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Electrodeposition of Single Crystalline Co$_{56.48}$Ni$_{43.52}$ Alloy Nanowires in AAO Template

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Abstract: Single crystalline cobalt nickel (Co-Ni) alloy nanowires are successfully fabricated using direct current (DC) electrodeposition with in the nanopore of highly ordered anodized aluminum oxide (AAO) template. SEM studies show that the average diameter of the alloy nanowires is approximately equal to 50 nm which corresponds to the pore size of the AAO template. Energy-dispersive X-ray (EDX) analysis confirmed that the Co-Ni alloy nanowires are deposited with 56.48:43.52 atomic ratios. We believe that at high potential the current density of Co nanowires is higher than depositing Ni nanowires which are clear by polarization curves, so content of Co increases in deposited Co$_{56.48}$Ni$_{43.52}$ alloy nanowires. Single crystalline Co$_{56.48}$Ni$_{43.52}$ alloys can be useful in future to compose and synthesize other metal nanostructures via template-based electrodeposition.

Keywords: Alloy Nanowires, Crystal Structure, Scanning Electron Microscopy, X-Ray Diffraction

1. Introduction

Ni and Co is a very important ferromagnetic material and received a lot of attention because of their potential application in ultra-high magnetic storage devices, microsensors and magnetoelectronics devices. Alloying by electrodeposition of Ni and Co is unique idea because of their high mechanical strength, magnetic wear resistance anti corrosive properties and electrocatalytic activity [1-3]. There has been lot of studies done on the electrodeposition of Ni and Co alloy nanowire and nanotubes by using various techniques but electrochemical deposition by using anodic alumina oxide (AAO) templates is one of the most versatile and cheap technique. The single nanohole in the AAO temple are arranged into a close-packed honeycomb like structure and the diameter and separation of each hole can be controlled by changing the anodization conditions [3, 4]. Electrodeposition of Ni-Co alloy has been recognized as an anomalous codeposition [5], many resarchers found that the anomalous codeposition is due to the formation of

hydroxides at the cathode surface due to increase in solution pH [6, 7]and deposition of monohydroxide of less noble metal is greater than more noble metal hydroxide [8]. In the Ni-Co alloy system the equilibrium phase at room temperature is an fcc structure up to about 65% of Cobalt and above this concentration the stable phase is hcp structure, and mixed structure of hcp and fcc phases has been observed in this system at Co$_{71}$Ni$_{29}$ alloy composition. Maqbol et al and Kawamori et al. [11, 13] found the mixed structure of fcc and hcp at 70:30 cobalt nickel ion concentration in solution. They found it to be the equilibrium phase of cobalt and nickel. This kind of behavior is also seen in cobalt nickel alloy films. Ali karpuz et al [12] obtained fcc cobalt up to 58% of cobalt content in the solution higher than this concentration they obtained the mixed structure of fcc and hcp. They use Scherrer formula [17] for obtaining the average grain size of the crystallite, by increasing the cobalt concentration the grain size increases through 16nm to 18 nm. On increasing the cobalt concentration in the solution cobalt content increases in the electrodeposited nanowires [12, 13], however they don't explain the reason of this behavior. S. Thongmee

et al observed bamboo and layer like structure in Ni-Co alloy nanowire at high current density with 15 and 25% of Co [13]. The structure of metal nanowires can be tuned to single or polycrystalline by controlling the deposition parameters. Previously single crystalline metal nanowires were deposited by AAO template [9, 10]. Electrodeposition of single crystalline of low melting point was done previously, but a growth of high melting point metal nanowires was difficult and claims to be impossible [11]. Minimization of internlal stress and surface energy inside pores of AAO template can help to form single crystalline metal nanowires. In our work single crystalline NiCo alloy nanowires was deposited in side AAO template, can have potential applications in electro-catalysis and in mechanics [12-14]. The reason of why the content of Co is more in electrodeposited Co-Ni alloy nanowires rather than used in electrolyte solution is also explained.

