

Growth Mechanism of Single Crystal Nanowires of fcc Metals (Ag, Cu, Ni) and hcp Metal (Co) Electrodeposited

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Using X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM), we have studied the growth of the single crystalline nanowires of Ag, Cu, Ni and Co metals in the small pores (50 nm). We find that the preferential growth surface of the single crystalline nanowires is on the atomically rough surfaces such as fcc(110) and hcp(10 $\bar{1}$ 0). We have proposed a new model to explain the growth of the nanowires of fcc and hcp metals. In this model we argue that the preferential growth should depend on the number of sites for dehydration of hydrated metal ions on a metal surface. The dehydration occurs only at the apex site of a protruding surface atom since the apex site of the protruding surface atom has an enhanced electrical field. The sites for the dehydration on the fcc(110) and hcp(10 $\bar{1}$ 0) atomically rough planes are in number much larger than those on the fcc(111) and hcp(0001) atomically smooth surfaces, thus leading to the preferential growth on the fcc(110) and hcp(10 $\bar{1}$ 0)planes. (© 2011 The Electrochemical Society. [DOI: 10.1149/2.034201jes] All rights reserved.

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Investigating the growth mechanisms of metal nanowires in the cylindrical pores of a template is of fundamental and technological interests. Such research efforts have been performed. For example, Tian et al. observed two interesting results.¹ First, the nanowires of Au, Ag, and Cu with an fcc structure are single-crystalline with a preferred [111] orientation under the low deposition potential, and polycrystalline under the high deposition potential. Second, the nanowires of Ni are polycrystalline, which is relatively insensitive to the deposition potential. They proposed that the formation of the single crystalline nanowires should be attributed to the larger critical nucleus formed at the lower deposition potential. The growth of nanowires along the [111] direction can be accounted for by the observation that the {111} surface is the energetically most favorable surface for fcc metals. However, other groups obtained different experimental results. Pan et al. prepared single-crystalline metal nanowires of Ni in an AAO template at the high deposition potential (-1.0 V and-4.0 V), which grow preferentially along the [110] direction.² They argued that this preferential growth was owing to the adsorption of H ions on the cathode, which stabilized the (110) face. However, several studies show that the pH value of electrolyte, ranging from 2 to 6, had no effect on the orientation of Ni nanowires.²⁻⁴ Therefore, their argument is not supported by the experimental observations. Wang et al. also observed the preferential growth of Ni nanowires along the [110] direction in an AAO template with pore diameter of 25-70 nm.^{5,6} Moreover, the nanowires of other fcc metals such as Ag and Cu also grow preferentially along the [110] direction.7,8

Metallic cobalt occurs as two crystallographic structures: hcp and fcc. The structure at room temperature is hcp. The transition temperature between hcp and fcc structures is 450° C. Huang et al. found that the single crystalline Co nanowires deposited at -1.5 V had an hcp structure, which grow along the $[10\bar{1}0]$ direction.⁹ Pan et al. also observed the growth of single crystalline hcp Co nanowires along the $[10\bar{1}0]$ direction at the deposition potentials of -0.4 V and -1.0 V. However, these authors do not explain why the growth of nanowires of hcp Co is along the $[10\bar{1}0]$ direction.

From the brief review given above, we can see two points. First, a lot of studies show that the growth surface of the single crystalline nanowires of fcc (Ag, Cu and Ni) and hcp(Co) metals is usually not on the closely packed surface (atomically smooth surfaces) such as fcc(111) and hcp(0001) but on the atomically rough surface like fcc(110) and hcp(10 $\overline{1}$ 0), respectively. Second, the growth mechanism of single crystalline metal nanowires is still poorly understood since the models previously proposed cannot explain why the growth surface of the single crystalline nanowires of fcc (Ag, Cu and Ni) and hcp (Co) metals is on the fcc (110) and hcp(10 $\bar{1}$ 0) surfaces. The purpose of the present paper is to elucidate why the growth surface of the single crystalline nanowires of fcc and hcp metals is on the (110) and (10 $\bar{1}$ 0) surfaces, respectively.

