature), thus setting up a steady state between growth and dissolution, both assisted by locally strong electric field at the pore bottom. A local Joule-heating phenomenon at the pore base contributes to an increased rate of dissolution and to an increased rate of current consumption by the anodization process. As a result, an effort must be made to cool and vigorously stir the solution in order to maintain temperature uniformity thereby avoiding pore branching and nodule formation.

The barrier layer thickness remains constant as long as steady state conditions apply and the pore growth remains self-perpetuating. The maximum thickness of the AAO layer is limited by
the mechanical properties of the alumina and by purely chemical dissolution of the alumina.

With AAO thickness reaching several hundred μm, the parallel pore walls become tapered near the mouth of the pore.

1.3.3 Arrays

The conditions expressed by eqn. 1-2 limit both the cell and the (unwidened) pore sizes to a narrow distribution of about 10% half-width value. Such variability is present due to small local deviations in voltage arising from irregular cells, occurring in the random pore packing observed in AAO grown on low purity aluminum or in the interstitial regions between the regularly packed cells on the single crystal domains of high purity aluminum. In such instances the equal distance between two adjacent centers of anodization may differ from that predicted by the geometrical relations. Irregular pentagonal and hexagonal cells are observed, however triangular and

Figure 3. SEM micrograph of top surface of AAO template, showing irregular cells and pore mouths.
quadrangular cells are rare because the minimum separation of two neighbouring cells must be observed \(^{(1,18)}\) (fig. 3).

The lateral field distribution around a prototypical, cylindrical pore is symmetrical, thus a close packed array of pores develops; ideally, a pore becomes surrounded by 6 other pores which mutually inhibit lateral growth. Influence of neighbouring pores sets up a hemispherical field at the bottom of the pore and results in a scallop-shaped oxide barrier and a conjugate structure in the underlying aluminum \(^{(1,19)}\) (see fig. 1b).

The development of periodicity and the different stages of solubilization of the porous alumina was simulated by Randon et al. \(^{(1,18)}\) based on the known graded solubility of the inhomogeneous oxide increasing towards the center of the cell. The simulations show very good agreement with the experimental observations of pore nucleation and cellular array development.

1.3.4. Coloured Appearance of AAO

The oxide film may appear light green, pink or yellow due to size-related optical properties of the pore/cell structure, forming at a particular voltage. A tinge of colour may also in part be associated with acid anion incorporation and specific impurities in the original aluminum and/or electrolyte \(^{(1,11)}\). For example oxides prepared on aluminum (Alcan) with approximately 2-3% of Mg, Fe, Si and Cu (all together) in 0.2 M oxalic acid, at > 40V, appear pale green, but the same anodizing conditions yield a colourless film on 99.9% pure aluminum (ESPI).

1.3.5. Electrochemical Polishing of Aluminum

Since the pores grow normal to the surface of the aluminum, any surface roughness would modify the local field which would in turn disrupt the parallel pore growth; therefore it is
important to begin with as smooth an aluminum as possible on the macroscopic as well as the microscopic scale. This was accomplished using electrochemical polishing, yielding a smooth, mirror-like finish to the aluminum. Jacquet\(^{(1,20)}\) explained the mechanism whereby anodic polishing dissolves protruding sites preferentially over the hollow sites. During polishing a concentrated, usually saturated and viscous layer of metal ion solution lines the surface of the polished metal. This highly resistant layer is parallel to the metal surface and planar due to convection in the bulk solution and thus promotes the dissolution of protruding sites over the cavities in an effort to minimize the local resistance by spreading the resistive layer evenly. Also the greatest diffusion gradient is at the protruding sites, thus further promoting smoothing of the metal surface\(^{(1,21)}\) by local dissolution.

Nanometer sized patterns of stripes or hills form on the aluminum during electropolishing depending on the polishing voltage and duration\(^{(1,22)}\) in certain electrolytes. The usefulness of such patterns with respect to the fabrication of highly periodic porous oxide is discussed in Chapter 4.
1.4.1 Electrodeposition of Metals

The technology of AAO is relatively inexpensive, the material is stable, uniform and porous over a wide range of pore sizes. Hence it is an attractive template for growth or synthesis of small particles.

A thin AAO may serve as a mask with nanometer sized features: Masuda & Satoh have used it as an evaporation mask (1,2) for producing gold nanodot arrays; Al-Mawlawi et al. (1,16) has ion etched a hexagonal hole pattern onto aluminum, silicon oxide and other materials through a sacrificial AAO mask.

1.4.2 AAO for Electrodeposition

In general, aluminum oxide is an insulating ceramic material. The barrier layer has an interesting electrical property – it is an electrical rectifier. That is, when sufficiently thin, the barrier layer conducts well only in the cathodic direction. No, or very little, anodic current passes through the barrier layer which ideally is insulating in this direction.

The unique morphology of AAO and the rectifying properties of its barrier layer make it a useful template for AC electrodeposition of metal or semiconductor particles. A crude version of this process has been used to colour anodic alumina for decorative purposes, as mentioned in the introduction. Heiman (1,23) first discovered that electroplated metal “keys in” the anodized aluminum, whereas adhesion to aluminum is often a problem in ordinary electroplating due to the native oxide.

Because of the rectifying properties of the barrier layer, metal ions in solution are reduced at the bottom of the pore, rather than along the much more insulating pore walls or at the top surface of the template. The rectification prevents the re-oxidation of the metal particles during the anodic half-cycle. Of course deposition can also occur on the aluminum substrate exposed at
cracks in the oxide for the cathodic current. The metal deposited there would be re-dissolved during anodic part of the cycle.

According to this mechanism, a nanowire gradually fills the pore from the bottom of the pore up (fig. 4 and 5). Branches and local swelling or narrowing occur because a nanowire is a faithful representation of the connected voids in its, at times imperfect, template. If the temperature and the electrolyte concentration are optimized then the process is independent of diffusion, and is proportional to the charge consumed in the cathodic half-cycle.
Figure 4. SEM micrographs of nanowires: free wires in a, b and c; d. section of the AAO template with short wires.
Figure 5. Bright field TEM images of free nanowires. The residue of alumina appears as the loose particles in the background (right).

1.4.2 Processes Competing with Electrodeposition

Several competing processes may hinder, or even halt the wire growth. The influence of these processes on electrodeposition has been studied only marginally. These processes include modification of the barrier layer structure and /or chemical composition, and its electrical conductivity, competing electrochemical processes and the obstruction of pores.

A porous aluminum oxide may be re-anodized, and if the anodizing conditions differ from the original (previous) anodizing conditions, the new growth will be morphologically and/or compositionally distinct. If, for example, the alumina is soluble in the electrolyte used for subsequent metal deposition, a new set of morphological dimensions (barrier layer thickness, pore and cell diameter etc.) will establish themselves by re-anodization as appropriate for the deposition voltage, temperature and the electrolyte. Such a modification of the pore base may thicken the insulating barrier layer sufficiently to slow or stop the electrodeposition due to low current density throughput.
A large portion of the current density may be unavailable for the electrodeposition process if competing processes occur. For example, in an aqueous electrolyte, water electrolysis with H₂ evolution competes with metal reduction. Hence an appropriate pH must be maintained using a buffer in order to restrict the former process.

Random faults in the AAO invite yet another competing process which may divert the charge away from the desired process. The current density may be unavailable to the electrodeposition because it is consumed by ordinary reduction/oxidation cycles occurring at bare aluminum exposed in random cracks and faults caused by handling, expansion stress created during oxide growth and drying, gas evolution, pitting and impurities in the electrolyte or the alumina. To minimize such faults one may use a high purity aluminum and ultra-clean electrolytes, fabricate AAO within specific forming-voltage and size ranges, and handle the samples with care.

Under normal electrodeposition conditions into the AAO, the wire growth rate is non-uniform on the micron scale (fig. 6a). Such observations imply non-uniformity in the original barrier layer over submicron length scales. This may entail differential thickness or local nano-cracks/channels more abundant in especially “productive” pores. The diversity may also stem from variations in the anionic or hydration-water content, a non-uniform fraction of intercrystalline volume etc. affecting the local conductivity of the barrier layer.

Non-uniform deposition rates cause preferential growth of a small population of wires up to the surface of template. These “opportunistic” wires then spread on the template surface to resemble “mushroom caps” (fig. 6a) which physically obstructs diffusion of fresh electrolyte into adjacent pores hindering wire growth in them (fig. 6b).
Electrodeposition depends on sufficient electrical conductance through the barrier layer of each pore. It is, therefore, reasonable to ascribe problems with wire deposition on the deterioration of the barrier layer.

Cd metal deposits relatively easily from an aqueous solution at elevated temperature (50-60°C) up to approximately 75% of the pore length. The thickness of the AAO template seems not to have an effect on the fractional filling of the pore. The growth will terminate once ~¾ of a template depth is filled, in a series of templates with pore lengths ranging from 0.8 to 6 μm. One
possible explanation is a progressive degradation of barrier layer during the Cd deposition via an unknown process, for example conductive microcracks/channels may heal. Pore blockage likely is an issue in Cd deposition. Loose black "particles" that are easily wiped off are often found on the AAO surface. The solution must be especially vigorously stirred in order to reach a deposition level of ¾ of pore length. It is worth noting here that deposition of other materials is successful at higher temperatures and the alumina/barrier layer structure does not appear to degrade. For example Ni and CdS (124) are deposited at above 100°C, albeit in a non-aqueous solvent.

A combination of these phenomena may be responsible for the inability to deposit nanowires of full length of the template for some of the metals: Cd, Co and Ni (the latter from aqueous baths).
1.5.1 Annealing of Ni Nanowires

Several techniques for preparing nanocrystalline (nc) Ni have been reported: inert gas condensation, electrodeposition, mechanical attrition, severe plastic deformation consolidation. Each method yields a unique micro and nanostructure, with potentially different properties. Annealing studies of such samples report the beginning of grain growth at temperatures as low as 175°C\(^1\) to as high as 550°C\(^2\), and variable resistance of films with comparable domain sizes. (Only electrodeposited nc Ni annealing studies were considered.)

