Ultra fast pulse-plating of Ni$_x$Cu$_{1-x}$ alloy nanowires

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Abstract. Since nanotechnology is one of the interesting new topics for scientists, fabrication of nanomaterials may be extremely important. This article shows that electrodeposition is one of the best techniques to fabricate metallic nanomaterials. Here we show that a Ni$_x$Cu$_{1-x}$ alloy nanowire of arbitrary composition may be grown within a nuclear track-etched polycarbonate membrane by electrodepositing well-defined submonolayer quantities of Ni and Cu in alternation. The microstructure of the alloy wires was investigated using TEM in both imaging and diffraction modes. Magnetic measurements were carried out at 5 K and 300 K using a SQUID magnetometer to characterize the compositional homogeneity of the electrodeposited nanowires.

Introduction

Electrodeposition is a versatile process for the fabrication of ultrathin metal films (2D), metal nanowires (1D), and metal quantum dots (0D). It can be carried out at ambient temperature and pressure, and therefore requires much less complex apparatus than vacuum-based techniques such as molecular beam epitaxy, sputtering, pulsed laser deposition or evaporation. It also offers considerable flexibility. For example, the combination of electrodeposition and extreme ultraviolet (EUV) lithography can be used to create much higher aspect ratio structures than vacuum-based 'lift-off' techniques, and is therefore widely used in nanoengineering.

Electrodeposition has the further useful attribute, that it is possible to fabricate extremely fine structures, in particular metal A/metal B multilayer films with A and B layer thicknesses below 1nm [1,2]. If these layer thicknesses are reduced even further, to submonolayer values, the result will be an alloy whose composition is determined by the ratio of the quantities of A and B deposited. This is of interest, because by varying the ratio during growth, an alloy film could be electrodeposited with an arbitrary composition profile that could be defined with sub-nm precision. We have recently reported that this is feasible [3], giving electrodeposition a flexibility that has previously only been possible with vacuum processes such as molecular beam epitaxy [4,5].

With electrodeposition, it is also possible to fill extremely small volumes with metals or other materials in highly controlled fashion. For example, metal wires a few tens of nm in diameter and a few µm in length may be fabricated by filling correspondingly dimensioned pores in an
insulator. Suitable nanoporous template materials include electrochemically oxidized aluminum and nuclear track-etched polycarbonate membranes prepared by etching damage tracks created when the plastic is irradiated with high energy particles. Both of these have been used successfully to grow single element, alloy nanowires, or superlattice nanowires [6]. In order to grow ultra fast pulse plating Ni-xCu1-x alloy nanowires we used our new method that has been already reported for the fabrication of heterogeneous alloy films [3].

**Experimental**

The electrolyte used contained 2.3 mol Ni sulphamate, 0.05 mol Cu sulphate and 0.49 mol boric acid per litre purified water, with the pH adjusted to 2.0 using sulphamic acid. Deposition was carried out at room temperature in a three-electrode cell, and the substrate potential was switched between -0.4 V and -1.9 V relative to a saturated calomel reference electrode to deposit Cu and a highly Ni-rich alloy respectively. The substrates used were Au-coated nuclear track-etched polycarbonate membranes, and were held in a sample holder which incorporated a Luggin capillary for the reference electrode and a cylindrical collar to improve the uniformity of the current distribution. Deposition was carried out at room temperature in a three-electrode cell, using a potentiostat controlled by a computer. The computer control of the deposition process was used to compensate for undesired electrochemical processes, such as partial re-dissolution of the Ni and co-deposition of the Cu. We assume that the Cu partial current at any time is given by its diffusion-limited value, measure the total current flowing in the cell, correct it for current efficiency which was measured as ~90%, and subtract the Cu partial current to obtain the Ni partial current. Knowing the Cu and Ni partial currents at any point, it is straightforward to monitor and control the alloy composition [3].

A large number of Ni-xCu1-x alloy nanowires were then deposited within the pores of the masked membranes under different deposition conditions. To separate the wires from the Au substrate and also from the membrane an area of about 4mm×4mm square of membrane was cut out and placed in a cleaned cylindrical glass container filled with chloroform, which dissolves the polycarbonate. In order to study the nanowires by TEM an Al mesh grid was first covered by a film of carbon and then some droplets of the milky solution involving large number of the nanowires were placed on the film.

