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Incoherent grain boundaries in CuO nanowhiskers

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Abstract. An array of CuO nanowhiskers have been fabricated by heating of copper coatings formed on stainless steel mesh substrate in air. Cross-sections of the nanowhiskers were studied by transmission electron microscopy. It was established that whiskers consist of two or more grains with incoherent boundaries. The mechanism of the formation of incoherent boundary is revealed. An important role of the incoherent boundaries in the formation of the nanowhiskers is discussed.

1. Introduction

Nanowires, also called nanowhiskers (NWs), are crystals with a high aspect ratio (diameter does not exceed 0.1 μ m and length can reach 100 μ m). NWs have a unique complex of mechanical, physical and chemical properties and are one of the most promising materials. It has long been known that metal whiskers have excellent mechanical properties [1]. Studies show that NWs have a nearly ideal (dislocation-free) structure. This excludes the usual mechanisms of plastic deformation and brings their strength closer to the theoretically possible. NWs possess pronounced crystalline anisotropy.

Over the years of NW research, many methods had been developed for their production such as gas vapor deposition, electrodeposition, thermal oxidation, etc. [2]. Currently, NWs are widely used in various fields of science and industry as gas detectors [3], heterogeneous catalysts and photocatalysts [4 - 6], electrodes in batteries [7, 8], probes [9], emitters [10, 11], solar cells [12] and highly sensitive sensors [13].

Semiconductor NWs (e.g. CuO and TiO₂) are already used as highly efficient photocatalysts [5, 14]. In this case tenorite (CuO) NWs are more preferable due to they are *p*-type narrow-gap semiconductors (band gap is 1.2 eV) and their application is possible at photocatalysis under the visible range of radiation while TiO₂ actives under ultraviolet light only.

Specific surface area, structure, internal defects, mechanical stresses, and surface morphology of the catalyst are great importance for catalysis and photocatalysis. The catalytic properties of metallic nanocrystals in many reactions are determined by their faceting [15]. For example, the Fe (111) facet in the synthesis of ammonia from nitrogen has a catalytic activity 430 times higher than the (110) facet [16]. Large contact area with the substrate, high specific surface area, as well as anisotropic morphology and corresponding improvement in mass transfer make NWs attractive electrocatalysts for the oxygen reduction reaction [17].

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In particular, CuO NWs can be used in photocatalysis for wastewater treatment [5]. This technology requires the placement of NWs on a strong metal mesh. The copper mesh does not have sufficient mechanical strength; therefore, in this case the copper layer is electrodeposited onto a stainless steel mesh. As shown in our previous studies [18], the copper layer consists of particles with a high density of defects. As a result of subsequent annealing, NWs are formed on this layer. On the other hand, it is known [19] that the structure and thickness of the copper layer have an effect on the size, density, and structure of NWs, all affect to their catalytic activity.

Transition metal oxides are intensively studied as materials for anodes of lithium-ion batteries. Copper oxide is one of the promising candidates due to its high theoretical capacity (tenorite and cuprite have 673 and 374 mA \cdot h/g respectively), non-toxicity and relative cheapness. In addition, the use of NWs as the active material of an anode increases mechanical stability, improves the kinetics of the electrochemical reaction and charge transfer in the electrode material [8].

Despite the fact that studies of the properties of CuO NWs have been performing for more than a decade [20], important questions remain regarding their structure and growth mechanism. To date, it has been established [20, 21] that CuO NWs are bi-crystals having a twin structure, twin planes are parallel to the growth direction. At the same time, it remained unclear by which channels copper cations are transported to the growth surface of the NWs. The side surface of NWs is excluded due to at annealing temperature copper interacts with the atmosphere results formation of chemical bonds copper cations with oxygen before they reach the growth surface. In [22, 23], it was shown that incoherent boundaries between bi-crystal components can play a role of copper cation transport channels. The existence of incoherent boundaries in CuO NWs was confirmed by transmission electron microscopy (TEM) studying cross-sections of NWs [23]. The aim of this work is to reveal the mechanism of incoherent boundary formation in CuO bi-crystals.

2. Methods

Copper oxide NWs were grown by annealing of copper coatings in air at the temperature range 250– 500° C. The copper coatings were formed on the stainless steel (type AISI 321) mesh substrate (wire diameter is 30 μ m, mesh size is 40 μ m) by electrodeposition from aqueous solutions of copper sulfate (250 g/l CuSO₄ and 90 g/l H₂SO₄). Electrolysis was carried out in a standard three-electrode electrochemical cell at the potentiostatic regime. A copper plate of the ASTN C10200 type was used as the anode as well as a copper wire of the same type served as the reference electrode. The duration of electrodeposition process with overvoltage of 160 mV was 15 minutes. NWs were separated from the substrate by ultrasonic treatment in an alcohol bath.

The morphology and surface of the NWs was examined by scanning electron microscopy on Tescan Mira 3.

For TEM studies the ultrathin cross-sections of NWs were prepared using a technique similar to proposed for studying nanotubes in [24]. The cross-sections of NWs investigation was performed with a JEOL2100F microscope operated at 200 kV. Electron micrographs obtained in the diffraction contrast regime and corresponding microdiffraction patterns were analyzed. Additionally, the samples were investigated in a high-resolution mode, and the corresponding images were analyzed by the fast Fourier transform method.

3. Results and discussion

In the thermal oxidation process of an electrolytic copper coating at the temperature of 400 $^{\circ}$ C, the so-called forest of nanowhiskers is formed (figure. 1 a).