2. Experimental Details

Our previous paper has given the detailed experimental procedure for preparation of the porous anodic alumina oxide (AAO) templates [15]. The detailed experimental procedure for preparation of the templates is as follows. Prior to anodizing, high-purity aluminum foils (99.999%) were first degreased in acetone and were annealed in a vacuum of 10^{-5} Torr at 500°C for 5 h to remove the mechanical stress, and then electro polished in a solution mixture of ethanol and perchloric acid with a committed ratio. The electro polished phase make the surface of aluminum foil appearances like a lively silver mirror thus obtaining the aluminum foils with a homogeneous structure over a large area. The spotless and electropolished aluminum foils were fixed in an anodization cell，these foils were first anodized in a 0.4 M H$_2$SO$_4$ solution for 6 hours, creates pores having diameter in the range of 40-50 nm. A DC voltage of 45 V was used between the electrodes. The temperature was 2°C to 5°C sustained by using a refrigeration system. To remove the alumina layer formed in the first anodization, these foils were dissolved in a solution of chromic acid (1.8 wt%) and phosphoric acid (6 wt%) at 60°C. To achieve an ordered nanoporous layer, a second anodization process was done on the substrate. The same arrangement with the same parameters and electrolyte were used just anodization time was kept 12 hours for this step. The hexagonally arranged and ordered honeycomb pores was formed as shown in fig. 1

The templates obtained by this procedure have the cylindrical and hexagonally arranged pores of about 50 nm in diameter. Potentiostatic deposition was conducted in a three-electrode cell at room temperature as shown in fig. 2. The area of the working electrode for growth of nanowires was 0.608cm^2 ($= 0.25\pi(0.88cm)^2$) and the area of the graphite counter electrode was 14.7cm^2 ($= 4.2cm \times 3.5cm$). The reference electrode was the saturated calomel electrode (SCE). The electrolyte was $0.35M\ CoSO_4 \cdot 7H_2O + 0.35M\ NiSO_4 \cdot 6H_2O + 0.65M\ H_3BO_3$. The concentrations of Co^{2+} and Ni^{2+} ions in the electrolyte

were 50% of Co and 50% of Ni. The *pH* of electrolyte was adjusted to 2.5 by adding 1M H$_2$SO$_4$ solution. Potentiostatic deposition was conducted in a three-electrode cell at the bath temperature of 25°C as shown in Fig. 2. The template area for depositing nanowires was 0.608cm^2. The area of the graphite counter electrode was 14.7 cm^2. The reference electrode was the saturated calomel electrode (SCE).

The Co-Ni nanowires were analyzed using XRD (X'Pert PRO MRD, PANalytical, Netherlands) with CuKα radiation, and FE-SEM (NOVA 400 Nano) with EDS (Le350 PentaFETx-3). To analyze the composition of single nanowire, AAO template was fully dissolved with 5 wt% NaOH solution, then rinsed with deionized water for several times, and finally, dispersed in absolute ethanol by ultrasonic. To analyze the composition of standing nanowires, AAO template was partly dissolved with 5 wt% NaOH solution, and then carefully rinsed with deionized water for several times.
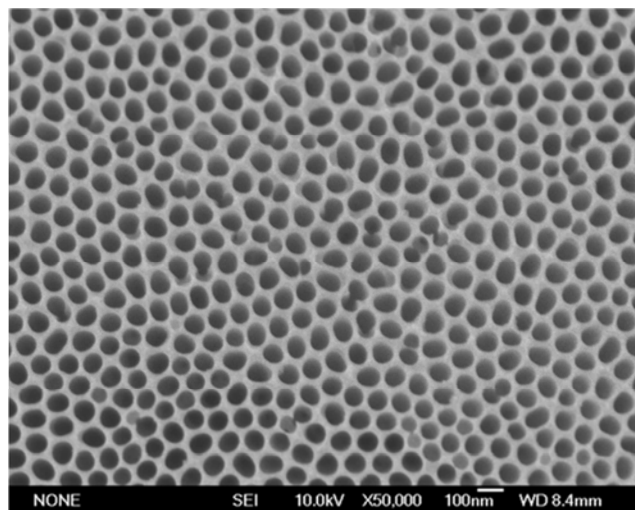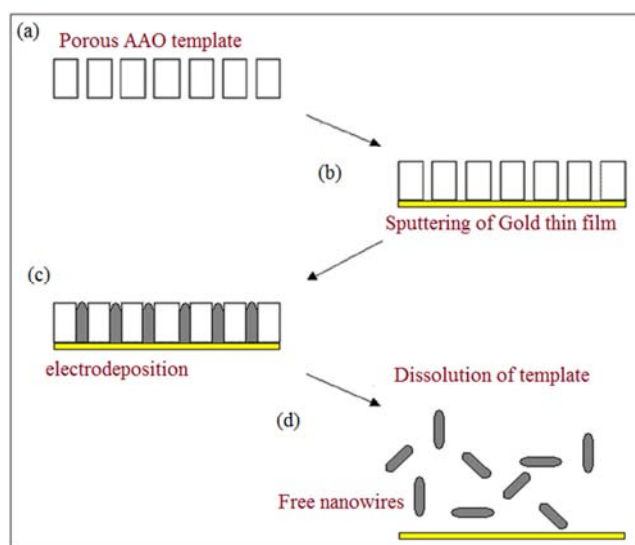

