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K_2SO_4 nanowires a good nanostructured template

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Abstract

K_2SO_4 nanowires with the width of 66–100 nm were fabricated by ice-subliming method. Under the heat radiation, the surface of K_2SO_4 nanowires presented ordering K_2SO_4 dots of 3.5 nm and arrays of narrow wires with the width of 3 nm due to the remnant H_2O molecules are released. Using these K_2SO_4 nanowires as the substrate, ZnO nanowires were also fabricated by vapor-phase deposition.

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Keywords: Nanowires; Ice-subliming method; Vapor deposition; Semiconductors

1. Introduction

Progress in the fabrication and characterization of one-dimensional (1D) nanostructured materials has attracted much interest, owing both to their novel physical properties, which differ from those of bulk materials, and to their potential application in nanodevices [1–7]. Many methods succeed in fabricating nanowires and nanotubes such as metal catalysis [8], carbon nanotube template [9–11] and porous alumina template [12–15]. Because the template and catalysis should be removed for getting the pure 1D materials, it is important to find a template which can be easily removed. In this Letter, K_2SO_4 nanowires template is introduced for its high melting point of 1362 K and being easily washed off. Specially, these K_2SO_4 templates are more suitable to the vapor deposition method due to their loose structure permit the fabrication of the nanowires with different thickness or different materials. In addition, ordering QDs and narrow wires with size of several nanometers can form on the surface of K_2SO_4 nanowires. Because ZnO is an n-type, direct band-gap semiconductor with $Eg = 3.35$ eV [16,17] and particularly interesting for nanodevice applications, ZnO nanowires with ordering QDs is also fabricated.

2. Experimental

The fabrication of K_2SO_4 nanowires by ice subliming method [18]: 0.251 g, 0.0251 g and 0.00251 g K_2SO_4 with AR purity was dissolved in 50 ml water, respectively. After the solution of 0.5 wt% was filled into a 10 ml weighing bottle, it was immersed into liquid nitrogen (77 K). The ice containing K_2SO_4 formed in a minute. Then the weighing bottle was placed into a vacuum chamber before liquid nitrogen had vaporized entirely. Finally the chamber was kept at about 10 Pa by being continually vacuumed with a steady rate of 4 L/s. After this lasted for 24 h, we got the residual white floccules. We also fabricated the products from the solution of 0.05 wt% and 0.005 wt% by the above process.

The fabrication of nanostructured ZnO on K_2SO_4 nanowires: A molybdenum piece between the two electronic rods was used

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as the heat source. ZnO with 99.999% purity was placed on the molybdenum piece. K_2SO_4 white floccules were placed on a copper net (∅3 mm), 5 mm far away above ZnO source. The Mo piece was heated to 1373 K at 1×10^{-3} Pa. ZnO started to grow on K_2SO_4 substrate. The growth process lasted for 30 minutes.

3. Results and discussion

The crystal structure of K_2SO_4 product was charactered by X-ray diffraction (XRD). Fig. 1 is XRD spectrum of the products with the radiation of Cu K_α. The peaks show an orthorhombic structure with $a = 5.770$ Å, $b = 10.07$ Å and $c = 7.477$ Å (PDF #830681). The morphology was charactered by transmission electron microscopy (TEM) with HITACHI TEM H-8100 IV at 200 kV. Fig. 2 shows the morphology of K_2SO_4 product fabricated by ice subliming method. As shown in Fig. 2(a) (from 0.5 wt% solution), the structure is mainly composed of nanowires with the widths of 66–100 nm and some bridge conjunctions. Fig. 2(b) (from 0.05 wt% solution) and (c) (from 0.005 wt% solution) also show the nanowires with similar width, but they present more fractional segments.

We think the formation of the K_2SO_4 nanowires as follows. When the sample temperature is very low (77 K), the sublimation rate of ice is also low, and the absorbed heat of the sample was larger than the heat loss induced by the sublimation of ice. This led to raise the sample temperature. The final temperature should balance the absorbed heat and the loss heat. The sublimation mainly progressed at this final temperature. The sample temperature in our experiments should be about 273 K for its permitting the high sublimation rate.