**Results and discussion**

Microstructure of Ni_xCu_{1-x} alloy wires were studied using image and diffraction TEM modes. A typical bright field image from a Ni_{0.81}Cu_{0.19} alloy wire is shown in figure 1. The contrast along the wire due to the existence of multiple grains can easily be seen. The size of the grains can be estimated by the contrast, whereby the larger the dark (or bright) area the bigger is the grain size. The grain length varies from 5nm to 100nm, while the individual grain boundaries in some parts occupy the full width of the wires. Therefore the average grain size is relatively large. This can be confirmed from the discontinuity in the selected area diffraction pattern of such a wire, shown in figure 2. This figure also shows that the growth is polycrystalline.

![Figure 1. Bright field image of a Ni_{0.81}Cu_{0.19} alloy nanowire. The image shows that the wire has relatively large grain size.](image-url)
EDX analysis was used to obtain the chemical composition of the alloy nanowires and indicated that good control over composition had been achieved. To determine the relative composition of Ni and Cu from each spectrum, the integrated areas under the Ni and Cu peaks were obtained using two separate windows to eliminate the background contribution. Table 1 shows the composition of a typical Ni$_{0.52}$Cu$_{0.48}$ nanowire obtained from 10 points along the wire. These data show that the distribution of Ni and Cu along the wire is almost constant.

| Point number | Programmed Ni composition (atomic %) | Counts in Ni $K_{\alpha}$ peak ($I_{Ni}$) | Count in Cu $K_{\alpha}$ peak ($I_{Cu}$) | $I_{Ni}/I_{Cu}$ ($\cong C_{Ni}/C_{Cu}$) | Measured Ni composition (atomic %) |
|--------------|-------------------------------------|------------------------------------------|------------------------------------------|----------------------------------------|----------------------------------|
| 1            | 52%                                 | 4679                                     | 4598                                     | 1.02                                   | 50%                             |
| 2            | 52%                                 | 3629                                     | 3208                                     | 1.13                                   | 53%                             |
| 3            | 52%                                 | 3914                                     | 3726                                     | 1.05                                   | 51%                             |
| 4            | 52%                                 | 4215                                     | 4461                                     | 0.94                                   | 48%                             |
| 5            | 52%                                 | 2941                                     | 2806                                     | 1.05                                   | 51%                             |
| 6            | 52%                                 | 3512                                     | 3763                                     | 0.93                                   | 48%                             |
| 7            | 52%                                 | 2418                                     | 2230                                     | 1.08                                   | 52%                             |
| 8            | 52%                                 | 3261                                     | 3385                                     | 0.96                                   | 49%                             |
| 9            | 52%                                 | 4078                                     | 3820                                     | 1.07                                   | 52%                             |
| 10           | 52%                                 | 3732                                     | 3861                                     | 0.97                                   | 49%                             |

Magnetic measurements were carried out to characterize the homogeneity of the electrodeposited nanowires on an atomic scale. Figure 3 shows the magnetic dipole moment of an electrodeposited Ni$_{0.52}$Cu$_{0.48}$ nanowire measured at 5 K and 300 K as a function of applied field. A homogeneous alloy with this composition would not be ferromagnetic at 300K [7], so the observation of hysteresis at this temperature indicates that there is some clustering of the Ni. However, the magnetization at 5 K is much greater than at 300 K, confirming that the extent of
the clustering is limited. Preliminary results suggest that it is possible to control the cluster size distribution by varying the deposition potential and/or the amount of each component deposited per cycle.

![Figure 3. Hysteresis loops for an electrodeposited Ni_{0.52}Cu_{0.48} alloy nanowire measured using a SQUID magnetometer at 5K and 300K.](image)

**Conclusion**

This article showed that it is possible to grow a Ni_{x}Cu_{1-x} alloy nanowire of arbitrary composition within a nuclear track-etched polycarbonate membrane by electrodepositing well-defined sub-monolayer quantities of Ni and Cu in alternation. TEM studying of the alloy wires showed that the growth is polycrystalline and the grain length varies from 5nm to 100nm. Homogeneity of the electrodeposited nanowires was investigated using a SQUID magnetometer at 5 K and 300 K, and a low level of Ni clustering in the wires was observed.

**References:**

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