Mehta \textit{et al.}\(^3\) heated nc-Ni up to 320°C. They observed significant grain growth only above 240°C, with a corresponding grain diameter increase from 25 nm (as deposited) to 250 nm (at 260°C) and to microcrystalline (0.5-1 \(\mu m\)) at 320°C. Throughout the annealing, selected grains grew preferentially at the expense of smaller grains — this abnormal growth was attributed to the presence of “low angle grain boundaries” and to the grain size distribution effect, pointed out by Hillert\(^4\). According to this theory only grains with diameters larger than a critical value (1.8 nm) will grow, by coalescence with smaller grains, until they encroach upon others developing in the same manner, resulting in a wide grain size distribution until completely annealed to a microcrystalline phase.

Wang \textit{et al.}\(^5\) proposed that such “abnormal growth” applies to coalescence of adjacent and slightly misoriented nano-grains, rather than random events.

All studies confirm that the highly defective grain boundary volume may be considerably minimized by thermal annealing. Our nanowires, electrodeposited in a confined matrix, structurally fall between a nc and an amorphous phase, and may thus become more crystalline upon annealing. The specific annealing procedure chosen for our Ni nanowire samples is described in more detail in the experimental section 2.3 (also see fig. 8).
References

2. Experimental

2.1. AAO Preparation

High purity grade of aluminum (99.9% - 99.999%, ESPI) was typically cleaned ultrasonically in acetone, methanol and water for about 20 min. each. Some clean Al strips were then thermally annealed (refer to Chapter 4). All Al samples were electropolished in EtOH:HClO₄ (Aldrich) aqueous bath (in 5:1 v/v ratio), at 0-5°C, 25V for 30s; then anodized (fig. 7) in 0.3 M H₂C₂O₄ (aq), while stirring vigorously \(^{1,2}\). Constant temperature was maintained by a solid state relay temperature controller, ± 0.5 °C (ΩE Omega, model CN76000). The temperature ranged from 1°C to room temperature, at approximately 22°C (table.1).

![Diagram](image)

**Figure 7.** Anodization scheme.

The forming voltage was normally 25 V, decreased to 8-10 V at the end of the final anodization to reduce the barrier layer thickness for metal deposition \(^ {1,2}\). At least 1 hr rinse in
running, deionised water was necessary to remove debris and residual oxalic acid solution from the pores. This was followed by 2 weeks of air drying. Vacuum drying was attempted, however it resulted in macroscopically uneven drying and blotchy metal deposits. Chemical pore widening is known to remove debris from pore bottoms. This method was not utilized, since pores as small as possible with oxalic acid fabrication were desired.

Table 1. Anodization Conditions.

<table>
<thead>
<tr>
<th>sample</th>
<th>Al purity %</th>
<th>electro-polishing</th>
<th>temp. oC</th>
<th>time min.</th>
<th>voltage V</th>
</tr>
</thead>
<tbody>
<tr>
<td>N01</td>
<td>99.9</td>
<td>no</td>
<td>23 rm. temp</td>
<td>30</td>
<td>25 – 15*</td>
</tr>
<tr>
<td>N02</td>
<td>99.9</td>
<td>yes</td>
<td>10 C</td>
<td>105</td>
<td>25 – 10</td>
</tr>
<tr>
<td>N03</td>
<td>99.9</td>
<td>yes</td>
<td>7C</td>
<td>120</td>
<td>25 – 8</td>
</tr>
<tr>
<td>N04</td>
<td>99.9</td>
<td>yes</td>
<td>2C</td>
<td>255</td>
<td>25 – 8</td>
</tr>
</tbody>
</table>

electrolyte: 0.3 M H₃C₂O₄ (aq)

* expression: 25 – 8 means that anodization voltage was 25V (for the duration mentioned) with subsequent stepwise voltage reduction to 8V in order to reduce barrier layer thickness (1.2, 1.11).

2.2. Ni Deposition

Deposition of Ni into dry AAO templates from aqueous solutions yielded short (few hundred nm in length) nanowires, regardless of the template height (pore length, l). An organic solution was used to prepare the Ni nanowire samples (table 2): 0.5-0.8M NiCl₂ (98%, anhydrous, Strem Chemicals) in DMSO (anhydrous, < 0.1% H₂O, kept under Ar and over 3A molecular sieves; ACE). 130°C was found to be the optimal temperature for Ni deposition, maintained by the same solid state relay temperature controller as used for anodization, ± 5°C (ΩE Omega, model CN76000). The AC voltage used was 12-16 V, depending on the thickness of barrier layer, at a frequency of 100-150 Hz, for 15-25 min. A UH-grade N₂ (Matheson), equipped with a drying cartridge (Gas Purifier, model 450, Matheson), was bubbled through the solution continuously, except during deposition.
2.3. Ni Annealing

Ni wires were annealed to 200°C, 300°C, 400°C, and 500°C within the intact AAO template. The melting point of bulk Ni is 1455°C \(^\text{(2.1)}\), however several workers noted a significant reduction in melting point of materials in a finely divided phase \(^\text{(2.2)}\). In choosing the annealing temperature we were limited by the melting point of the aluminum substrate (660.37°C \(^\text{(2.1)}\)).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp (°C)</th>
<th>Time (hr)</th>
<th>Voltage</th>
<th>Current</th>
<th>Other Treatments</th>
<th>Wire Length (nm)</th>
<th>Wire Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N01</td>
<td>136</td>
<td>100</td>
<td>16</td>
<td>30</td>
<td>no</td>
<td>6.1-6.2</td>
<td>30-32</td>
</tr>
<tr>
<td>N02</td>
<td>135</td>
<td>100</td>
<td>14</td>
<td>40</td>
<td>no</td>
<td>4-4.3</td>
<td>18-20</td>
</tr>
<tr>
<td>N03</td>
<td>135</td>
<td>100</td>
<td>11-12</td>
<td>45</td>
<td>ion etch 15 min, 3kV/3mA</td>
<td>3.5-3.6</td>
<td>15-18</td>
</tr>
<tr>
<td>N04</td>
<td>130</td>
<td>100</td>
<td>9</td>
<td>80</td>
<td>ion etch 5 min, 3kV/3mA</td>
<td>3.2-3.4</td>
<td>10-13</td>
</tr>
</tbody>
</table>

Figure 8. Temperature programs for thermal annealing of Ni nanowires within AAO template.
Fig. 8 shows the temperature programs. The oven temperature was regulated by a programmable temperature controller (model CN3201TC1-DC1, Omega) and verified with an independent thermocouple. Constant N₂ (UH grade, Matheson) flow at 25-30 mL/min, equipped with a drying cartridge (Gas Purifier, model 450, Matheson). Prior to annealing, the samples were cleaned in acetone and methanol, each for 30 min. to dissolve any residual NiCl₂/DMSO solution and remove loose surface Ni deposits.

Annealed Ni wires were examined by SEM and TEM, and found to remain structurally intact and robust (fig. 9). Their size (length and diameter) did not change.

![Figure 9 a. TEM image of an unannealed Ni nanowire; b. annealed at 300°C; c. SEM micrograph of Ni wires annealed at 200°C.](image)
2.4. Preparation of SEM/TEM Samples

SEM samples were prepared on the day of the imaging. The side sections and top view images of the alumina, empty or loaded, were prepared by bending the sample over a knife blade. The aluminum substrate bent, while the alumina being more brittle snapped, exposing a fresh section of the porous structure. To image free nanowires deposited on the surface of aluminum substrate, the alumina matrix was chemically dissolved in 0.1M NaOH, at 50°C, for a few seconds to minutes followed by a careful rinse in deionized water and air drying. A standard conductive carbon tape or paste were used to affix the sample to the stage. The gold or carbon coating to reduce surface charging were not utilized, because the sputtered particles were on the order of the AAO/wire features. Most samples were reasonably conductive.

TEM is a suitable imaging technique for single nanowires, being only 20-30 nm thick. A suspension of nanowires was prepared by dissolving AAO in 0.1 M NaOH. After centrifuging, the caustic supernatant solution was replaced with water. Following 6 such rinses, the water was replaced with ethanol, sonicated to separate bunches of nanowires, and dropped onto a standard carbon-coated, Cu TEM grid. A 99.99% pure Ni standard TEM grid was used as a control sample for Electron Diffraction.

2.5. Density

The density of the nanowire material was determined as follows. The mass was determined from measurements of dissolved samples by Ion Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), while the volume was elucidated from SEM micrographs of the wires and template.

ICP-AES is a quantitative method for rapid elemental analysis of liquid samples. Atoms are thermally ionized and excited, emitting a photon upon decay to the ground state. The instrument
model used was Perkin Elmer Optima 3000DV, with ICP-WinLab software that collected the data, adjusted background noise and performed instrument calibration and calculations. Three wavelengths of characteristic Ni transitions were used: 232.003 nm, 231.604 nm, 221.647 nm. The detection limit of Ni was approximately 20 ppb. A four point standard calibration included zero.

A series of identical alumina template samples was prepared simultaneously and loaded with Ni nanowires of varying lengths corresponding to varying deposition times. The alumina and nanowires were digested in concentrated H₂SO₄, then diluted as listed in table 3, and the resulting sample was subjected to the ICP-AES analysis. Undissolved slivers of the aluminum substrate settled to the bottom of the ICP-AES tubes, and so their removal was not necessary. Suitable Ni standard solutions were prepared in the same acid matrix as the nanowire samples. Control samples of the solvent (blank) and void AAO template were also analyzed.