Experimental

Preparation of the AAO templates .- The porous anodic alumina oxide (AAO) templates were prepared via a two-step anodization procedure.^{5, 10, 11} Prior to anodizing, high-purity aluminum foils (99.999%) were first degreased in acetone and then were annealed in a vacuum of 10⁻⁵ Torr at 500°C for 5 h to remove the mechanical stress, thus obtaining the aluminum foils with a homogeneous structure over a large area. The aluminum foils were anodized in a 0.3 M H₂C₂O₄ solution at 2°C for 6 h. After removing the alumina layer formed in the anodization in a mixture of phosphoric acid (6 wt%) and chromic acid (1.8 wt%), the aluminum foils were anodized again at the same conditions as the first step for 12 h. The templates that experienced the above two-step anodization were etched in a saturated CuCl₂ solution to remove the remaining aluminum on the back side. The alumina barrier layer was then dissolved in a 5 wt% phosphoric acid solution at 40°C. In order to deposit metal into the pores of AAO templates, a gold film was sputtered onto the back side of the AAO templates to serve as the working electrode.

Electrodeposition of the metal nanowires.— The electrolyte for preparation of Ag nanowires was a mixture of AgNO₃ (45 g/L) and H_3BO_3 (45 g/L) solutions, with pH of 2 by adding a HNO₃ solution. The electrolyte for the preparation of nanowires of Cu and Ni was a mixture of CuSO₄ (90g/L), H_3BO_3 (45 g/L) solutions, and NiSO₄ · 6H₂O (100g/L), NiCl₂ · 6H₂O (20g/L), H_3BO_3 (45 g/L) solutions, respectively, and the pH value of the solution was adjusted to 2.5 with 1 M H₂SO₄. The electrolyte for the preparation of Co nanowires was a mixture of CoSO₄ (100 g/L) and H_3BO_3 (45 g/L) in aqueous solutions, with pH of 2.5 by adding 1 M H₂SO₄ solution. Direct current (DC) electrodeposition for formation of nanowires of Ag, Ni and Cu was performed at the deposition potentials of -0.2 V and at a room temperature (about 25°C), respectively. The Co nanowires were prepared at deposited potential of -1.6 V at room temperature.

Characterization.— The metal nanowires was characterized by X-ray diffraction (XRD, Y-2000) with CuK_{α} radiation (λ = 0.154178 nm). The images of deposited metal nanowires were obtained by scanning electron microscope (SEM, JEOL JSM-6700F) and transmission electron microscope (TEM, Tecnai G20 Philips). For XRD measurements the film of Au was mechanically polished away. For SEM observations, the AAO templates were partly dissolved with

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Figure 1. SEM images of the top and side (inset) views of highly ordered AAO template.

5 wt% NaOH solution, and then carefully rinsed with deionized water for several times. For TEM observations, the AAO was completely dissolved in a 5% NaOH solution, then rinsed with deionized water several times, and finally dispersed in absolute ethanol by ultrasonic.

Results

Figure 1 gives a top-view SEM image of AAO template, indicating that the pores on AAO template are hexagonally arranged and highly ordered. The average diameter and spacing of pores are estimated to be 50 and 100 nm, respectively. The inset of Figure 1 is a side-view image of AAO template, demonstrating that these cylindrical pores are perpendicular to the AAO template surface.

