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Controlled crystallinity and crystallographic orientation of Cu nanowires fabricated in ion-track templates

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Abstract

The hallmark of materials science is the ability to tailor the structures of a given material to provide a desired response. In this work, the structures involving crystallinity and crystallographic orientation of Cu nanowires electrochemically fabricated in ion-track templates have been investigated as a function of fabrication condition. Both single crystalline and polycrystalline nanowires were obtained by adjusting applied voltages and temperatures of electrochemical deposition. The anti-Hall–Petch effect was experimentally evidenced in the polycrystalline nanowires. The dominant crystallographic orientations of wires along [111], [100], or [110] directions were obtained by selecting electrochemical deposition conditions, i.e., H₂SO₄ concentration in electrolyte, applied voltage, and electrodeposition temperature.

1. Introduction

In the past two decades, one-dimensional nanostructures, e.g. nanowires, nanorods, nanotubes, and nanobelts, have attracted great research attention stimulated by their unique properties which are considered to be the bases of future practical applications [1–7]. It is widely accepted that the performance of a given nanostructure is not only affected by its intrinsic properties but also influenced by its structure such as crystallinity and crystallographic orientation [8]. Therefore, understanding and controlling structure have been actively pursued as means of manipulating electrical, mechanical, magnetic and optical properties of nanomaterials.

To date, a large variety of methods for forming one-dimensional nanostructures have been reported [2, 3, 5]. Among them, the template method in combination with electrochemical deposition has shown unique advantages and therefore has been widely used [7, 9–15]. One of the attractive advantages is that the structural characteristics of fabricated nanomaterials can be artificially controlled. For instance, both polycrystalline and single crystalline Au nanowires were achieved by using gold sulfite and gold cyanide electrolytes, respectively [11]. Due to the interface energy minimum principle, the size effects on the crystallographic orientation of electrodeposited nanowires have been investigated both theoretically and experimentally [16–18]. In the recent past, a number of publications have further shown that the applied...
voltage and deposition temperature of electrodeposition have pronounced influences on the nanowires’ structural properties [12, 13, 18–24]. Undoubtedly, these structural characteristics will consequently dictate the functional performances of one-dimensional nanostructures via changing mechanical, electrical, magnetic properties and so on [10–13, 20, 24].

Recently, Cu nanowires have been of peculiar interests thanks to their important role in the current electronics industry based on their excellent electrical and thermal conductivity. However, to our knowledge, there has been no systematic investigation on control over structural properties. Here we report a comprehensive study for controlling and understanding the structural features of Cu nanowires electrochemically deposited into the nanopores of home-made polycarbonate ion-track templates. The effects of fabrication conditions including \( \text{H}_2\text{SO}_4 \) concentration in electrolyte, applied voltage, and electrodeposition temperature on the wires' structures involving both crystallinity and crystallographic orientation have been systematically investigated.

2. Experimental section

2.1. Swift heavy ion irradiation and chemical etching

Polycarbonate (PC) foils (Makrofol N, Bayer Leverkusen) of thickness 30 \( \mu \text{m} \) were irradiated at the UNILAC linear accelerator of GSI (Darmstadt, Germany) with \( \text{Pb} \) ions (kinetic energy 11.4 MeV \( \text{u}^{-1} \), fluence \( 5 \times 10^{8} \) ions \( \text{cm}^{-2} \)) at normal incidence. The damaged regions produced by the lead ions along their trajectories, called latent tracks, were selectively dissolved in 5 M \( \text{NaOH} \) at 50 \( ^\circ \text{C} \) leading to the formation of cylindrical nanopores in the membranes. Prior to chemical etching the foils were exposed to UV light for 2 h from each side in order to enhance the selectivity of the etchant and, thus, to increase the track etching rate [9, 11]. This track sensitization is necessary to produce highly cylindrical nanopores. During etching, an ultrasonic field was employed to achieve a homogeneous etching.

2.2. Electrochemical deposition of Cu nanowire arrays

A thin gold film was sputtered onto one side of the membrane and then reinforced electrochemically by a Cu layer with a thickness of several micrometers. This backing layer (Au + Cu) served as the cathode during the following electrochemical deposition of the Cu nanowires. The electrolytes consisted of an aqueous solution of 75 g l\(^{-1}\) CuSO\(_4\) \( \cdot 5\)H\(_2\)O and varied H\(_2\)SO\(_4\) concentrations. To prepare the Cu nanowires, direct current electrochemical deposition was employed. The deposition processes were monitored by recording current versus time curves. To make sure the nanopores were fully filled, overgrowth of nanowires was intentionally adopted until the wire caps were formed on the template top surface.