Figure 1. Hexagonally arranged AAO template.

Figure 2. Schematic illustration of (a) AAO template (b) Sputtered conductive layer(c) electrodeposition of alloy nanowires (d) Free nanowires.

3. Results

Fig. 3 shows current vs time curve measured during the deposition of Co and Ni alloy nanowires with 50:50 concentration for pH 2.5 using -3.0V, respectively. The time required for depositing alloy nanowires is half hour, Fig. 3 shows initial part of current vs time curve (0-10sec). It can be seen that the maximum value of current (i_{max}) increases with potentials while the t_m (at which the current has a the maximum value) decreases with potential. The values of i_{max} and t_m are determined to be -186.08 mA/cm^2 and 0.505 sec for the deposition at –3.0 V.
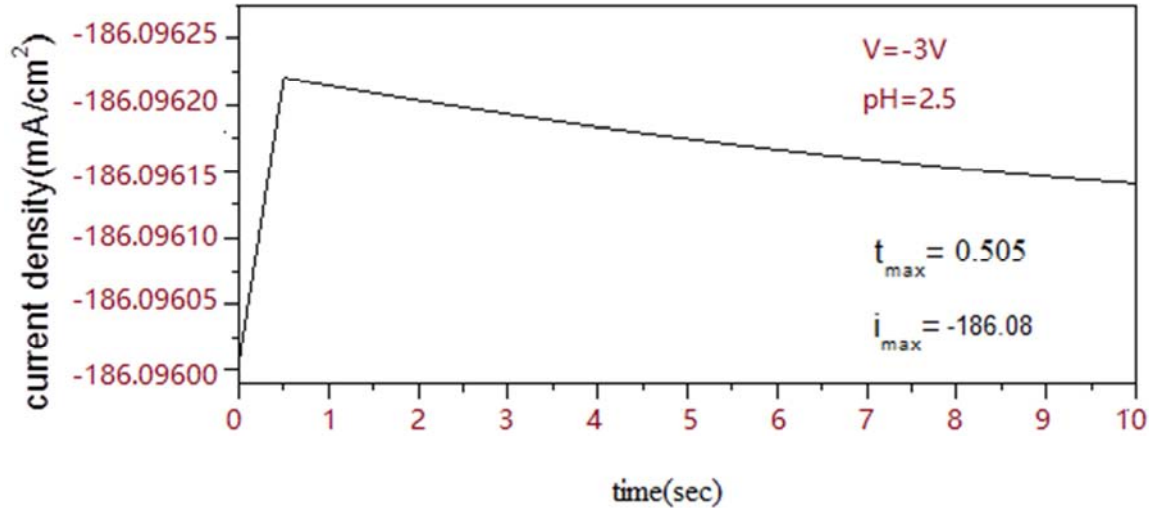

Figure 3. Initial current density vs time curve deposited at pH 2.5 with -3V.