Figure 2 shows the XRD patterns of Ag, Cu, Ni and Co nanowires, which were collected from the top side of nanowires. The nanowires of Ag, Cu and Ni were prepared at a room temperature under the negative deposition potential of 0.2 V. The position of the peak of Ag, Cu and Ni are in good agreement with those of the face-centered cubic (fcc) Ag (JPCDS, 04-0783), Cu (JPCDS, 04-0836) and Ni (JPCDS, 04-0850), respectively. The sharp peak is due to (220) plane diffraction. The above XRD results of Ag, Cu and Ni nanowires have pre-viously been observed by other researchers.^{2,5,7,12} Using HR-TEM, those researchers have demonstrated that these nanowires with only one diffraction peak is single crystalline.^{2,12} The nanowires of Co were prepared at -1.6 V. The nanowires of Co prepared at -1.6 V have a sharp peak at $2\theta = 41.6$ degrees. Our XRD results of Co nanowires are in agreement with those obtained by Huang et al.⁹ Using HR-TEM, Huang et al. demonstrated that the nanowires of Co with one peak are single crystalline.⁹ The peak at $2\theta = 41.6$ degrees are due to the hcp $(10\bar{1}0)$ plane diffraction.⁹ From the above results, we can see that the growth surface of single crystalline nanowires is on the atomically rough surface like fcc(110) and hcp($10\bar{1}0$).

Figure 3 shows SEM (Fig. 3a) and TEM (Fig. 3b) images of nanowires of Ag. We can see from Figure 3 that the growing surface of nanowires is not a completely flat surface but rather a protruding surface at the nanometer scale.

Discussion

The XRD experimental results given above are not new since these results have previously been observed. However, we are the persons who have for the first time taken into consideration all the results of single crystalline nanowires of fcc and hcp metals and found that the growth surface of single crystalline nanowires is usually not on the atomically smooth surface like fcc(111) and hcp(0001) but on the



Figure 2. XRD patterns of metal nanowires deposited at different deposition potentials: (a) fcc Ag, -0.2 V; (b) fcc Cu, -0.2 V; (c) fcc Ni, -0.2 V (d) hcp Co, -1.6 V.

atomically rough surface like fcc(110) and hcp(10 $\bar{1}$ 0). Here we will explain why the growth surface of single crystalline nanowires is on the fcc(110) and hcp(10 $\bar{1}$ 0).

In the electro-deposition of metal, a metal ion Mⁿ⁺ is transferred from solution into the ionic metal lattice, meanwhile electrons are provided from the external electron source (power supply) to the electron gas of the metal M.13 This electro-deposition process can be pictured as the following four steps in the atomic-level scale. First, hydrated metal ions in an aqueous solution diffuse to a metal surface and are adsorbed on this surface. (In a hydrated metal ion, the water molecules of hydration are electrostatically attached to the metal ion.) Second, when an adsorbed hydrated metal ion captures electrons from the surface by quantum-mechanical tunneling, the metal ion is neutralized. The electrostatic attractive interaction between the neutral metal atom and water molecules is zero and then the water molecules of hydration are displaced. Third, the neutral metal atom is adsorbed on the surface. Fourth, the adsorbed metal atom diffuses to a surface site (such as kink site) where it incorporates into the ionic metal lattice, thus leading to the growth on the surface on which the dehydration occurs. In the four steps described above, the second step plays a crucial role in the growth of metal nanowires. This is because the metal nanowires can grow only when the water molecules that are attached to the metal ions are displaced on a metal surface. The dehydration involves electron transfer from a metal surface to hydrated metal ions by tunneling.¹⁴ (see page 8 of this reference). In the following, we argue that the probability of electron tunneling is much higher on the atomically rough surfaces such as fcc(110) and hcp($10\overline{1}0$) than on the atomically smooth surfaces like fcc(111) and hcp(0001) and so the dehydration rate is faster on the fcc(110) and hcp(10 $\overline{1}$ 0) surfaces than on the fcc(111) and hcp(0001) surfaces. This means that the preferential growth surface is on the fcc(110) and hcp($10\overline{1}0$).



(a)



Figure 3. SEM(a) and TEM(b) images of Ag nanowires.



Figure 4. Schematic surface structure of fcc and hcp metals, not drawn to scale: (a) fcc(100); (b) fcc(111) and hcp(0001); (c) fcc(110) and hcp(10 $\bar{1}$ 0), if the distance between two atoms along the close packed direction is a, then the distance between two atoms is 1.414a along the $\langle 100 \rangle$ direction and 1.633a along the $\langle 0001 \rangle$ direction, respectively. The fcc(001), fcc(111) and hcp(0001) surfaces are relatively smooth at the atomic scale. However, the fcc(110) and hcp(10 $\bar{1}$ 0)surface is atomically rough with the troughs.