Figure 1(b) is demonstrated high-resolution electron microscopy (HREM) image of the CuO NW cross-section. It is clearly seen the NW consists of two grains. For convenience, let us write down these two grains as G1 and G2. It should be noted the boundary between these grains is incoherent. The boundary is parallel to the (001) planes of G1 and herewith it almost parallel to the $(11\overline{2})$ plane of G2. In the diffraction pattern (figure 1(c,d)), two array of diffraction spots formed by the translation

of parallelograms OABC and OFED can be noted. In the figure 1(d) diffraction spots A, C, B, L correspond to reflections from the $(00\overline{1})_1$, $(110)_1$, $(11\overline{1})_1$, $(11\overline{2})_1$ planes, respectively. Then zone axis, which we take for the direction of growth, has indexes $[\overline{1}10]$. However, it must also be noted that the figure 1(b) does not allow us to unambiguously distinguish the growth directions $[\overline{1}10]$ and [110]. Similarly, parallelogram OFED corresponds to reflections from G2.



Figure 1. (a) Low-magnification scanning electron microscopy image of CuO NWs. (b) TEM image of a bi-crystal cross section. (c) The diffraction pattern of the bi-crystal. (d) The enlarged central part of the picture diffraction pattern.

An analysis of the figure 1(b) showed that G2 is the result of two successive mirror reflections: first reflection in $(11\overline{1})$ plane, then in $(00\overline{1})$ plane. The 180 degree rotation of the parallelogram OABC about OB gives the parallelogram OC'BD. In the direct space this operation corresponds to reflection in $(11\overline{1})_1$ plane. The parallelogram OFED corresponding to G2 of the bi-crystal can be obtained by translating the parallelogram OC'BD along DB followed by 180 degree rotation about OD which is equivalent of reflection in $(00\overline{1})_2$ plane. The calculation shows that the angle between the $(00\overline{1})_1$ and $(001)_2$ planes of the bi-crystal should be 48.4 °, which coincides within the experimental error with shown in the figure 1(b) angle $\angle A'OA = 49^\circ$. The small deviations can be attributed to the fact that it was not possible to achieve the coincidence of the zone axis and the electron beam due to required large tilt of the sample. Direction of the reciprocal lattice vector $g(11\overline{2})_1$ practically coincides with the direction of the vector $g(\overline{110})_2$. According to the calculation, the angle between them is 1.97 °, which is larger than the angle between the corresponding line segments LO and FO, as

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shown in the figure 1b. The discrepancy can be explained by a small rotation of G2 about the direction $[1\overline{10}]$, as a result of which the angle between the $(001)_1$ and $(00\overline{1})_2$ planes increased slightly, and the angle between $(11\overline{2})_1$ and $(\overline{110})_2$ decreased.

Confirmation of the above assumptions can be an image of the cross-section of a multiply-twinned nanowhiskers and corresponding diffraction pattern which are presented in the figure 2. In the diffraction pattern, two reflex arrays can be distinguished similar to those shown in figure 2b, and figure 2a clearly demonstrates the effect of successive twining with respect to the $(\overline{111})$ and $(00\overline{1})$ planes. Region II is the result of the reflection of region I relative to the $(\overline{111})$ plane, region III is the result of the reflection of region I relative to the $(00\overline{1})$ plane. Thus, region III is the result of two successive reflections: first relative to the $(\overline{111})$ plane, then relative to the $(00\overline{1})$ plane.



Figure 2. TEM image of a multiply-twinned nanowhisker. (b) Diffraction pattern of the nanowhisker.

Nowadays, there are a few proposed CuO nanowhiskers growth mechanisms include vapor-solid growth, stress-induced formation, and short-circuit/grain boundary diffusion [22]. The vapor-solid growth mechanism cannot produce the high NW growth rates in the reason of the vapor pressure of copper oxide at 400° C is about 10^{-9} Torr [25]. The stress-induced formation of CuO NWs was discussed in [23]. There it is argued that the internal stresses arise from the volume mismatch produced during annealing, and they are the driving force for the diffusion of copper cations to the top of the whisker.

It is well known one- and two-dimensional defects such as dislocation lines, dislocation walls, grain and phase boundaries can be considered as short circuits in materials. Short-circuit diffusion paths in metals and alloys are importance in the oxidation process. Thermal oxidation demands consideration of interface- or dislocation-enhanced diffusion and other complex phenomena [26].

As a rule self-diffusion is fastest along a free surface where the activation energy constitutes 0.1-0.3 of the activation energy of the bulk diffusion. Diffusion rates along high-angle grain boundaries are slower with the activation energy, which amounts typically to (0.4-0.6) of the activation energy of the bulk diffusion. Low-angle grain boundaries possess typically slower diffusion rates. As well as, the diffusion coefficients of the low-angle grain boundary and of individual dislocations do not typically exceed 1-10 % of the values which correspond to the diffusivities of high-angle grain boundaries [26].

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It should be noted that the incoherent interface can act as a source or sink for thermal vacancies, thus enabling the relief of strains in the growing NWs.

Observed grain boundary runs along the entire length of the NW and acts as a path for short-circuit diffusion transport of Cu ions to the NW tip. The growth of CuO NWs occurs via stress-induced diffusion of Cu cations across multilayered oxide substrate followed by short-circuit diffusion along the CuO NW grain boundary to the NW tip where subsequent oxidation and growth processes occur.

4. Conclusions

CuO NWs fabricated by annealing of copper coatings in air at 400 °C have been studied by TEM. It is revealed that the NWs consist of two or more grains with incoherent boundaries. The incoherent boundaries are the results of two successive reflections in non-equivalent planes. The NWs grow by short-circuit diffusion transport of copper cations along internal boundaries from the substrate to the top of NWs. Studies of internal structure of NWs are important not only for understanding their mechanisms of growth, but also to predict the structurally dependent properties such as strength, catalytic activity and others.

Acknowledgments

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