2.3. Characterization

The texture of the wire arrays was investigated by x-ray diffraction (XRD, X’Pert PRO, Panalytical, Cu K\(\alpha\), \( \lambda = 0.154056 \text{ nm} \)). For these examinations the wires were left embedded in the templates, and both the caps and the backing layer were removed. After dissolving the polycarbonate templates by dichloromethane (CH\(_2\)Cl\(_2\)), the morphology, the composition, and the crystallinity of wires were studied by means of scanning electron microscopy (SEM, Philips XL30 and JEOL JSM-6701F), high resolution transmission electron microscopy (HRTEM, JEOL JEM-3010), energy dispersive x-ray spectroscopy (EDS) and selected area electron diffraction (SAED). In the process of TEM sample preparation, an ultrasonic field was used to detach the wires from the backing layer.

3. Results and discussion

The low magnification SEM micrograph shown in figure 1(a) displays a representative overview of the sample. The wires are aggregated and homogeneously distributed on the backing layer after dissolving the template matrix by dichloromethane. The aggregation of wires is ascribed to surface tension effects of solvent droplets when drying the sample. The detailed description of this phenomenon can be found elsewhere [9]. The high magnification SEM image presented in figure 1(b) reveals that the wires have excellent cylindrical shape, and smooth and homogeneous contours along the wires’ length.
The wire diameter is around 75 nm. The corresponding template was etched for 3 min. Since the wire length equals the template thickness of 30 μm, the aspect ratio of the wires is expected to be as high as 400. For the preparation of this sample, the H2SO4 concentration, the applied voltage, and the deposition temperature were selected to be 30 g l⁻¹, 200 mV, and 50 °C, respectively.

The elemental composition of the as-prepared Cu nanowires, after liberating them from the PC template, was examined by EDS. The EDS spectrum of the nanowires is given in figure 2. It is obvious that only Cu signals are observed, indicating that the wires exclusively consist of elemental Cu.

It has been demonstrated that the morphology of the wires’ cap is an indirect indication of the crystallinity of the nanowire [11]. Namely, regular faceted caps are indicative of single crystalline nanowires, and caps consisting of irregular shapes, e.g. rounded shape, are hints of polycrystalline nanowires. In this work, this strategy has been employed to prejudge the crystallinity of the as-prepared Cu nanowires. Figure 3 displays the two representative shapes of caps. To fabricate these samples, the H2SO4 concentration was fixed to be 30 g l⁻¹. For the wires deposited at an applied potential of 100 mV and deposition temperature of 50 °C, the caps of wires are regularly faceted in spite of different shapes, as shown in figure 3(a), revealing that the wires are single crystalline. These faceted caps are clearer when their sizes are small, see figure S2 in the supplementary data (available at stacks.iop.org/Nano/21/365605/mmedia). However, for wires prepared at a higher applied potential of 400 mV and a lower deposition temperature of 22 °C, some grain boundaries are observed, as shown in figures 3(c) and (d). The corresponding SAED pattern shown as an inset in figure 3(c) confirms the polycrystalline characteristic. Interestingly, some bended wires were frequently observed in the polycrystalline sample, which is shown by the TEM micrograph in figure 3(d). To understand the growth mechanism of electrochemically deposited nanowires, a two-dimensional (2D) nucleation-growth mechanism, a three-dimensional (3D) nucleation-growth mechanism, and a modified critical dimension model have been proposed to explain the formation mechanism of crystallinity of electrochemically deposited nanowires [19–21, 23]. In these models, new grains will grow when the size of an initial grain nucleus exceeds the critical dimension \( N_c \), and the \( N_c \) is inversely proportional to overpotential. Namely, the lower the overpotential, the larger the critical dimension. In addition, the overpotential could be decreased by an elevated temperature and an ultrasonic environment, respectively [14, 25]. Taking the aforementioned factors into account, in the present work, a lower applied
Figure 4. TEM images of Cu nanowires. (a) Single crystalline wire, the applied potential and the deposition temperature were 100 mV and 50°C, respectively; (b) HRTEM image of the edge of single crystalline wire corresponding to (a); (c) and (d) TEM images of polycrystalline Cu nanowires, the applied potential and the deposition temperature were 400 mV and 22°C, respectively. The arrows are indicative of grain boundaries. The inset images in (a) and (c) are the corresponding SAED patterns. Note that, in the pictures, the layer on the wire’s surface is the residual polycarbonate after dissolving the template by dichloromethane.