Little is known on the tunneling processes occurring in the dehydration. In order to understand the tunneling processes in the dehydration, we first describe briefly the tunneling processes in field ion microscopy (FIM),¹⁵ (See page 11 of this reference) which is well understood. In the presence of a high electrical field of a few V/Å, an electron in an atom near a metal surface can transfer to the metal surface by tunneling. The higher the electrical field is, the higher the probability of tunneling is (this is because the width of tunneling barrier is reduced by the electrical field). In FIM, the metal is applied a positive bias voltage, the electron of the image gas atom tunnels into





Figure 5. Schematic illustration of a possible growth mechanism for the single crystalline metal nanowires. Atom 1, originating from dehydration at terrace, diffuses to a kink site for growth; atom 2 originating from dehydration at step either goes to the layer immediately below and then diffuses along step to a kink site to join the lattice, or diffuses to a kink site to join the lattice on the same layer; atoms at the topmost layer of growing surface will form a new layer by diffusing.

the metal surface. In the case of electro-deposition, a metal surface is biased a negative voltage. The value of overpotential should be on the order of a few V with respect to adsorbed hydrated metal ions, which have a zero potential.¹³ If the surface metal atom and adsorbed hydrated metal ion are regarded as the hard balls, the distance between

the centers of them is several Å. Therefore there is a high electrical field between the surface metal atom and adsorbed hydrated metal ion.¹⁴(see page 5 of this reference) It is the high electrical field that leads to adsorption of hydrated metal ion on a metal surface and then electron tunneling from the metal surface to the adsorbed hydrated metal ion.

The electrical field is never uniform everywhere as a jellium model of metal surface would imply. Instead, the field is enhanced near a protruding atom.¹⁵ (See page 73 of this reference) The protruding atoms may include atoms located at the sites of step, kink and surface edge. In FIM, a tunneling event occurs only at the apex site of a protruding atom and only protruding atoms are imaged.¹⁵ (See Fig. 1.3 of this reference) In the case of electro-deposition, therefore, we suggest that the dehydration, which is an electron tunneling process, should occur only at the apex site of a protruding atom.

Fig. 4 shows the surface structure of (111), (100), (110), (0001) and $(10\bar{1}0)$ planes of fcc and hcp metals. We can see from Fig. 4 that the terrace atoms on the fcc(110) and hcp($10\overline{1}0$) surfaces have two nearest first-layer atoms while the terrace atoms on the fcc(100), fcc(111) and hcp(0001) have four and six nearest firstlayer atoms, respectively. Thus, the terrace atoms on the fcc(110) and hcp $(10\bar{1}0)$ surfaces can be also regarded as protruding atoms while the terrace atoms on the fcc(100), fcc(111) and hcp(0001) are not protruding atoms. This observation is confirmed by FIM experimental results.¹⁵ (See Fig. 1.3, Fig. 4.7 and 4.9 of this reference) The electrical field above smooth planes like fcc(100) and fcc(111) is too uniform and so field adsorption of image gas atoms and electron tunneling will not occur above the terrace atoms of these surfaces. Adsorption and tunneling induced by the field occurs only at the apex sites of edge atoms of the smooth planes since they are protruding atoms. Therefore only edge atoms are imaged. For example, only edge atoms are imaged for the nearly circular shape of the (100) layers of an Ir tip.¹⁵ (See Fig. 4.9 of this reference) However, for the nearly circular shape of the (110) layers of a Pt tip, all the atoms on the (110) surface including the terrace atoms are observed in the FIM image.¹⁵ (See Fig. 4.7 of this reference) These FIM results indicate that all the atoms on the (110) plane including terrace atoms can be regarded as protruding atoms. Therefore we believe that all the atoms on the (110) and (1010)surfaces can be regarded as protruding atoms. On the other hand, for the (111), (100) and (0001) surfaces, only atoms located at edges and surface defects such as steps and kink are protruding atoms. Thus, the sites for the dehydration of hydrated metal ions are in number much larger on the (110) and $(10\overline{1}0)$ surfaces than on the (111) and (0001) surfaces.