The volume taken up by the nanowires was deduced from the sample area, pore density, wire height and diameter (table 4). The sample area was measured using calipers. The pore density and wire lengths were estimated from SEM micrographs of AAO from the same samples that were analyzed by ICP-AES, mean wire diameters were obtained from SEM micrographs of the free wires, also taken from the same samples.
**Table 3a. ICP-AES Nanowire Sample Preparation Conditions (volume).**

<table>
<thead>
<tr>
<th>sample</th>
<th>dep. time min</th>
<th>template</th>
<th>deposition</th>
<th>nanowire radius</th>
<th><em>mc = mushroom caps</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>n/a</td>
<td>0.3 M H₂C₂O₄, 25 → V, °C, min.</td>
<td>0.5 M NiCl₂(DMSO)₃, 130-135 °C, under N₂, dry templates</td>
<td>11.5 nm</td>
<td></td>
</tr>
<tr>
<td>n8</td>
<td>0</td>
<td>0.109%</td>
<td>0.0129%</td>
<td>35.14%</td>
<td></td>
</tr>
<tr>
<td>n1</td>
<td>0.5</td>
<td>0.180%</td>
<td>0.0212%</td>
<td>4.92%</td>
<td></td>
</tr>
<tr>
<td>n2</td>
<td>1</td>
<td>0.245%</td>
<td>0.0955%</td>
<td>3.019%</td>
<td></td>
</tr>
<tr>
<td>n3</td>
<td>2</td>
<td>0.202%</td>
<td>0.0755%</td>
<td>6.692%</td>
<td></td>
</tr>
<tr>
<td>n4</td>
<td>4</td>
<td>0.112%</td>
<td>0.0304%</td>
<td>4.350%</td>
<td></td>
</tr>
<tr>
<td>n5</td>
<td>10</td>
<td>0.107%</td>
<td>0.0204%</td>
<td>2.617%</td>
<td></td>
</tr>
<tr>
<td>n6</td>
<td>12</td>
<td>0.108%</td>
<td>0.0290%</td>
<td>4.064%</td>
<td></td>
</tr>
<tr>
<td>n7</td>
<td>18</td>
<td>0.114%</td>
<td>0.0271%</td>
<td>3.991%</td>
<td></td>
</tr>
</tbody>
</table>

**Table 3b. ICP-AES Concentration Data (mass).**

<table>
<thead>
<tr>
<th>sample</th>
<th>concentration</th>
<th>mean conc.</th>
<th>N mass</th>
<th>density</th>
<th><em>mc = mushroom caps</em></th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>232.003</td>
<td>-872.5254</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>231.604</td>
<td>-216.4806</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>221.647</td>
<td>-540.1141</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>n8</td>
<td>232.003</td>
<td>-982.135</td>
<td>-0.167</td>
<td>0.0027</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>231.604</td>
<td>-195.4217</td>
<td>-0.0238</td>
<td>0.00045</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>221.647</td>
<td>-456.8614</td>
<td>-0.141</td>
<td>0.0079</td>
<td>20</td>
</tr>
<tr>
<td>n1</td>
<td>232.003</td>
<td>288.6356</td>
<td>0.490</td>
<td>0.0088</td>
<td>0.562</td>
</tr>
<tr>
<td></td>
<td>231.604</td>
<td>522.1919</td>
<td>0.635</td>
<td>0.0106</td>
<td>3.37</td>
</tr>
<tr>
<td></td>
<td>221.647</td>
<td>1816.784</td>
<td>0.561</td>
<td>0.0087</td>
<td>7.17</td>
</tr>
<tr>
<td>n2</td>
<td>232.003</td>
<td>3137.257</td>
<td>0.533</td>
<td>0.0059</td>
<td>0.608</td>
</tr>
<tr>
<td></td>
<td>231.604</td>
<td>5620.706</td>
<td>0.684</td>
<td>0.0022</td>
<td>3.65</td>
</tr>
<tr>
<td></td>
<td>221.647</td>
<td>1965.072</td>
<td>0.607</td>
<td>0.0076</td>
<td>5.62</td>
</tr>
<tr>
<td>n3</td>
<td>232.003</td>
<td>9412.285</td>
<td>1.60</td>
<td>0.036</td>
<td>1.671</td>
</tr>
<tr>
<td></td>
<td>231.604</td>
<td>1424.066</td>
<td>1.73</td>
<td>0.044</td>
<td>10.03</td>
</tr>
<tr>
<td></td>
<td>221.647</td>
<td>5448.026</td>
<td>1.68</td>
<td>0.050</td>
<td>3.743</td>
</tr>
<tr>
<td>n4</td>
<td>232.003</td>
<td>19116.04</td>
<td>3.25</td>
<td>0.14</td>
<td>3.34</td>
</tr>
<tr>
<td></td>
<td>231.604</td>
<td>27868.91</td>
<td>3.39</td>
<td>0.13</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>221.647</td>
<td>10954.96</td>
<td>3.38</td>
<td>0.13</td>
<td>3.75</td>
</tr>
<tr>
<td>n5</td>
<td>232.003</td>
<td>19901.86</td>
<td>3.242</td>
<td>0.060</td>
<td>3.354</td>
</tr>
<tr>
<td></td>
<td>231.604</td>
<td>28043.14</td>
<td>3.413</td>
<td>0.057</td>
<td>2.012</td>
</tr>
<tr>
<td></td>
<td>221.647</td>
<td>11029.71</td>
<td>3.406</td>
<td>0.071</td>
<td>4.525</td>
</tr>
<tr>
<td>n6</td>
<td>232.003</td>
<td>13566.41</td>
<td>2.303</td>
<td>0.038</td>
<td>2.386</td>
</tr>
<tr>
<td></td>
<td>231.604</td>
<td>20041.92</td>
<td>2.439</td>
<td>0.032</td>
<td>1.432</td>
</tr>
<tr>
<td></td>
<td>221.647</td>
<td>7827.599</td>
<td>2.417</td>
<td>0.040</td>
<td></td>
</tr>
<tr>
<td>n7</td>
<td>232.003</td>
<td>15865.23</td>
<td>2.69</td>
<td>0.13</td>
<td>2.80</td>
</tr>
<tr>
<td></td>
<td>231.604</td>
<td>23548.9</td>
<td>2.86</td>
<td>0.13</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>221.647</td>
<td>9219.424</td>
<td>2.85</td>
<td>0.12</td>
<td></td>
</tr>
</tbody>
</table>

Each sample was digested in 1.00 mL of concentrated H₂SO₄, then diluted with 5.00 mL of water (dilution factor of 6).

* average value of emission signal from three replicate spectra at each wavelength
Table 4. Measurements of nanowire dimensions and pore density from the SEM micrographs.

<table>
<thead>
<tr>
<th>Ni (nm)</th>
<th>d (nm) ± s (nm)</th>
<th>N</th>
<th>Nme (µm²)</th>
<th>α (%)</th>
<th>ρp (227 ± 8 pores/µm²)</th>
<th>Np = 618</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>0.0975±0.005</td>
<td>238</td>
<td>n/a</td>
<td>n/a</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0.225±0.02</td>
<td>108</td>
<td>n/a</td>
<td>n/a</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.596±0.03</td>
<td>84</td>
<td>n/a</td>
<td>n/a</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.61±0.07</td>
<td>45</td>
<td>0.034±0.01</td>
<td>337</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.60±0.06</td>
<td>32</td>
<td>0.038±0.01</td>
<td>1427</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>1.62±0.06</td>
<td>27</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>1.61±0.07</td>
<td>36</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ni is the sample size of nanowire lengths measured
Nme is the sample size of mushroom caps measured
α % of pores with mushroom caps
pore density is 227 ± 8 pores/µm², Np = 618

Figure 10. Examples of SEM micrographs used to measure the nanowire dimensions to determine the density of the nanowire material.
a. surface of AAO with pores visible used to find the pore density,
b. side view of AAO used to measure the lengths of the pore and full-length nanowires,
Figure 10. Examples of SEM micrographs used to measure the nanowire dimensions to
determine the density of the nanowire material.
c. short wires within template and d. free used to measure the average length and diameter,
e. long wires within template (sideways) and f. free used to measure the average length and
diameter,
g. surface view with mushroom cap-like overgrowth of long wires, used to measure the
average radius of the caps.
2.6.1 Conductance Samples

The value of the electrical conductivity of a metallic nanowire, especially as it compares to that of the bulk metal, may shed light on the degree of disorder, impurity content and possibly quantum size effects. In this study we measured the resistance of a single nanowire.

A sharp probe of a Scanning Tunneling Microscope (STM) was used to approach and contact a small number of wires at a time.

When attempting to measure the electrical conductivity of such a small system, making proper contacts is not a trivial problem. Since the nanowires in the Ni-loaded AAO are conveniently parallel, a common macroscopic electrode may be deposited to short all wires on one side of the template. One can then determine the resistance of a single wire if it is contacted

![Diagram]

Figure 11. STM sample preparation scheme.
at the other side to close the circuit. The stages of sample preparation are illustrated in fig. 11.

The barrier layer side of an AAO template is more uniform and flat, therefore it was chosen as the side from which to approach single wires with the STM tip. We call this side "the barrier layer side" or "the underside" to distinguish it from the surface of the AAO template as formed. To expose the nanowire tips from the barrier layer side all underlying layers must be carefully removed: the AAO on the other side of the aluminum substrate, aluminum, and finally the barrier layer.

2.6.2. Preparation of STM Samples

The surfaces of the samples used were first cleaned by ion milling (Ar at 2.3 mtorr; 3.0 kV; < 2-4 mA, 5-10 min at etching rate of 20 nm/min), which also removed any Ni overgrowth. Thick (>500 μm), conductive Ag film was evaporated to short the Ni wires; a Ag wire contact was glued to this electrode with conductive epoxy (type H21D, Epo-Tec) and covered with a non-conductive epoxy to protect and support the thin structure (fig.11). The Ni-containing AAO on the other side of the sample was dissolved in 0.1M NaOH, at 40°C. The Al layer was dissolved in a CuCl2/HCl(ω) solution, at room temperature. At this stage the Ni wires were only covered with a thin (~20 nm) barrier layer of alumina, which was then removed by placing the sample in H₃PO₄ solution (35 mL/L), at 50°C, for 12-14 min. SEM micrograph (fig.12) shows the Ni nanowire tips exposed after the barrier layer was removed. The sample was throughoutly rinsed with deionised water and air dried between all chemical dissolution steps.
2.6.3. Scanning Tunneling Microscope (STM)

The experiment was performed in ambient air at room temperature. The design of the STM chamber is for Ultra-High Vacuum (UHV) experiments (2,3). It sits on a limestone table supported by 4 pneumatic legs (Newport). The sample block and STM probe are isolated by 3 stages resting on viton loops. The sample mount is additionally isolated by glass rod and bead support (2,3).

