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Microstructure characterization of Al_2O_3 nanowires with networked rectangular nanostructure

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Abstract. L-shaped and U-shaped Al_2O_3 nanowires were synthesized using a vapor phase deposition method. The as-grown nanowires are single crystalline and structurally uniform at the junction of the branches. Detailed TEM analysis revealed that the growth direction of the nanowires is parallel to the *a*- or *b*-axis directions, and switched growth from one direction to another forms the rectangular morphology of the peculiar L-shaped or U-shaped nanowires. Possible growth mechanism of the Al_2O_3 nanowires was explained. Our results can provide evidence to understand the growth mechanism of the complicated nanostructure.

PACS. 73.63.Bd Nanocrystalline materials – 74.62.Bf Effects of material synthesis, crystal structure, and chemical composition

1 Introduction

Since the discovery of carbon nanotubes in 1991 [1], one dimensional nanoscale materials have attracted extraordinary attention owing to their potential applications in electrical [2], optical [3], magnetic devices [4,5]. Al_2O_3 is one of the most important structural materials due to its high-elastic modulus, optical characteristics [6,7], thermal and chemical stability [8]. Al_2O_3 is expected to have potential applications especially in high-temperature composition materials and nanodevices, such as mechanical enhancement materials in polymer, ceramic and glass based composites. Different methods have been used to synthesize alumina nanowires, such as carbon nanotube template method [9], iron catalyst involved thermal evaporation method [10], carbon-assisted synthesis [11] and electrochemical synthesis of ordered alumina nanowire arrays [12]. Here we reported Al_2O_3 nanowires with networked rectangular morphology prepared using vapor phase deposition method.

2 Experimental

The synthesis of Al_2O_3 nanowires was conducted in a tube furnace. Aluminum powder (99.9%) and alumina powder (99.9%) were mixed together with a molar ratio of 25:1 and put in an alumina boat, which was covered with a silicon wafer. The boat was then put in a quartz tube. A constant argon flow ∼100 sccm was introduced into the system, and the pressure inside the tube was kept at 0.06 MPa. Afterwards, the furnace was heated to 1000 °C for 2 h. After cooling down, a transparent layer was deposited on the Si wafer. Scanning Electron Microscopy (SEM) and a Tecnai F30 Transmission Electron Microscopy (TEM) were used to characterize the morphology of the as-grown Al_2O_3 nanowires. High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were implemented to study the microstructure of the as-grown Al_2O_3 nanowires and the chemical compositions of the products were analyzed with energy-dispersive spectroscopy (EDS).

3 Results and discussions

Figure 1a shows scanning electron microscopy image revealing the general morphology of the Al_2O_3 nanowires. It is visible from the SEM image that the nanowires were grown in a bulk quantity on the Si substrate. Nanowires with networked rectangular nanostructure can also be found everywhere in the SEM image. A magnified SEM image was shown in Figure 1b, which reveals a typical U-shaped morphology of the Al_2O_3 nanowires. The diameters of the nanowires are ∼100 nm and the length of the nanowires can be up to several micrometers.

The morphology and microstructure of the Al_2O_3 nanowires were further studied by using transmission electron microscopy (TEM). Figures 2a and 2b show a typical U-shaped and L-shaped Al_2O_3 nanowire, respectively.