The XRD data were collected from the top side of nanowires, fig. 4 shows that the single crystalline Co$_{56.48}$Ni$_{43.52}$ alloys nanowire. The Co$_{56.48}$Ni$_{43.52}$ alloy nanowires deposited at –3.0 V have fcc structure and peak lies at $2\theta = 76°$ ($d = 1.252$ Å). Co-Ni phase diagram [16] shows that for Co$_{56.48}$Ni$_{43.52}$, Co and Ni exhibit complete solid solution in the fcc phase. Therefore, the peak at $2\theta = 76°$ is unambiguously attributed to the diffraction of (220) plane of fcc Co$_{56.48}$Ni$_{43.52}$ alloy nanowires.
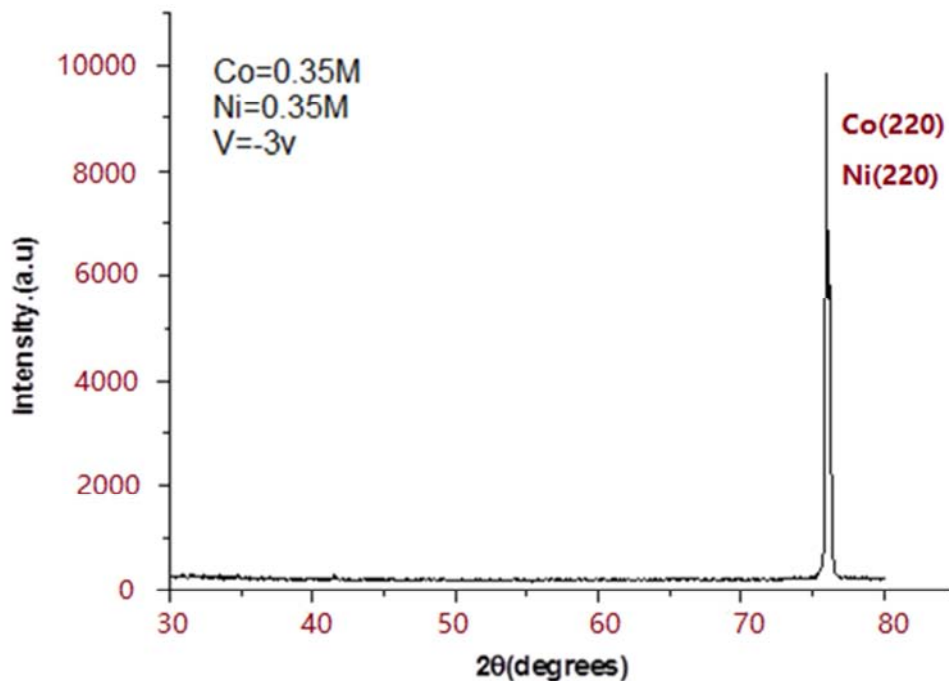

Figure 4. XRD patterns of single crystalline Co-Ni nanowires deposited at –3.0 V.

The EDX results in Fig. 5 shows that Co Ni alloy nanowires are deposited with atomic ratio 56.48:43.52 and there is no peak of single cobalt and nickel it means that cobalt and nickel formed an alloy instead of separate grains.
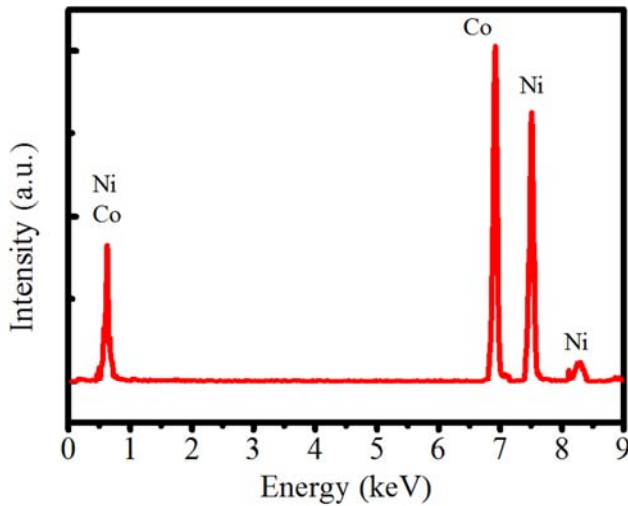
Figure 5. *EDX spectrum of single crystalline Co-Ni nanowires deposited at –3.0 V.*