Coarse approach to sample is carried out by a linear piezoelectric inchworm (Burleigh Instruments). The scan tube mounted within the inchworm permits fine control of the probe in the perpendicular direction (inner electrode, Z) and laterally (4 outer electrodes,
X+, X-, Y+, Y-). The inchworm and scanner are controlled by RHK STM-100 electronics and software.

The STM tip fits into a metal tube within a Macor nosepiece glued onto the scanner tube. The STM tips are cut from Pt-90%, Ir-10% wire (0.010" in diameter, ESPI) (fig.13).
References

3. Results & Discussion

3.1.1. STM Measurements

The nanowire resistivity was measured using the Scanning Tunneling Microscope (STM). Two types of measurements were carried out: in the first set (of the STM measurements) the tip is pressed into the sample surface and withdrawn. The tip-sample current is analyzed as a function of tip displacement, both towards and away from the sample (I-Z measurements).

The I-V spectra are the second set of STM experiments: the current (I) response is recorded as a function of varying voltage (V) while the tip is pushed against the nanowire sample, at various levels of approach.

The nanowire conductivity is calculated from both types of experiments, knowing the wires' structural parameters and the measured conductance, according to:

\[ G_w = \sigma_w \times \frac{l}{\pi r^2} \quad (3-1) \]

where \( G_w \) is the measured conductance, \( \sigma_w \) is conductivity, \( l \) is the template thickness (approximating the nanowire length) and \( r \) is the average radius of nanowire cross section.

3.1.2. Contact

To obtain the resistance of nanowires, a contact must be established at both ends of every measured nanowire. Their size poses a major problem in handling and providing a reliable and reproducible contact. The minute size and the large density of nanowires in a sample means that we need to be able to determine the number of individual nanowires being contacted in some independent fashion.
All nanowires are shorted on the surface of AAO by a thick Ag electrode (section 2.6.1). It is likely that a thin NiO layer covers the tips of the nanowires, between the Ni and the Ag. (In the preparation procedure a sample was momentarily exposed to air between surface cleaning (by ion-milling) and Ag evaporation in order to deposit a mask to prevent interlayer shorting). The nanowire tips at the barrier layer side are also covered with air grown NiO, since that side of the sample is open to air to perform STM measurements.

At room temperature the conductivity of NiO is high; however, electron scattering may occur at Ni/NiO and NiO/Ag interfaces.

The contact from the barrier layer side is created with a sharp probe of the STM microscope touching one or a few nanowires at a time. The local geometry of each contact is unique and irreproducible, however the basic stages of contact development are the same. First, the STM tip must traverse a barrier consisting of the air gap, barrier layer residue and air-formed NiO layer. During retraction, elongated junctions may arise. Due to the microscopic sizes of both electrodes, constricted point contacts are likely to form during the approach and retraction stages. Then the ohmic contact may be established once the barriers are overcome.

All macroscopic contacts in the other parts of the circuit are assumed perfectly ohmic.

3.1.3. Quantum Conductance

Dynamic conductance fluctuations at the atomic-scale contacts were predicted and observed (for example: 3.1, 3.2). The aggregation geometry of the atoms at, and the size of junction determine the properties of such a contact, rather than the characteristics of the bulk material, so much so that nanowire junctions have been successfully described with concepts derived from cluster models (3.3).
During the physical separation of the electrodes involved in a nanometer-scale contact, the evolving junction experiences a series of atomic rearrangements. Certain shapes and structures of the narrowing have enhanced stability, (similar to the "magic numbers" phenomenon in clusters) and sustain certain amounts of stress before further elongation of the junction. The observed step-like conductance quantization is due to a limited number of allowed conducting states, and correlates well with a series of atomic rearrangements \(^{(3,3)}\).

Our STM measurements involve very small structures (tip and nanowire). It is, therefore, likely that contacts form in the size range where conductance quantization occurs and evolve during the tip's advance and retraction. It has been shown that a point contact can be drawn even between two macroscopic conductors \(^{(3,4)}\). Constricted contacts may form through tunneling barriers (air, partly broken NiO/bl) during tip approach or through elongated protrusions drawn out of the sample/tip material during the retraction. The Pt/Ir tip we use is softer than the Ni wires, therefore an elongated nanojunction should be composed of the tip material interacting with the sample, during the final moments before the contact is lost.

3.1.4. Point Contact Current Fluctuations

Conductance oscillations are observed in Mechanically Controlled Break Junctions (MCBJ) and other transport measurements in constricted systems (for example: 3.4, 3.5, 3.6).

In point-contacts with a diameter comparable to the Fermi wavelength, \( \lambda_F \), of the free carrier the conductance, \( G \), should be quantized according to:

\[
G(n) = \frac{2e^2}{h} \times \sum_{i=1}^{N} T_i(n)
\]  

\[ \text{(3 - 2)} \]
where $T_i$ is the transmittance for the $i$th channel ($T_i(n) = T_{is}(n)$ for diamagnetic wires for a given atomic configuration $n$ in a nanowire). This function suggests that the steps are dependent on specific atomic arrangements, the units of steps being $2T_i(n) e^2/h$, rather than simply in units of $2e^2/h = G_Q$ as previously suggested. Only in the strict absence of backscattering due to surface roughness and disorder in an ideal constriction, is the conductance purely ballistic and $T_i(n) = 1$, and conductance steps are in intervals of $G_Q = 2e^2/h$. Therefore, the units of quantized conductance may vary from sample to sample, and also depend on the experimental setup (temperature, atmosphere, speed etc.). This further complicates the task of differentiation of the steps arising from size effects from those due to the consecutive contact to several nanowires.

A control STM measurement on gold (99.999% pure, annealed in air) surface produced the expected staircase behaviour on breaking a contact between the STM probe tip and the Au sample.

The current step size in our I-Z spectra on Au is close to $2e^2/h = G_Q$ in agreement with several other studies \(^{(3.6,3.7,3.11)}\) of quasi-ballistic conductivity when only a small degree of disorder is present in the surface and in the nanoneck formed in the final stage of tip-retraction just before the contact is lost.

3.1.5. The Probe Approach and Feedback

IZ measurements record current changes versus the varying physical separation of the two electrodes: the nanowire tips in the sample and the sharp STM probe, connected to an outside circuit and driven by a piezoelectric drive device. The radius of curvature of our STM tip is of the order of 100 nm flaring out to a macroscopic wire where it is mounted. The inter-wire spacing is about 30-80 nm (the cell and pore dimensions of the template both depend on the forming voltage and temperature). This ratio allows us to contact a single wire or a few wires when brought in close contact with a sample surface. We are confident that we obtained the properties of a single...
wire since these were deduced from a large number of approaches in several fresh areas of a sample.

Guided by the feedback mechanism, the STM probe approaches the sample until a specified current is attained. Then the feedback maintains a steady current and the voltage between the sample and the tip is held at a selected level by fine tuning the separation using a feedback circuit. This tip position, with respect to the sample, is assigned as a reference point of 0 nm tip displacement. Once the reference interelectrode separation is established, the instrument is ready to perform an IZ measurement. The feedback mechanism is disconnected for the duration of the measurement: tip displacement in case of IZ measurement, or voltage sweep during the IV spectra.
3.2.1. IZ Measurements

During the IZ measurements, the probe approaches the sample and then retracts by a specified distance, with the feedback momentarily disconnected. The typical tip displacement, 300-600 nm (approximately from ± 150 nm to ± 300 nm), is manually optimized to the sample response. During the tip's approach and retreat, several jumps in current are normally observed and recorded (fig. 14).

![Graphs of conductance jumps](image.png)

Figure 14. The conductance jumps in typical IZ measurements, for 4 different samples.

The conductance steps that are large enough to be clearly resolved may be ascribed to a number of phenomena. First, semiconducting, native NiO coats the nanowire tips, since they are
exposed to air (see fig. 11). This layer is broken or crushed by the STM probe pushing into the sample surface. The details of this process are rather complex, taking into account the variable geometry of tip and sample, the distribution of wire sizes and variable barrier (NiO/residue of barrier layer/adsorbates) characteristics. The immense variability in each of the above mentioned properties are sources of noise throughout the measurement, as a distinct, new barrier must be overcome on every nanowire approached.

The smallest, barely resolved and rather flat steps are associated with tunneling current. The tunneling current should normally increase smoothly. However the contact may not evolve uniformly due to the previously mentioned surface oxide, sample roughness and the limited number of conductance channels available. Chaotic, disordered and restricted contact channels are likely to form and break during a given measurement. Those and other causes contribute to the observed fluctuations in tunneling current.

Once the NiO barrier is broken, further approach brings the tip into a metallic contact with one or a few nanowires exposed at the surface of the sample. The current changes from tunneling to ohmic. Meanwhile the probe continues advancing towards the sample and additional current bursts are recorded as adjacent nanowires are contacted in parallel.

3.2.2. Unit of Conductance Jumps

Dr. D. Davydov has observed that during an IV measurements taken in the same experimental setup, the initial contact is established to a single nanowire, and only very rarely two or more wires are initially contacted simultaneously. One might assume that the contact
resistance is identical for both IZ and IV measurements. If so, the IZ spectra might be understood using the $R_Q$, contact resistance obtained from the IV measurements.

Initial events in the said IZ spectra, as usual, may be attributed to tunneling through a barrier and to the breaking of the NiO barrier. Those events will have a rather high resistance, and thus only contribute to a slow increase in current or to very shallow conductance steps. Once those barriers are overcome, the magnitude of the early conductance steps often corresponds to fractions of $2e^2/h$, and may hence be attributed to wire conductances whose inverse would be $R_w$. Therefore, in those particular spectra, the steps would presumably be predominantly due to the resistance of nanowires modified by the contact resistance.

The magnitudes of such conductance jumps are found to lie in the range 0.1 to several $G_Q$ depending on the specific arrangement of nanowires contacted during a particular measurement plus any contact resistance present.