Voltage and a higher temperature are the favorable conditions to form single crystalline wires.

It is not doubted that the as-prepared nanowires were originally straight since they were the replicas of the straight nanopores within the ion-track templates. The bended wires were probably formed during the process of sample preparation for TEM observation. The mechanical force induced by the employed ultrasonic field could be responsible for the bending of wires. As shown in figure 4(d), the bended regions were only found at the grain boundaries, suggesting that the grain boundaries are the preferred places to bend wires. It has been demonstrated that the hardness and yield stress of a bulk material typically increase with decreasing grain size, a phenomenon known as the Hall–Petch effect [26, 27]. However, the computer simulations of the deformation of nanocrystalline copper showed that the plastic deformation is due to a large number of small ‘sliding’ events of atomic planes at the grain boundaries. Therefore, the nanocrystalline Cu became soft and this observation is understood as the anti-Hall–Petch effect [28].

The fabrication conditions not only influence the crystallinity of the Cu nanowires, but also affect their crystallographic orientation simultaneously. In the present work, XRD was employed to evaluate the crystallographic orientation of wire arrays fabricated at various deposition conditions. For these examinations the wires were left embedded in the templates. In order to eliminate the external diffraction signals, before XRD measurement both the wires’ caps and the backing layer (Au + Cu) were carefully torn away. Note that, after this process, the samples were still kept undamaged, see figure S1 in the supplementary data (available at stacks.iop.org/Nano/21/365605/mmedia). The diffraction patterns of nanowire arrays deposited as a function of the \( H_2SO_4 \) concentration of electrolytes, and at fixed applied voltage of 90 mV and deposition temperature of 50°C are shown in figures 5(b)–(j). All the Bragg peak positions are in agreement with those of the standard Cu powder sample (JCPDS, 04-0836) shown in figure 5(a). It is clearly seen that the relative intensities of the diffraction peaks of (111), (200), and (220) planes change dramatically with increasing \( H_2SO_4 \) concentration. In the case of 30 g l\(^{-1}\) (figure 5(i)), the diffraction peak of the (220) plane is the most intensive, whereas, the other two peaks are rather weak, indicating that the wires strongly possess the [110] growth direction. Thus, the \( H_2SO_4 \) concentration plays a significant role in determining the crystallographic orientation of wire arrays. To quantitatively evaluate the degree of preferred orientation, the texture coefficients (TC) of the three strongest reflection
planes (111), (200), and (220) are calculated by the Harris formula [9, 11]:

$$TC(h_{i}k_{i}l_{i}) = \frac{I(h_{i}k_{i}l_{i})/I_{0}(h_{i}k_{i}l_{i})}{(1/N) \times \sum_{j=1}^{N} (I(h_{j}k_{j}l_{j})/I_{0}(h_{j}k_{j}l_{j}))}$$

where $I_{0}(h_{i}k_{i}l_{i})$ are the intensities of the $(h_{i}k_{i}l_{i})$ lattice plane of the standard Cu powder sample, $I(h_{i}k_{i}l_{i})$ are the intensities of the $(h_{i}k_{i}l_{i})$ lattice planes under analysis. $N$ is the total number of diffraction planes taken into account for calculations and represents the maximum value of the texture coefficient. For $TC(h_{i}k_{i}l_{i}) > 1$ a preferred crystallographic orientation perpendicular to the $(h_{i}k_{i}l_{i})$ planes exists. By this formula, the calculated texture coefficients of the (111), (200), and (220) planes are shown in figures 5(k)–(m), respectively. Note that all texture coefficients are calculated according to Gaussian fitting of each peak, see figure S3 in the supplementary data (available at stacks.iop.org/Nano/21/365605/mmedia). It is clear that the H$_2$SO$_4$ concentration has little impact on $TC(200)$, but has pronounced influence on $TC(111)$ and $TC(220)$. As shown in figure 5(m), the value of $TC(220)$ increases when the H$_2$SO$_4$ concentration increases from 2.2 to 5.1 g l$^{-1}$ and from 11 to 30 g l$^{-1}$. The value of $TC(220)$ decreases when the H$_2$SO$_4$ concentration increases from 5.1 to 11 g l$^{-1}$ and from 30 to 35.5 g l$^{-1}$. Whereas, $TC(111)$ shows completely opposite trends compared with $TC(220)$.