Fig. 5 schematically gives a possible growth mechanism for the single crystalline metal nanowires. Atom 1, originating from dehydration at terrace of fcc(110) and hcp(10 $\bar{1}$ 0), diffuses to a kink site

where it incorporates into the metal lattice. Atom 2, originating from dehydration at step, either goes to the layer immediately below and then diffuses along step to a kink site to join the lattice, or diffuses to a kink site to join the lattice on the same layer. Atoms at the topmost layer of growing surface of the nanowires can form a new layer by diffusing. It can be seen from Fig. 5 that the growth can occur dominantly on the fcc(110) and hcp(10 $\bar{1}$ 0) surfaces since the fcc(110) and hcp(10 $\bar{1}$ 0) surfaces have an overwhelmingly number of the sites for the dehydration, compared to the fcc(111) and hcp(0001) surfaces.

SEM and TEM results show that the growing surface of a metal nanowire is a protruding surface at the nanometer scale, indicating that the growing surface has a lot of steps. Such protruding surface has more sites for dehydration than flat surface and therefore favors the growth of nanowires.

The data of workfunctions of single crystal metal surfaces corroborate the above argument that the electron tunneling is much easier on the atomically rough surface than on the atomically smooth surface. The value of workfunction represents the height of energy barrier for electron departing a metal surface. The value of workfunction is related to probability of electron tunneling. The larger the value of workfunction is, the lower the probability of electron tunneling is. For a metal, the value of workfunction is usually lower on the atomically rough surface than on the atomically smooth surface.¹⁵ For example, the workfunction of the (110) and (111) surfaces is 4.52 eV and 4.74 eV for Ag,¹⁶ 5.04 eV and 5.35 eV for Ni,¹⁶ 4.48 eV and 4.94 eV for Cu,¹⁷ respectively. The workfuction of cobalt single-crystal surfaces is not available. It can be seen from the workfunction of metal that the electron tunneling is much easier on the atomically rough surface than on the atomically smooth surface. Therefore, the dehydration occurs dominantly on the atomically rough surface.

It is well understood for surface scientists that single neutral metal atom is very active chemically. It sticks to and grows on any surface which it contacts. This means that one neutral metal atom cannot select a surface for growth. However, hydrated metal ions in an aqueous solution can select the rough surface like fcc(110) and hcp($10\bar{1}0$) for dehydration and grow on this surface. This is because the rough surfaces can make dehydration happen much more easily. Therefore it is this selection that leads to the dominant growth on the surfaces of fcc(110) and hcp($10\bar{1}0$).

The growth of crystals in nanowires can be influenced by the pore size of a template. When the pore size is large, several critical nuclei would form on the Au (or deposited metal) surface of one pore and polycrystalline growth occurs. In this case, one can expect to observe the diffraction peaks of not only the (220) plane but also the (111) and (100) planes. Wang et al. observed the diffraction peaks of the (111), (220) and (100) planes on the nanowires of Ni, which grew in the larger pores of 90–225 nm.^{5,6}

Conclusions

This work has two interesting points. First, we find that the dominant growth of single crystalline nanowires usually occurs on the atomically rough planes such as fcc(110) and hcp(10 $\bar{1}$ 0) rather than the atomically smooth planes like fcc(111) and hcp(0001). Second, we suggest that the growth on a metal surface should be controlled by the number of sites for dehydration of hydrated metal ions on the metal surface. The dehydration occurs only at the apex site of a protruding surface atom. The sites for the dehydration on the fcc(110) and hcp(10 $\bar{1}$ 0) rough planes are in number much larger than those on the fcc(111) and hcp(0001) smooth planes. Therefore the growth of single crystalline nanowires of fcc and hcp metals can occur dominantly on the fcc(110) and hcp(10 $\bar{1}$ 0) planes.

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