The final contact is made to one or a few nanowires at a time with a contact cross-sectional area of hundreds of $\text{nm}^2$ -- a rather large contact area, therefore the large conductance "jumps" or "steps" correspond to integer multiples of the nanowires being contacted and therefore conducting in parallel, including any contact resistance. If:

$$G_{\text{wire}} < G_{\text{Quantum}}$$

(3-3)

then the measured conductivity is $G_{\text{wire}}$. For the opposite case, where:

$$G_{\text{wire}} > G_{\text{Quantum}}$$

(3-4)

the observed steps will be $G_{\text{Quantum}}$ rather than $G_{\text{wire}}$. 

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3.2.3. Resistance shift

The notion that the conductance steps (expressed in units of $G_0$) are representative of the nanowire conductance is also supported by the observed dependence of the measured resistance as a function of the wire dimensions. The diameter and length of wires in the various samples studied vary. The changes in size of the wires are assumed insignificant with respect to the contacts at either side of measured wires. Therefore, the measured resistance, $R_m$, should remain constant since it is independent of wire dimensions if the contact resistance, $R_C$, is the sole contributor to the measured resistance. However $R_m$ is expected to change from sample to sample if

$$R_m \propto R_w$$  \hspace{2cm} (3-5)

according to the relation

$$R_w = \rho_{\text{wire}} \cdot l/\pi r^2$$  \hspace{2cm} (3-6)

A linear dependence in measured resistance with respect to the quantity $l/d^2$ is observed (fig. 15). The best fit line does not pass through zero $\Omega$, rather the y-intercept is at $15 \pm 3 \ \Omega$. This residual resistance is approximately equal to the resistance quantum, $R_Q \approx 13 \ \Omega$, the resistance of a single point contact.

This finding implies that the appropriate model for our nanowire resistance measurements is a very narrow wire (in an array of wires) connected to the STM tip via an even narrower junction which contributes a resistance in series with the resistance of the nanowire. The resistance of these junction resistors would correspond to the permissible quantized values representing the allowed quantum states for the particular atomic arrangement in the connecting "nanoneck". The
Figure 15. Measured resistance of nanowires is linearly dependent on the nanowires' dimensions, the quantity \( l/d^2 \). The shaded area represents the resistance due to the nanowires, while the area below that represents the residual resistance.

Sources of noise described below occasionally contribute additional resistance of a lesser value, over and above \( R_Q \).

The shaded area in the plot represents the wire resistance, \( R_w \), while the residual resistance underneath it represents the constant contact resistance, \( R_C \).
3.3.1. Why is the Conductance (IZ) Distribution Broad and Overlapping

Steps are clearly visible in most IZ measurements, however the step heights are highly variable among different sets of measurements obtained even for the same sample. As a result, the peaks in histograms constructed from the observed current step heights (in units of $G_0$) become broadened to the point where peak assignment is uncertain (fig.16).

The peaks in the Distribution of Conductance Steps are well defined in two of the four samples studied. The peaks in sample N01 coincide with integer multiples of $G_0$, suggesting that what is being observed is quantized conductance at a point contact rather than the conductance due to multiple nanowires. For sample N02, the distribution is uncorrelated with the conductance quantum, however it does not correspond to the conductance derived from the IV spectra for this sample. For the other two samples, N03, N04, the conductance step height distribution shows no distinct peaks.

The resistance values obtained from the histograms of current step height, from the IZ measurements of two samples (N01, N02) do not correlate with the resistance obtained from the IV measurements. We propose that the difference in the conditions of the measurements is responsible for these differences. The IZ measurements are performed while in motion, whereas only bias changes during the IV measurements and the inter-electrode separation remains constant. The dynamic nature of the IZ measurements creates more variability in the contact and is more prone to artifacts, thus the resistance obtained from the IZ measurements is found to be less reliable than that found from the IV measurements.

Several factors may contribute to the observed variability in the results of the IZ measurements: contact phenomena, variability in the wire dimensions and composition, intrinsic and surface impurities.
Figure 16. Conductance step height distribution histograms for 4 samples. Bin unit is $2e^2/h = G_0$. 
3.3.2. Point-contact disorder

The current steps often display dips and edge rounding (fig. 17). This phenomenon was previously experimentally reported\(^{(3,4)}\) and simulated\(^{(3,9)}\) in terms of point-contact transport. The depth of the simulated dips is proportional to the increase in disorder\(^{(3,9)}\) during structural transformation of the contact. Our STM measurements involve relatively small structures that may form a constricted contact conductance channel which evolves during the tip's advance and retraction. Actually small contact size is not totally essential, point contact can be drawn between two macroscopic conductors\(^{(3,4)}\). The Pt/Ir tip we use is softer than the Ni nanowires, therefore the elongated neck is likely composed of the tip material interacting with the sample, during the final moments before the contact is lost. Quantized conductance resulting from such constricted contacts will generate steps in the IZ spectra, and thus smear the nanowire conductance-step distribution. The magnitude of the conductance quantization would be \(\leq G_Q\) and indeed many

![Figure 17. Examples of dips and edge rounding in the current steps of IZ measurements.](image-url)
such steps are observed. Now we turn our attention to the effect of the resistance of a point contact, $R_Q$, in series with the resistance of a nanowire, $R_w$, as a source of added system resistance. The maximum resistance contribution is $R_Q = 13 \text{k}\Omega$, the resistance of a single point contact. This value is of the same order of magnitude as the resistance of a single nanowire and cannot be easily ignored in the measurements, thus it is a significant source of broadening.

![Example of differences in approach and retreat measurements](image)

**Figure 18.** An example of the differences between approach and retreat IZ measurements. Note the abrupt raise in current in the approach measurement compared to the shallow initial steps in the retreat.

The current response is recorded during both the retraction and the approach of the tip to the nanowires. Both sets of measurements should result in steps of equivalent heights. There are however some structural differences between the the two. The approaching tip encounters intact NiO/bl barrier which must be crushed or breached before ohmic contact is established. Several point contacts may contribute conductance channels at any moment. The retracting probe
withdraws an elongated, constricted "nanoneck" and loses the last contact abruptly. Therefore the retraction (IZ) spectra should be somewhat different from the approach spectra (fig. 18).

The recorded current fluctuations for the approach have slowly increasing initial current, which probably correspond to tunneling and the arduous process of breaking the existing barriers (barrier layer, NiO). In comparison, most retraction measurements lose their conductance abruptly near the end of measurement, as expected for a process involving the separation of electrodes. Additionally the saturation currents observed in the approach and retraction measurements vary somewhat. However this appears to be random and is probably due to thermal drift.

3.3.3. Few Wires Fill Pores Completely

The deposition of Ni into AAO template is non-uniform (see fig. 6c), thus only a fraction of the nanowires exposed to the STM tip actually make contact to the Ag electrode film. From the Ni density experiments we estimate that as much as 10-50% of the pore volume may be completely empty, which is due either to empty pores or very short wires. This increases the real spacing between the conductive wires and allows us to contact only a few wires with a probe whose radius of curvature is large compared to the wire diameter (compare figures 12 and 13).

The density of the nanowire material was deduced indirectly from two sources: the mass was found using ICP from the Ni concentration in aqueous samples produced by digesting the wires, and the volume of the nanowires was deduced from SEM micrographs of those samples (section 2.5). The density of the nanowire material (fig. 19) was found to be significantly less than the density of bulk Ni, 8.90 kg/L \(^{2-1}\). The calculated density ranges from 45% to 80% of bulk Ni.
density, with the highest density of approximately 80% obtained for the very shortest wires 
(deposited for only 30 s).

![Graph of Ni Nanowire Density vs. Deposition Time]

Figure 19. Density of Ni nanowires as a function of the electrodeposition time. Dashed horizontal line represents the density of bulk Ni.

This finding implies that a significant portion of the pore volume is devoid of nanowires. There may be two types of such vacant spaces: small spaces encapsulated within a wire body, and unoccupied (empty or incompletely filled) pores.

The former type of spaces may likely be filled with the electrolyte fluid occluded during the electrodeposition of Ni into the pores (section 3.5.4.). Gas inclusions are another possibility where fluid inclusions were incompletely encapsulated within the Ni matrix and thus remained open to air. With time, some of the encapsulated fluid would evaporate and/or seep out leaving behind a void space within the wire.

We propose that such bubble inclusions, whether liquid or gas filled, may only account for a
relatively small portion of the unoccupied pore space. A large number of small inclusions would cause wires to become fragile, which is contrary to the observed resilience of nanowires to mechanical stress such as boiling or centrifuging. Both liquid and gas inclusions are non-crystalline regions, and should be detectable by TEM as low contrast areas, if their mean diameter is larger than about 2 nm. Variable contrast domains are indeed observed, however no obviously low contrast regions are visible, therefore we conclude that there are few or very small (< 2 nm) occluded bubbles.

Small, nanometer sized, inclusions would drastically reduce the effective diameter of a wire, when its total diameter is 12-30 nm. Such sites may affect the conductance when the reduced local wire cross section is comparable to the mean free path of electrons. In small domains additional electron scattering would occur as a result of electrons interacting with wire boundaries, and measured resistance of wires would increase.

Empty pores are often observed in SEM micrographs. Variable deposition efficiencies in adjacent pores and over larger distances is commonly observed (fig.20). The pore structure appears uniform, besides, the pore walls act only as boundaries of the deposition process. It is the barrier layer that takes active part in the electrodeposition, by delivering the current in the cathodic half of the AC cycle. Hence any inhomogeneity in barrier layer properties would affect the uniformity in the wire growth. Our observations imply that the electrical properties of the barrier layer are inhomogeneous over a micron size scale as well as with respect to the immediately adjacent pores.

We estimate that 10-50% of all pores must be completely or largely empty in order to account for the calculated density of ~90% of bulk Ni, which also takes into account a small (up to 10%) amount of inclusions, impurities, oxide layers etc.
Figure 20. Variable deposition efficiency results in nanowires (seen as bright spots in pore openings) with variable lengths. Diagonal cut through alumina template, SEM image.