Figure 6 displays the XRD patterns and the calculated texture coefficients of the (111), (200), and (220) planes of Cu nanowires deposited at varied applied voltages and at fixed H$_2$SO$_4$ concentration of 30 g l$^{-1}$ and temperature of 50$^\circ$C. By the Harris formula, the calculated texture coefficients of the (111), (200), and (220) planes are shown in figures 6(i)–(k), respectively. It is seen that, with increasing applied voltage from 90 to 300 mV the $TC(220)$ decreases from 2.7 to 0.1 and then keeps fixed $\sim 0.1$ as voltage further increases. At the same time, the $TC(200)$ keeps almost constant at $\sim 0.2$ as voltage increases from 90 to 300 mV and increases quickly from 0.2 to 2.8 as the voltage varies from 300 to 500 mV, then drops rapidly from 2.8 to 0.3 as the voltage is further increased from 500 to 600 mV. The $TC(111)$ increases as voltage increases from 90 to 300 mV and from 500 to 600 mV, and decreases as voltage goes up from 300 to 500 mV.

In addition to the effects of H$_2$SO$_4$ concentration and applied voltage, the impact of electrodeposition temperature on the crystallographic orientation of Cu nanowire arrays has been investigated. Figure 7 shows the XRD patterns and the calculated texture coefficients of the (111), (200), and (220) planes of arrays deposited at varied electrodeposition temperatures, and at fixed applied voltage of 200 mV and H$_2$SO$_4$ concentration of 30 g l$^{-1}$. From figure 7(j), it is obvious that $TC(200)$ is insensitive to deposition temperature and keeps its value $\sim 0.3$. However, comparing with $TC(200)$, $TC(111)$ and $TC(220)$ are remarkably influenced by temperature and display opposite trends, see figures 7(i) and (k). With increasing temperature from 24 to 70$^\circ$C, $TC(111)$ decreases from 2.3 to 0.4. But, if the temperature is further increased to 80$^\circ$C, it is restored to the value of 0.8.

In the electrochemical deposition, the growth of metallic nanowires is a complex process, which is influenced by
Figure 6. XRD patterns and calculated texture coefficients of the (111), (200), and (220) planes of Cu nanowire arrays deposited at varied applied voltages, and at fixed H₂SO₄ concentration in electrolytes of 30 g l⁻¹ and a deposition temperature of 50 °C. (a) XRD standard pattern of the Cu powder sample (JCPDS, 04-0836); (b)–(h) measured XRD patterns of Cu nanowires deposited at varied voltages from 100 to 600 mV, respectively; (i)–(k) calculated texture coefficients of the (111), (200), and (220) planes by the Harris formula, respectively. The dotted lines are only used to guide the eye.

Figure 7. XRD patterns and calculated texture coefficients of the (111), (200), and (220) planes of Cu nanowire arrays deposited at varied electrodeposition temperatures, and at a fixed applied voltage of 200 mV and H₂SO₄ concentration in electrolyte of 30 g l⁻¹. (a) Standard pattern of the Cu powder sample (JCPDS, 04-0836); (b)–(h) measured XRD patterns of Cu wire arrays deposited at temperatures increasing from 24 to 80 °C, respectively; (i)–(k) calculated texture coefficients of the (111), (200), and (220) planes by the Harris formula, respectively. The dotted lines are only used to guide the eye.
Therefore, the [110] crystallographic orientation was obtained above, the increased temperature diminishes the overpotential. It could disturb the absorption of H ions. Besides, as discussed below, the relatively low voltages from 100 to 600 mV were used suggested by the authors, could produce H ions in the solution than 1 V, we employed [17–19, 22]. Such a high voltage, as the deposition of Ni nanowires, higher voltages, usually greater than 3 V, were employed [17–19, 22]. Such a high voltage, as suggested by the authors, could produce H ions in the solution and then accelerate the absorption of H ions. In this work, the relatively low voltages from 100 to 600 mV were used to deposit wires. The overpotentials within a lower range could disturb the absorption of H ions. Besides, as discussed above, the increased temperature diminishes the overpotential. Therefore, the [110] crystallographic orientation was obtained by using lower voltage and higher temperature. However, the probabilities coming from the differences of materials’ intrinsic properties cannot be excluded. The discrepancy between results of Cu and Ni nanowire arrays suggests that this research topic needs to be further investigated. Additionally, it is interesting to note that, in figure 6(f), the peak (200) dominates the whole pattern, indicating that the (200) plane has the minimum surface energy when the applied voltage is ~500 mV, and the temperature and the H2SO4 concentration are fixed to be 50°C and 30 g l−1 respectively.