Table 1. *The composition of Co and Ni in Co-Ni nanowires deposited at -3V.*

Element	At. wt%
Co	56.48
Ni	43.52
Total	100

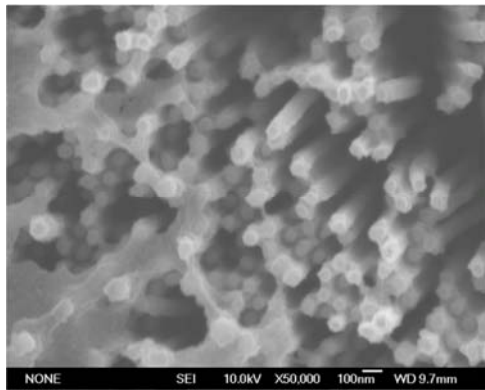**Figure 6.** *SEM images of deposited Co$_{56.48}$Ni$_{43.52}$ alloy nanowires at 50,000 magnification.*

The diameter of nanowires is the same as that of the pores of AAO template (_50 nm), indicating that the cylindrical pores were filled with Co and Ni atoms during deposition.

In order to explain why concentration of Co is more than Ni in deposited nanowires CV curve were measured at sacn rate of 0.1 mV/s. The electrolytes used were $0.3M\ CoSO_4 \cdot 7H_2O + 0.65M\ H_3BO_3$ for Co nanowires and $0.3M\ NiSO_4 \cdot 6H_2O + 0.65M\ H_3BO_3$ for Ni nanowires. It is clear in the fig that the current density increases linearly with potential does not obey the Butler -Volmer equation [17] and current density of Co nanowires increases more rapidly at potential than current density of electrodeposited Ni. The current density ratio (j_{Ni}/j_{Co}) is calculated to be 0.74 at -3.0V.
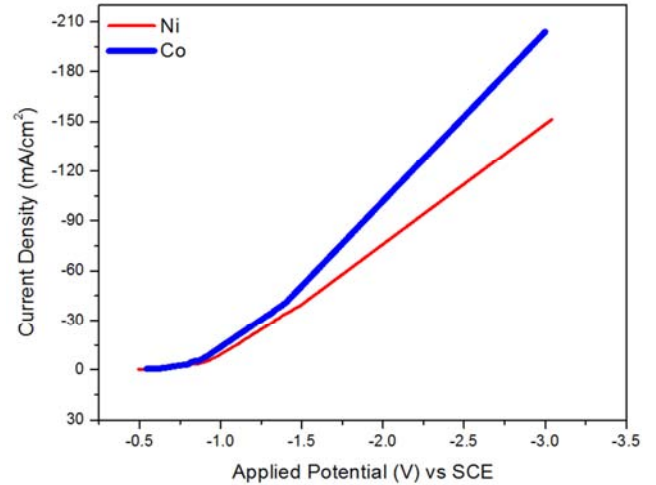

Figure 7. *The polarization curves of depositing Co and Ni nanowires, measured at a scan rate of 0.1 mV/s.*

4. Discussion

When the negative potential is applied to the working electrode, divalent metal ions of cobalt and nickel which are surrounded by hydration shells move towards the cathode, the valence electron neutralize these ions by following chemical reaction,

$$Co^{+2} + 2e^- \rightarrow Co \qquad (1)$$

$$Ni^{+2} + 2e^- \rightarrow Ni \qquad (2)$$

and after the neutralization (as the attractive interaction between water molecule and neutral metal atom is zero) water molecules of hydration are displaced and neutral metal atom of cobalt and nickel gives an intermetallic phase according to the chemical reaction

$$Co + Ni \rightarrow CoNi \qquad (3)$$

Than cobalt and nickel diffuses to surface sites where it incorporates in to metal, leading to growth of alloy nanowires [18]. The growth of alloy nanowires follow the same trend as for single nickel and cobalt nanowires, there are four stages for the growth of nanowires (a) first there is a sharp decrease in the value of faradic current due to the progress in nucleation. (b) than the growth of alloy nanowires starts in the 50nanoholes with the hemispherical head, at that time current seems to increasing. (c) The nanoholes are filled up to the top and heads are formed on each of the nanowires, current shows their maximum value. (d) Heads reach together and cover the whole electrode area and after that overdeposition start with sharp increase in current. In electrochemical deposition of metal nanowires using AAO template, higher deposition temperature and voltage minimize the growth of nanowires because of the polarization phenomenon and formation of bubbles in the very initial stage of deposition which hinders the movement of metal ion and stops growth of alloy nanowires, which results in incomplete filling of the nanopore [19].