3.3.4 Variability in Wire Diameter

The wire conductance as determined from the current steps is a function of the dimensions of the wire. Therefore any variability in the nanowire dimensions would be expected to affect the distribution of conductance values. It is known that low periodicity AAO templates have a 10-15% half-width value for the distribution in pore diameters sizes (3,10). Since the conductance is proportional to the square of radius, a broadening of up to 30% in conductance distribution would be anticipated.

We assume our nanowires to be cylindrical, however electron microscopy (SEM and TEM) shows them to be faithful representation of the template, with pore walls not always parallel and sometimes branching, swelling or locally narrowing (see figures 4, 5, 6, 9, 10).
3.3.5. Adsorbed Material

The nanowire samples are cleaned with ethanol and/or acetone prior to the resistance measurements performed in air. There are adsorbed gases/water or a native nickel oxide covering the surface of nanowires and contributing to additional impurity scattering and thus to the broadening of the observed conductivity distribution. This conclusion is based on observed deviation in tunneling current between metallic electrodes in MCBJ caused by gas adsorbed on the surface.

3.3.6. Tip-Sample Geometry

Additional noise may come from the random geometry of the tip and sample for example, multi-tip probes. Both, the probe and sample, become physically deformed during a measurement. Indentations of a few hundred nm were observed by optical microscopy on the surface of a nanowire sample following a series of STM measurements. Deeper holes of the order of 1-2 µm were sometimes observed after the tip crashed into a poorly conductive region of a sample.

A similar effect may result from the probe sliding on the sample rather than moving in a direction strictly perpendicular to the surface of the sample. Exposed nanowire tips are assumed to be of equal height, based on the low mean roughness of the barrier layer side of the AAO, which may be as low as a few nanometers, depending on the quality of the original aluminum surface and its pretreatment. However, the plane of wire tips is not necessarily normal to the STM tip due to the details of the sample preparation and mounting. This may affect local tip-sample geometry as the tip skids on the sloped sample rather than being pressed down perpendicular to the sample surface.
3.3.7. The Speed of Measurement

To observe point-contact current oscillations, the electrodes must be parted with angstrom resolution. Costa-Krämer (3.11) noted that the speed of measurement affects the deformation process of point contact channels, and it, therefore, affects the observed conductance quanta. He considered a speed range of 200-100 000 Å/s on nanochannels pulled from a gold surface. The approach of our probe is smooth at the rate of approximately $7 \mu m/10 ms = 70 000 000$ Å/s. The highest electrode separation speed considered by Costa-Krämer is 100 000 Å/s, at which the position of the first conductance peak is decreased by 5%. Extrapolating the trend, the first conductance peak would be at $0.8 - 0.7 \left(2e^2/h\right)$ for the estimated speed of electrode separation in our STM measurements. Subsequent steps would still have a $2e^2/h$ magnitude, shifted by $0.8 - 0.7 \left(2e^2/h\right)$, according to Costa-Krämer. With such a shift, the point contact fluctuations become comparable to the nanowire conductance steps.
3.4.1. IV spectra

The current response to a voltage sweep at constant interelectrode distance is the second type of our STM experiments.

The feedback mechanism maintains a constant current and voltage at a manually set level. During a measurement the feedback is momentarily disconnected and the tip-sample separation remains constant. However, between the series of individual IV measurements the tip is brought closer to the sample to break the NiO layer by gradually reducing the tip-sample bias manually, while required to register the same current by the feedback mechanism. Several IV spectra are recorded at each stage of tip approach. Such a series of IV spectra shows a transition from a tunneling regime initially in air and ultimately through a NiO layer, to a metallic conductance when that oxide barrier is mechanically crushed.

In the tunneling regime, the IV curve is non-linear and the resistance,

$$ R = \frac{I}{V} \quad (3-7) $$

is due to tunneling through the nickel oxide barrier. The first derivative, dI/dV, has an even more exaggerated, almost parabolic curvature, which quickly becomes a flat function when the tip finally makes metallic contact and the IV function becomes linear.\(^{1,9}\) (fig. 21). It is impossible to pinpoint the exact resistance at which this transition occurs, due to the variability in the wire diameter, the local thickness of NiO barrier and other random contributions. Therefore the transition is qualitatively assigned to a narrow range where the non-linear character of tunneling resistance initially subsides giving way to the linear IV relationship, based on a large number of measurements.\(^{3,4}\) (fig. 22).
Figure 21 a. An example of IV (inset dl/dV) dependence near the tunneling-to-metallic transition for NO1 sample.

**linear IV dependence, NO1**

![Linear IV dependence graph](image)

**non-linear IV dependence, NO1**

![Non-linear IV dependence graph](image)
Figure 21 b. An example of IV (inset dI/dV) dependence near the tunneling-to-metallic transition for NO2 sample.
Figure 21 c. An example of IV (inset dI/dV) dependence near the tunneling-to-metallic transition for NO3 sample.
Figure 21 d. An example of IV (inset dI/dV) dependence near the tunneling-to-metallic transition for N04 sample.
Figure 22. Histograms composed of the measured resistance values for each sample. Hatched bars represent the linear (metallic) IV dependence, gray bars represent the non-linear (tunneling) IV dependence.
The metallic resistance at the transition from tunneling to metallic transport represents the resistance of one nanowire. The distribution must encompass the variability range for the wires and their environment at the time of measurement.

Knowing the average microscopic dimensions of the wires, their resistivity may be obtained from the reciprocal of conductivity (eqn. 3-1):

$$\rho_{w+c} = \frac{1}{\sigma_{w+c}}$$

where $\sigma_{w+c}$ is the measured conductivity of nanowires including a contact resistance of $\sim 15 \pm 3$ kΩ (approximately equal to $R_Q \equiv 13 k\Omega$). The wire resistivity is approximately $1.4 \pm 0.3 \times 10^{-4}$ Ω cm. Figure 23 shows that the resistivity is consistently two orders of magnitude higher than that of bulk Ni, $\rho_{\text{bulk NI}} = 6.03 \times 10^{-6}$ Ω cm$^{(2.1)}$.

![Nanowire Resistivity vs. Wire Dimensions (l/d^2)](image)

Figure 23. Ni nanowire resistivity (triangle/solid line) as a function of quantity $l/d^2$. Note that at $1.4 \pm 0.3 \times 10^{-4}$ Ω cm, the resistivity is two orders of magnitude larger than the bulk Ni resistivity and it is independent of the wire dimensions.
3.5.1. Large Resistivity of Nanowires

The resistivity of Ni nanowires is found to be 100 times greater than that of bulk Ni, even after the contact resistance is subtracted. The fabrication method of this material offers a partial explanation for this increase.

3.5.2. Chemical Composition, Electron Diffraction

A series of electron-diffraction patterns (in TEM microscope) of free Ni nanowires consistently show that Ni metal is the major component of the wire, even after the strongly oxidizing TEM-sample preparation process. The spots in the electron diffraction correspond to the reflection from the index planes, similar to the X-ray diffraction. An X-ray database was used for reference. While X-ray diffraction is a very rigorous and quantitative technique, electron diffraction is more qualitative and comparative.

Figure 24. Electron diffraction pattern for Ni nanowires (left pattern is for the unannealed, right is for the annealed Ni wires). Spots b, c, d, e and h may be attributed to Ni. Spot a is due to γ-NiOOH, spot b is due to Ni/NiO/γ-NiOOH; spot c is due to Ni/γ-NiOOH/Ni₂O₃; spot d is due to Ni/γ-NiOOH; spot e is due to Ni; spot f is due to NiO; spot g is due to Ni₂O₃; spot h is due to Ni/NiO.
While the e-diffraction patterns were found to be complex, the metallic fcc-Ni is the main component of the nanowires. That conclusion is drawn from an analysis of the relative intensities of the spots possibly corresponding to the fcc-Ni indices\(^{(3,12)}\) comparing them to the intensity of many other spots present, mostly attributable to a host of Ni oxides and hydroxides\(^{(3,12)}\). The characteristic Ni pattern is present in all the wires studied, except for the fully oxidized sample that was purposely oxidized during preparation as a control sample. The Ni pattern is significantly more intense than the oxide/hydroxide patterns (fig. 24). The oxidized sample not only lacks the Ni spots, but also has a much simpler oxide/hydroxide pattern (fig. 25d).

A thin layer of material with an electron density, and therefore contrast, different than that of the inner part of a wire appears to coat all wires examined by TEM, including those samples for which e-diffraction was taken. The coating is not as visible on the fully oxidized sample, which shows uniform contrast throughout (fig. 25).

We propose this coating layer to be due to nickel oxides/hydroxides covering the wires. The e-diffraction spots for many Ni oxides and hydroxides coincide with each other and with spots due to metallic Ni, therefore it is not possible to deduce accurately which oxides are present and in what ratios. Rather, we assume the coating to be a complex mixture of Ni oxides and possibly hydroxides formed mainly during the preparation of the samples for TEM microscopy, since a strong oxidizing agent is used in that process.
Figure 25 a. unannealed Ni nanowire, b. nanowire annealed at 500°C, c. purposely oxidized Ni nanowire, and d. the e-diffraction pattern of the oxidized sample (diffuse rings are due to NiO and γ-NiOOH). Notice the low contrast coating on the wires marked by arrows, the coating is not as obvious on the oxidized control sample.
3.5.3. Crystallite Size, X-Ray Diffraction and TEM

X-ray diffraction of whole AAO films with Ni wires embedded shows a broad, low intensity 200 line corresponding to scattering off the (100) plane; the highest intensity Ni line 111 (2θ ~ 44 deg) is obscured by a strong Al 200 line \(^{(2-12)}\) (fig. 26). The presence of the Ni 111 peak on the left shoulder of the Al 200 line is indicated by strongly asymmetric appearance of the Al 200 line. Other Ni lines are not observed probably due to their much lower intensity.

![X-ray diffraction of Ni nanowires within AAO matrix on Al substrate.](image)

Figure 26. X-ray diffraction of intact Ni nanowires within AAO matrix on Al substrate. The top plot is a control sample of empty alumina template. The inset shows the calculated X-ray powder diffraction pattern of fcc-Ni. Note the low intensity Ni 200 line at ~52 deg, and Ni 111 line on the left shoulder of the strong Al 200 line at ~44 deg. The broad peak at ~27 deg is due to alumina.