One should mention that the effective applied voltage (Ueffective) should be less than the real applied voltage (Ureal) because a part of the real applied voltage is exhausted by the electrolyte (Uelectrolyte) inside the nanopore of the template. The effective applied voltage can be written as Ueffective = Ureal − Uelectrolyte. The magnitude of Uelectrolyte is mainly determined by the resistance of the electrolyte inside nanopores and therefore finally determined by the amount and the mobility of conductive carriers in the electrolyte. As known, the higher the amount and the mobility of carriers, the lower Uelectrolyte is, and consequently the higher Ueffective is. Thus, increasing H2SO4 concentration not only increases the number of H ions which benefits the [110] crystallographic orientation, but also enhances Ueffective which promotes formation of the [111] orientation. Obviously, increasing the H2SO4 concentration could give rise to two competitive orientations, i.e. [110] and [111]. This is the reason why TC(220) decreases and TC(111) goes up as the H2SO4 concentration increases from 5.1 to 11 g l−1 and from 30 to 35.5 g l−1, as shown in figure 5. Similarly, increasing temperature could enhance carrier mobility and therefore diminishes Ueffective which is favorable to produce the [111] orientation. Due to this, TC(111) is restored from 0.4 to 0.8 as temperature is increased from 70°C to 80°C, as displayed in figure 7.

Taking the aforementioned findings into consideration, it seems that arrays with strong [110] orientation are difficult to obtain since increased H2SO4 concentration and deposition temperature could increase the effective applied voltage which induces the [111] orientation. However, we believe this increased part of the effective applied voltage would be eliminated by decreasing the real applied voltage. Therefore, an array with extremely strong [110] orientation can be obtained, see the XRD spectrum shown in figure 8. The inset table shows the calculated texture coefficients of the (111), (200), and (220) planes. The value of TC(220) is 2.98, indicating a strong [110] texture. For preparation of this Cu nanowire array, the real applied voltage, the electrodeposition temperature, and the H2SO4 concentration were chosen to be 40 mV, 80°C, and 35.5 g l−1, respectively. We should address the fact that the applied voltage of 40 mV is not sufficiently high for the deposition of Cu wires at the temperature of 50°C, and the H2SO4 concentration of 30 g l−1.

For XRD spectra of one piece of bulk single crystal of Cu, peaks for (111), (200) and (220) cannot show up in the same spectrum because these planes are not parallel to each other. In all XRD spectra of the Cu nanowire arrays plotted in figures 5–7, when all (111), (200) and (220) peaks appear, either it means that each wire is made of many crystalline
grains or segments with different growth directions of [111], [100] and [110], or, it means that single crystalline wires have these three preferred growth directions. In the first case, each wire is typically polycrystalline. Figure 8 shows a nanowire array with a highly preferred growth orientation of [110], while figure 6(b) is a case for moderately [110]-preferred growth. Figures 6(d), (h), and (b) show cases with preferred growth orientation of [111], and figure 6(f) is a case for [100]-preferred growth. In the remaining samples, two or three of the three major peaks appear in the same XRD spectrum. Therefore, it is reasonable to suggest that all these three preferred crystallographic orientations, i.e. [111], [100], and [110], could be controlled for the Cu nanowire arrays, respectively.

4. Conclusions

The crystallinity and crystallographic orientation of electrochemically deposited Cu nanowires in ion-track polycarbonate templates were controlled by deposition conditions. At low voltage and high temperature, single crystalline wires were obtained. Otherwise, polycrystalline wires were achieved. In the polycrystalline wires, the grain boundaries were the preferred regions for bending, evidencing the anti-Hall–Petch effect. In addition, Cu nanowire arrays with preferred [111], [100], or [110] crystallographic orientations were obtained. The H₂SO₄ concentration, the applied voltage, and the temperature coherently influence the crystallographic orientation of wires via their effects on H ion absorption and consequently the wires’ surface energy which ultimately dictates the wires’ growth orientation.

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