The size of a critical cluster (N_c) can be determined by classical electrochemical nucleation theory [20, 21],

$$N_c = \left(\frac{2b}{3ze\eta} \right)^3 \tag{4}$$

where z is the valence of hydrated metal ions, e is the electron charge, η is the overpotential, b is the constant which depends on geometrical shape of the cluster. It is clear from Eq. (4) N_c has an inverse relation with overpotential: higher overpotential smaller critical clusters can be formed. Higher potential of -3v in our case smaller critical clusters can be formed; smaller critical clusters favor the formation of fcc structure [22]. It is known [23] that the saturation nucleus density (N_s) is related to maximum value of current (i_{max}) and time (t_m) at which the current has maximum value, so smaller t_m and larger i_{max} can corresponds to larger N_s. Therefore the deposition at -3.0 V (higher potential) has smaller t_m and higher i_{max} (as shown in Fig. 3), which favours larger number of N_s. The large number of N_s means smaller nuclei, smaller nuclei favours fcc structure. So deposition voltage of -3.0 V fcc $Co_{56.48}Ni_{43.52}$ alloy nanowires are formed.

The electrodeposition of an alloy is the codeposition of two metals. The compositions of alloy can depend upon the current density ratio obtained from the polarization curves of depositing these two metals [20]. The current density ratio (j_{Ni} / j_{Co}) has calculated to be 0.73 at deposition voltage of -3.0 V. We believe that the current density ratio nearly represent the ratio of Ni to Co deposited atoms. As measured current arises from reduction of hydrogon (i_H) and metal (i_M) and ions is given by

$$\frac{j_{Ni}}{j_{Co}} = \frac{i_{Ni} + i_H}{i_{Co} + i_H} \tag{5}$$

Where j_{Ni} and j_{Co} is the current density obtained from Fig. 6, i_{Ni}, i_{Co} and i_H is the current arising from reduction of metal ions (Co and Ni) and hydrogen ions. Hydrogen evolution is largely because of proton reduction, so i_H does not very much change with potential [24]. in case where current density is higher than 30 mA/cm^2, the current efficiency will be very high [24] which indicates that i_H is very small compared to i_M. In our results the deposition current at -3.0 V is higher than 30 mA/cm^2 which is clear in Fig. 7. Therefore, eq (5) can be written as

$$\frac{j_{Ni}}{j_{Co}} \approx \frac{i_{Ni}}{i_{Co}} \tag{6}$$

This shows that the current density ratio (j_{Ni} / j_{Co}) can almost represent the ratio of Ni to Co atoms deposited.

The current density ratio (j_{Ni} / j_{Co}) of Co and Ni at -3V is 0.74, we suggest that deposition of 1 Co atom corresponds to the deposition of 0.74 Ni atom. At -3 V when 50 Co atoms are produced, 37 Ni atoms (50 x 0.74) would be produced. Thus the alloy nanowires with 50 Co atoms and 37 Ni atoms

will incorporate into the lattice and alloy composition is calculated to be,

$$Co = \frac{50}{50 + 0.74} = 57.47\% \tag{7}$$

$$Ni = \frac{50}{50 + 0.74} = 42.52\% \tag{8}$$

The calculated composition of $Co_{57.47}Ni_{42.52}$ is very close to the composition of electrodeposited alloy nanowires $Co_{56.48}Ni_{43.52}$, calculated from EDX.

5. Conclusion

We have successfully deposited single crystalline $Co_{56.48}Ni_{43.52}$ alloy nanowire arrays by electrochemical deposition using dc power supply with AAO template. EDX results confirmed that cobalt and nickel are equally distributed with atomic ratios of 56.48:43.52. XRD results shows that the single crystalline $Co_{56.48}Ni_{43.52}$ alloy nanowires with fcc structure are deposited in the nanohole of AAO template. Believe that at high potential the current density of Co nanowires is higher than depositing Ni nanowires so content of Co increases in deposited $Co_{56.48}Ni_{43.52}$ alloy nanowires. Results shows that crystalline structure of $Co_{56.48}Ni_{43.52}$ alloy nanowires depends upon current density during Direct current deposition.

Acknowledgment

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