This indicates that nanowires are crystalline rather than amorphous, however the crystallite size is small as calculated from the peak width of the 200 line, from the Scherrer equation

\[
D = \frac{0.93 \lambda_{\text{X-ray}}}{B \cos \theta}
\]

where \(D\) is the average crystallite size in Å, \(\lambda_{\text{X-ray}} = 1.54056\) Å, \(\theta\) is the position of the line in radians, and \(B\) is a constant calculated from the difference of the half-width of the peak for the sample and the standard,
\[ D = \frac{0.93 \times 1.54056}{0.007167 \times \cos 0.4343} = 220.34 \, \text{Å} \quad (3-10) \]

The wire diameter of this sample was 36-40 nm, therefore, the average crystallite size of 22 nm indicates polycrystalline Ni nanowires. Small crystallite size also does not indicate a strongly preferred orientation of crystallites which might be expected of a material deposited in narrow pores where two directions are restricted (radial) and one is not (axial). One has to remember that the calculated value of \( D \) is an average, thus a weak (axial) orientation may still occur.

For CdS nanowires fabricated in similar AAO templates, an average crystallite size was also calculated from the intensity and width of several XRD peaks \(^{(1,24)}\) and found to be 6-20 nm, depending on the pore size.

Very narrow wires are comprised of a large number of crystallites, at least in the axial direction, with a large number of crystallite boundaries. It is well known that electron scattering at boundaries contributes to the overall electrical resistivity of metals. Considerable increase in resistivity has been observed in nanocrystalline phase in Ni, Fe, Cu, Pd \(^{(3,13)}\) and many other metals. The excess resistivity of electroplated nc Ni films \(^{(3,13)}\) has been found to increase almost linearly with increasing intercrystalline volume fraction. At a mean grain size of 15 nm the resistivity was +10 \( \mu \Omega \text{cm} \) above the conventional polycrystalline Ni with negligible intercrystalline component, 6.2 \( \mu \Omega \text{cm} \); at grain size of 34 nm, the resistivity was only +4 \( \mu \Omega \text{cm} \) above \(^{(3,13)}\). It is, therefore, reasonable to assume an increase in resistivity by a factor of 2-3 due to the small crystallite size of 22 nm and a high proportion of intercrystalline component in our nanowires.

Contrast in TEM micrographs is a measure of the differential electron density, and although one cannot determine grain size based on the contrast alone, it does qualitatively suggest the presence of grains smaller than a single wire (see fig.25). According to Wang et al. \(^{(1,29)}\) the volume fraction of a crystalline component is approximately 60%, at a mean grain size of 10 nm.
Naturally the intercrystalline component (grain boundary, triple line and quadruple node) makes up the remainder of the volume. These component ratios apply to bulk nc material, however an analogous relationship may exist for spatially restricted nanostructures, perhaps considering even smaller crystallite sizes. Therefore, if our nanowires are polycrystalline, we conclude that a highly defective, intercrystalline material makes up an appreciable fraction of the nanowire's volume. Even so, such an intercrystalline component can only be responsible for a 20-30% increase in resistivity\(^{(3.13)}\).

### 3.5.4. Impurities

A second major source of resistive electron scattering is a possibility of electrolyte fluid inclusions and a relatively high concentration of impurities.

Fluid (also see section 3.3.3.) may become occluded by the reduced nanowire material during Ni deposition in the pores of template. The composition of such inclusions would be identical to that of the depositions solution: NiCl\(_2\) \text{an.} in DMSO.

Impurities within the nanowire material can act as a source of resistive electron scattering. The reactants used are all of reagent quality and the template is produced from a high purity Al foil (99.9% - 99.999%). The relatively low purity of anhydrous NiCl\(_2\) (98%) is by far the greatest source of contaminants derived from reagents. The deposition was carrier out under N\(_2\) at atmospheric pressure, however the glass line has been frequently opened to air to replace leads.

Besides airborne impurities, there may be a contamination inherent to the chemical nature of the solution. Chloride is the anion in the deposition solution, it is known to be highly corrosive and may cause additional Cu contamination from copper alligator clips. In an effort to minimize the Cu contamination of the NiCl\(_2\)/DMSO solution, the position of the Cu clip was adjusted to be at least 7-10 mm above the solution level. Additionally the clip was entirely covered with several tight layers of inert teflon tape, throughoutly cleaned between use and kept inside the flask only.
for the duration of the electrodeposition process. Despite these efforts, some corrosion of the Cu surface was observed after several months of use. The clips were replaced whenever signs of wear became apparent, however it is possible that an unknown amount of Cu contaminated the solution and codeposited along with Ni into the template.

Although the possible sources of impurities are mentioned, we in fact do not have any evidence of Cu. The electron diffraction patterns of Ni nanowires do not indicate presence of significant impurities.

3.5.5. NiO Barrier

The Ag electrode deposition is yet another feature of the sample preparation method that may contribute to the unusually high resistivity. The samples are ion etched to remove loose Ni surface deposits and air-formed NiO before silver is evaporated. Protective coats of clear, colourless nail polish was applied to parts of the sample between the etching and evaporation in order to prevent shorting, thus the sample was momentarily exposed to air and a thin barrier of NiO might be formed.

Semiconducting NiO is a good conductor at room temperature, however it is a considerably worse conductor than Ni metal \(^{(2,1)}\).

3.5.6. Quasi Quantum Effects

Electron scattering events become significant when the wire diameter is less than, or at least comparable to the mean free path of charge carriers.

For pure, bulk Ni the literature values for electronic mean free path range from 36Å \(^{(3,14)}\) to 60 Å at room temperature \(^{(3,15)}\). A factor of 2 or 3 difference in these values should be attributed to the variable purity and crystallinity of the Ni samples, often not clearly described in the literature. We must consider that the electron mean free path will be somewhat less for our nanowires than that for bulk Ni due to the high concentration of defects including the
intercrystalline fraction and impurities discussed above (sections 3.5.2 – 3.5.5). However, with a mean wire diameter of only 12-30 nm, the occurrence of such local nano-constrictions is still highly probable, especially in view of the fact that locally narrow and swollen sections are observed on SEM and TEM micrographs (see figures 4, 5, 6, 9, 10, 25).

Possible void inclusions within a wire would drastically reduce the effective diameter of a wire, and thus increase the likelihood of quantum confinement. This effect is discussed section 3.3.3.

The low calculated density of the nanowire material suggests that, if the wires are in fact grainy, as observed in the TEM micrographs as discussed in section 3.5.3., the contact between adjacent grains/crystallites may be limited. The effective conductive channel may be significantly less than the diameter of a 12-30 nm thick nanowire. A complex structure like this has a high probability of constricted contacts within it.

In addition to constrictions occurring within the body of a wire, quantum size effects are expected in the point contacts formed with a sharp probe during STM measurements. Such contacts are especially likely to form during measurement of IZ spectra involving electrode separation, which is potentially able to draw a constricted conductance channel from the softer of the two electrode materials, the Pt/Ir tip in our case.

Such quasi-quantum confinement effect would increase the measured mean resistance of nanowires. The occurrence of this effect would be expected to be distributed randomly throughout a given sample and become more pronounced as the mean diameter diminishes from 30 nm to about 12 nm. Instead the resistivity remains constant, within the experimental error limits.

Recapping the above discussed sources of electrical resistance account partly for the increase in the resistivity of Ni nanowires by 2 orders of magnitude compared to the bulk Ni resistivity. The high resistance is mostly due to the disordered nature of the electrodeposited Ni.
References

4.1.1. Results and Discussion - AAO Periodicity

A more uniform porous alumina template is desirable in its own right as a novel material (compare alumina in figures 1b and 6b), but also because it yields a more uniform array of nanoparticles: nanodots, nanowires or nanotubes. The nanowires synthesized in such periodic templates have considerably more parallel walls and less local narrowings and swellings compared to those from the random templates (compare wires in figures 4b - periodic template and 6b - random template). Incidentally the barrier layer of periodic or nearly periodic alumina is more consistent, than that in a disordered alumina template so the efficiency of electrodeposition into the template is more uniform.

An ideal hexagonal cell array of AAO develops via a competition between growth and dissolution. The balance between the two processes can be disturbed by impurities, temperature or concentration fluctuations, local changes in the strength of the electric field etc. causing excessive dissolution or growth, chaotic pore initiation, branching or a change in the direction of pore growth. All of which destroys the periodic hexagonal structure of alumina, and pentagonal or heptagonal cells form, as seen on a SEM micrograph (fig. 3).

It has been recently found that pore nucleation may be forced to occur at certain locations if the electric field can be locally distorted at appropriate, periodical positions.

4.1.2. Texture of Aluminum

During anodization, equipotential electric field lines form parallel to the surface. Therefore an uneven surface causes field distortions. Periodic indentations will, therefore, cause periodic points of strong field inducing preferential initial dissolution of alumina – pore nucleation.

If an aluminum surface is pre-textured with a regular hexagonal pattern with parameters appropriate to the anodization conditions applied – then an extremely ordered pore array
develops. Pre-texturing techniques create periodic indentations in aluminum, which then become indentations in the native aluminum oxide with locally strong electric field initiating pore nucleation in a well ordered array. A “stamping” technique was first described by Masuda (1,5,4,1) with excellent periodicity achieved over several tens of microns range. A hexagonal array of nanotips was patterned by electron lithography into a SiC stamp, which pressed against aluminum left periodic indentations, and then anodic alumina formed with periodic “defects”-indentations, where pores would initiate preferentially.

Electropolishing in specific electrolyte, voltage and duration has been reported to result in a periodic hill pattern formation on the surface of aluminum (1,22). Highly periodic porous oxide has been grown on such pre-treated aluminum.