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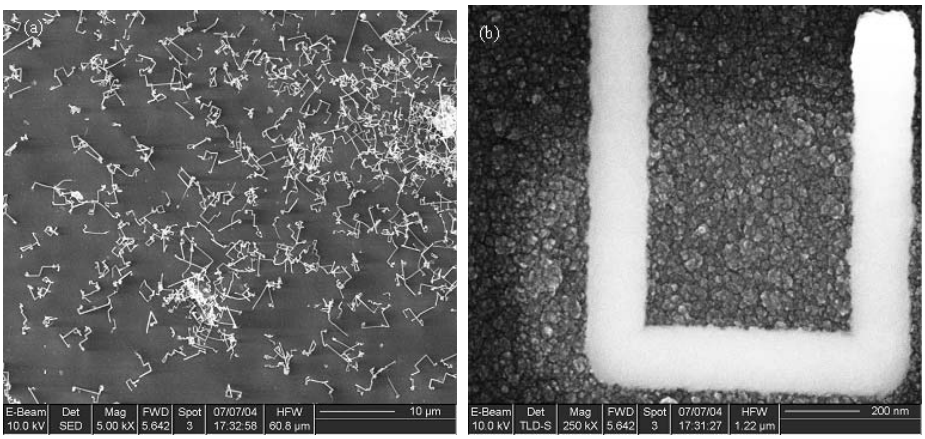
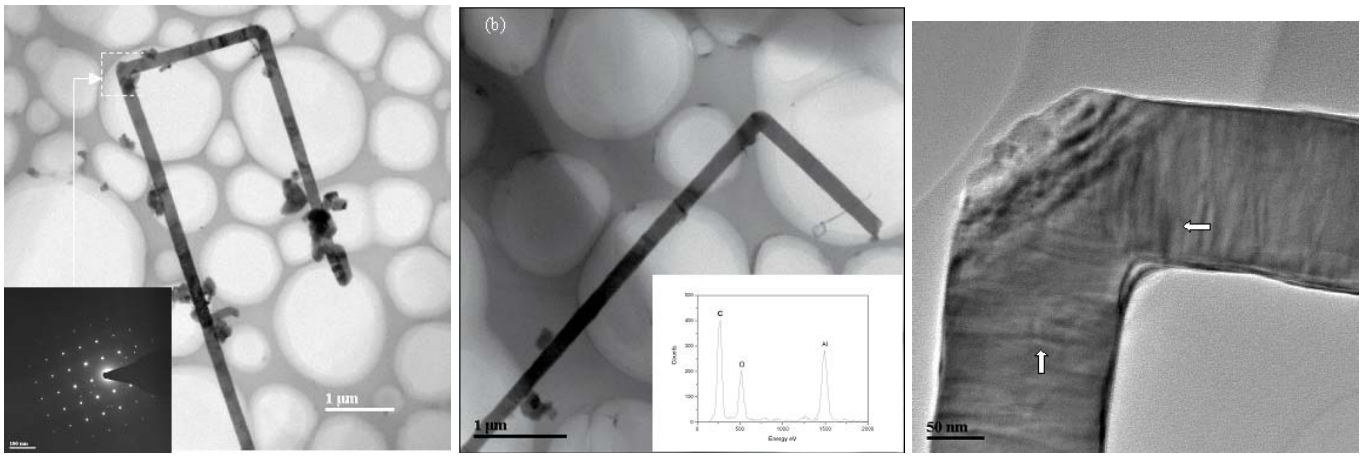


(a) (b)

Fig. 1. (a) SEM image of Al_2O_3 nanowires, in which abundant of nanowires take the morphology of rectangular L-shape or U-shape. (b) Magnification SEM image of a U-shaped Al_2O_3 nanowires.



(a) (b) (c)

Fig. 2. (a) TEM image of a U-shaped Al_2O_3 nanowires, the inset shows the SAED image recorded from area indicated by the arrow, revealing that the U-shaped nanowires are single-crystalline. (b) TEM image of a L-shaped Al_2O_3 nanowires. Inset shows the EDS spectrum taken from a single Al_2O_3 nanowires. (c) Magnification TEM image recorded from the junction of two branches. The arrow indicates stacking fault of the nanowires.

The diameters of the nanowires are ∼100 nm in average. The three branches of the U-shaped nanowires are about ∼10 μm, ∼3 μm and ∼6 μm, while the two branches of the L-shaped nanowire are about ∼10 μm and ∼2 μm respectively. It is obvious that the Al_2O_3 nanowires exhibit a uniform diameter throughout their length. The inset in Figure 2a is the select area electron diffraction (SAED) pattern taken from the area indicated by the arrow, which is along [001] zone axis of the Al_2O_3 nanowire. The SAED pattern revealed that the Al_2O_3 nanowire is single crystalline and structurally uniform at the two branches. Inset in Figure 2b shows the corresponding EDS spectrum taken from a single nanowire, which indicates that the as-grown nanowires are composed of Al and O, with an atomic ratio of 38.8:61.2, in a good agreement with the theoretical ration of bulk Al_2O_3. Figure 2c is a high-magnification TEM image revealing the morphology and microstructure details at the junction area of a single Al_2O_3 nanowire. It is visible that though there are some stacking faults on the nanowires, the nanowire remains single crystalline. As discussed in the work by Zhao et al. [13], these planar defects play an important role in the formation of the peculiar L-shaped or U-shaped Al_2O_3 nanowires. Figure 3 shows a high-resolution TEM image of a single Al_2O_3 nanowire with rectangular morphology, and the incident electron beam is parallel to the [001] zone axis of the nanowire. The inset corresponds to the diagraph of the fast Fourier transform (FFT). It is revealed that the growth direction of the Al_2O_3 nanowires is [200] direction. Several tens of such Al_2O_3 nanwires were studied with the similar networked rectangular structure, and it is found that they all grow along the [200] direction (the *a*-axis).