4.2.1. Sequential Anodizing and Stripping

Another way to pattern the aluminum, is to use the intrinsic texture formed during anodization underneath the anodic oxide layer. The bottom surface of the barrier layer is scalloped and leaves a perforated pattern on the underlying aluminum (fig. 27). The pattern molded into the aluminum is the negative of the scalloped texture of the barrier layer. It was found that each step of repetitive anodization and stripping, performed under identical conditions, significantly improves the spacing order of the scallop-like cavities within each grain on the aluminum surface (1,5,4,1,4,3). Excellent periodicity within each domain can be achieved with this technique. Of course the impurities and flaws at the grain boundaries must be eliminated by other means, for example annealing followed by electropolishing, and/or improving the purity of aluminum. Figure 28 shows the improved periodicity as the purity of aluminum increases, all Al samples were simultaneously annealed and anodized repeatedly (fig28 and table 5). Thermal annealing increases the mean size of grains and concentrates the impurities near the surface of the
foil, which then are (partially) removed by electropolishing. More of the surface aluminum enriched in impurities is removed in layers when it is converted to oxide during anodization and stripping cycles.

An obvious observation of array organization in fig. 28 is that the 0.1% impurity content in 3N (99.9%) aluminum is sufficiently high so that no periodic domains form in AAO after a series of 4 anodization/stripping cycles, whereas identical processing of 4N (99.99%) Al yields rather periodic, although small (approximately 1 µm) domains in the alumina. The size of such domains increases further on the 5N (99.999%) Al, due to the greatly reduced impurity content.

Fast Fourier Transform (FFT) is a measure of correlation, thus may be used to describe the periodicity of an array of points. An ideal hexagonal 2D lattice has a FFT pattern of 6 points at the corners of a regular hexagon. Figure 29 shows FFT of the array of points representing the xy coordinates of the pore centers visible at the surface of the anodic oxide formed on the annealed 3N, 4N and 5N aluminum (see anodize-strip conditions in table 5 and fig. 28). The pore centers
were extracted from the SEM images (fig. 28) of the alumina surface by an image processing software (Scion Image). The pore array of AAO grown on the 3N Al shows diffuse concentric rings in the FFT (fig. 29a) indicating a nearly radial distribution of points (pores) but no hexagonal order. A hexagon is clearly present in the FFT of the 4N and 5N samples (fig. 29b. and c. respectively). The hexagon pattern for the 5N sample is qualitatively less diffuse than that for the 4N sample, verifying the improvement in the periodicity as the purity of the Al substrate increases.

It is obvious from the SEM images of the pores (fig. 28) that the order only extends over small domains, representing single crystal domains present in the original aluminum substrate. There is a distribution of sizes of such domains. Order is lost at the boundaries of the domains. In addition the hexagonal pattern in any given domain is rotated by a random angle with respect to the adjacent domains. The Fast Fourier Transform cannot take into account multiple domains of different sizes nor the rotation. This is a source of error manifested by loss of sharpness in the ring, hexagon and/or 6-point pattern obtained by FFT.

Table 5. Anodization-Stripping Series for Annealed Al

<table>
<thead>
<tr>
<th>Al purity</th>
<th>annealing plateau temp. /°C</th>
<th>electropolishing bath</th>
<th>Al purity</th>
<th>annealing plateau temp. /°C</th>
<th>electropolishing bath</th>
</tr>
</thead>
<tbody>
<tr>
<td>3N</td>
<td>400</td>
<td>2:1:100:100</td>
<td>4N</td>
<td>400</td>
<td>2:1:100:100</td>
</tr>
<tr>
<td>4N</td>
<td>400</td>
<td>2:1:100:100</td>
<td>5N</td>
<td>400</td>
<td>2:1:100:100</td>
</tr>
</tbody>
</table>

* electropolishing bath 5:1 of ethanol:perchloric acid
Figure 28a. Random pores in alumina grown on annealed 3N aluminum, a SEM image and centers of the pores extracted from the image by the Scion Image software.
Figure 28 b. Quasi-periodic domains of pores in alumina grown on annealed 4N aluminum, a SEM image and the centers of pores extracted from the image by the Scion Image software.
Figure 28 c. Quasi-periodic domains of pores in alumina grown on the annealed 5N aluminum, a SEM image and centers of pores extracted from the image by the Scion Image software.
Figure 29. Fast Fourier Transform (FFT) of the array of points representing the xy coordinates of the pore centers pictured in figure 28. Figure 29. a. is the FFT for the 3N, b. is for the 4N, and c. is for the 5N aluminum substrate sample. Note the arrows pointing to one of the 6 corners in the hexagon pattern formed in the FFT in b. (4N) and c. (5N), d. FFT of an ideal hexagonal net. The presence of the hexagon is an evidence of the hexagonal periodicity present in the pore array on the 4N and 5N aluminum.
4.3. Pair Correlation

The periodicity of pore arrays is assessed using a computer program based on the pair correlation function. The xy coordinates of pore centers are extracted using an image processing software (Scion Image) and are treated as points in a 2 dimensional hexagonal lattice. The expression

\[ \rho(r) = \rho_0[r - u(r)] \] (4-1)

gives the mean square fluctuation of displacement, \( u(r) \), from ideal (expected) at any specified point of the 2D pore lattice. And the correlation between the fluctuations at different points \( r_1 \) and \( r_2 \) is determined by mean value

\[ \langle \rho(r_1) \rho(r_2) \rangle = \langle \rho_0[r_1 - u(r_1)] \rho_0[r_2 - u(r_2)] \rangle \] (4-2)

The function is normalized to a mean nearest neighbour distance, equal to the mean cell diameter for each analyzed image.

Figure 30a. Periodic pore structure produced by anodization of "stamped" aluminum by Masuda (4.1).
Pair Correlation Function of pore centers in periodic AAO (4.1)

Figure 30b. Pair Correlation Function of the pore centers in periodic AAO (fig. 30a). The inset shows long range order. Compare the fine peak structure to the pair correlation of an ideal hexagonal array in figure 31.

Our pair correlation program was tested on the hexagonal pore lattice obtained by Masuda et al. (4.1) (fig. 30) and the density pattern obtained matches closely the ideal hexagonal point-lattice (fig. 31). Assignment of pore center coordinates is done based on colour contrast in SEM images of AAO and contributes a small amount of noise. Also a number of misshapen cells in the interstitial regions are assigned multiple pore centers by the image processing software. Several (pair correlation) plots display this error as a small peak (or fine structure on the left shoulder of the nearest neighbour peak) of very short inter-pore distances, less than the average cell diameter (fig. 32 a and b).

Our pore arrays consist of small, periodic domains, misoriented with respect to each other, thus when the pair correlation is averaged for the entire image area, it resembles more smooth peaks of a radial than a hexagonal point distribution. However, fine structure on the first few peaks in the plot for the 4N and 5N sample lattice (fig. 32 b and c) are reminiscent of the ideal
hexagonal net (fig. 31): the 2\textsuperscript{nd} peak is split into a dublet, and the 3\textsuperscript{rd} peak has slight, although less resolved structure on its (right) shoulder.

The increase in fit to the ideal hexagonal pair correlation form the 3N to the 5N sample is a measure of an increase in periodicity of the pore domains in the AAO as the purity of the original aluminum substrate increases.

Figure 31. The xy coordinates of an ideal hexagonal net (top) and its Pair Correlation Function (bottom, inset shows the long range structure).
Figure 32 a, b. Pair Correlation Functions of the 2D array representing the pore centers of alumina produced on 3N (top, a) and 4N aluminum (bottom, b). Note the fine structure on the left shoulder of the nearest neighbour peak, which indicates smaller cells and contrast noise in the SEM image (mostly at domain boundaries).
Figure 32 c. Pair Correlation Functions of the 2D array representing the pore centers of alumina produced on 5N aluminum.
References

Conclusions

Arrays of Ni nanowires were fabricated by electrochemical deposition into porous anodic aluminum oxide templates. The electrical resistance of single wires was determined utilizing a sharp probe of a Scanning Tunneling Microscope (STM).

The results obtained from our STM measurements were interpreted in terms of a model which includes quantum contact between the two microscopic leads: the STM probe tip and the nanowire tips. We postulate that as contact is made, highly constricted structures evolve at the interface between the nanowire and the STM tip which results in a residual resistance \( \approx 15 \pm 3 \, k\Omega \) in series with the nanowire's resistance. This value is approximately equal to the resistance quantum, \( R_Q \approx 13 \, k\Omega \), corresponding to the resistance of a single point contact.

The resistance of single nanowires was measured for wires of varying length and diameter: 12 \( \pm 2 \, k\Omega \) (N01 - 6.1 \( \mu \)m, 32 nm), 17 \( \pm 3 \, k\Omega \) (N02 - 4.2 \( \mu \)m, 20 nm), 22 \( \pm 5 \, k\Omega \) (N03 - 3.6 \( \mu \)m, 17 nm), 42 \( \pm 8 \, k\Omega \) (N04 - 3.3 \( \mu \)m, 12 nm).

After subtracting the contact resistance from the measured resistances, the resistivity of the metallic nanowire material was determined to be \( 1.4 \pm 0.3 \times 10^{-4} \, \Omega \text{cm} \), two orders of magnitude larger than that of bulk Ni, \( 6.03 \times 10^{-6} \, \Omega \text{cm} \). The unusually large value of resistivity is believed to result from the disordered nature of the material and possibly quasi-one-dimensional size effects. X-ray diffraction study revealed the structure of the nanowires to be polycrystalline with mean diameter of 22 nm.

In an attempt to understand the nature of the material comprising the nanowires an attempt was made to measure the density of the nanowires using ICP. The resulting density was found to be very low (45-80% of bulk Ni density). Rather than interpreting this low density in terms of an unusual structure for the nickel in the nanowire we believe that it arises from an incomplete (45-80%) filling of the pores in the anodic film by the electrochemical deposition process used, resulting in a broad distribution of wire lengths. Small voids present within the
body of wires and some oxidation of the surface of the wires may also contribute slightly to the apparent low density of the nickel.

The nanowire arrays synthesized in the alumina templates are potentially a useful novel electronic material. An important future goal would be to perfect the fabrication methods so as to produce nanowires with more uniform morphologies and properties.