Since no catalyst was used in the growth process, the conventional vapor-liquid-solid (VLS) growth model that is usually used to explain the growth mechanism of

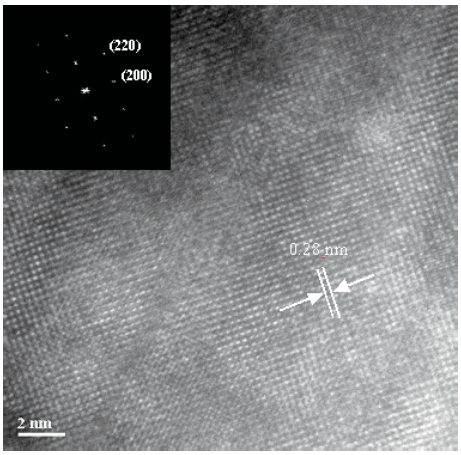


Fig. 3. Typical HRTEM image showing that the Al_2O_3 nanowires are single crystal, the left-top inset is the corresponding FFT pattern. The resolved spacing between the parallel fringes in the length direction is approximately 0.28 nm. It corresponds to the [200] lattice plane of Al_2O_3.

nanowires is excluded in our case. An alternative vapor-solid (VS) model was proposed to explain the growth of the Al_2O_3 nanowires in our work [14]. When the system temperature was headed up to 1000 °C, the following chemical reactions took place, resulting the formation of the Al_2O_3 nanowires:

$$\mathrm{Al(l)} + \mathrm{Al_2O_3(s)} \rightarrow \mathrm{Al_2O(g)}, \quad (1)$$

$$\mathrm{Al_2O(g)} + \mathrm{O_2(g)} \rightarrow \mathrm{Al_2O_3(s)}. \quad (2)$$

It is known that the melting and the boiling points of aluminum are 660 °C and 2467 °C, respectively. When the system temperature was hold at 1000 °C, the melting aluminum can continuously react with the solid powder alumina powder (melting point 2054 °C) to form gaseous Al_2O vapor as in reaction (1). The Al_2O vapor was metastable, and can act as self-catalyst. Afterwards, it was easily oxidized by the residual oxygen in the vacuum. Nuclei of the Al_2O_3 were formed on the silicon wafer. During the grown process at 1000 °C, melting Al can continuously react with alumina, and preferable elongation of the nuclei along the *a*- or *b*-axis directions occurred to form the Al_2O_3 nanowires. The formation of the peculiar U-shaped and L-shaped nanostructure in Al_2O_3 is ascribed to the alternating switch growth from [200] (the *a*-axis) to [020] (the *b*-axis). It is obvious that the change of grown direction is reasonable, because they are the two crystallographically equivalent directions. The exact mechanism of the formation of this hierarchically organized structure is not clear, which needs further investigation. However, the growth mechanism may be related to the existence of structure defects formed during nanowire growth. Very similar morphology was observed in MgO nanowires by Zhao et al. [13]. They explained the growth mechanism of the nanowires as follow: during the growth process, some defects such as vacancies and stacking faults were formed. These defects could play an important role in the growth of networked rectangular nanowires, which make it possible for the nanowires to change the growth directions to a perpendicular one, resulting the formation of the branches.

4 Conclusions

Al_2O_3 nanowires with networked rectangular morphologies have been synthesized by vapor phase deposition method. A VS model was proposed to explain the possible growth mechanism, but the exact growth mechanism for this peculiar nanostructure is not clear. These novel hierarchically organized nanostructure of Al_2O_3 nanowires may be used as building block for some nanodevices.

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