During the process of the sublimation, the pressure of the vacuum chamber kept at 10 Pa. It was far lower than the saturated vapor pressure of the ice at the experimental temperature.

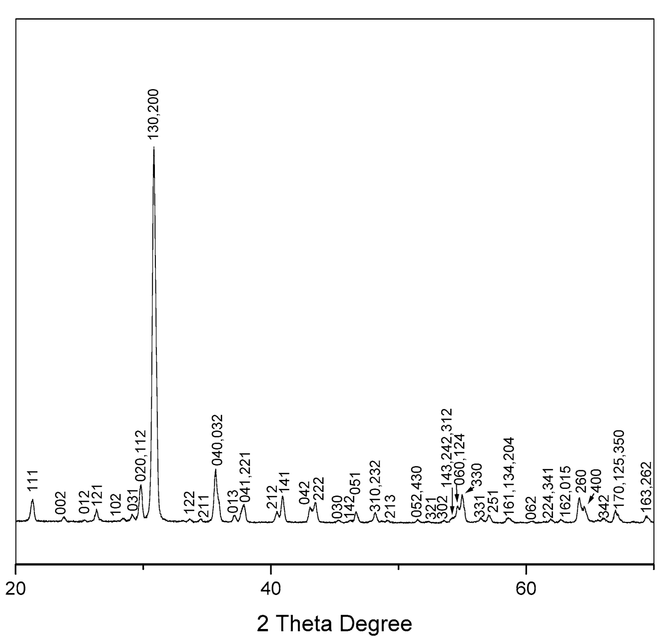

Fig. 1. XRD spectrum of K_2SO_4 nanowires.

This showed that the process of the sublimation was mainly limited by the surface of the sample. That is to say, there was a need for increasing the surface area. Just this led to the spontaneously formation of the nanostructures of 66–100 nm for it can multiply the surface many times.

K_2SO_4 nanowires from the 0.5 wt%, 0.05 wt% and 0.005 wt% K_2SO_4 solutions showed the nanowires with the similar width. So, we think the width of the K_2SO_4 nanowires may be determined by the critical thickness with which the ice-K_2SO_4 layers were strong enough to support themselves.

We can image the formation of K_2SO_4 nanowires. With the ice subliming, a groove first formed on the surface of the ice-K_2SO_4 layer, and the residual K_2SO_4 are dusted on to the two edges. These K_2SO_4 prevented the covered ice from subliming. And the nearest groove could only form on the other side of these residual K_2SO_4 bars. When this process took place all over the surface, a spacing structure of K_2SO_4 bar–groove formed. From Fig. 2(a), the groove can be validated by the white light strips on the middle of the nanowires with the width large than 100 nm. With the ice sublimation, the grooves were penetrated and K_2SO_4 nanowires formed.

Because some H_2O may be embedded in K_2SO_4 nanowires for a low fabrication temperature of about 273 K, the effect of electron radiation on the morphology of K_2SO_4 nanowires was studied. When an electron beam with acceleration voltage of 200 kV and beam currant of 15 μA were projected on the K_2SO_4 nanowires, some small holes formed on the surface of the wires. As shown in Fig. 3, these holes were not random but they were arranged in rows. This indicates that H_2O molecules were on the position of rows were easy to be picked off. The selective evaporation of H_2O molecules on the surface of K_2SO_4 nanowires may be related with the crystal structure of K_2SO_4 and heat conduction of the surface. Details research is undergoing.

With the increase of electron radiation, some ordered K_2SO_4 dots form on the surface of K_2SO_4 nanowires. As shown in Fig. 4, the even size of the dots is about 3.5 nm and the distance between two QDs is about 7.8 nm. With the further increase of electron radiation, as shown in Fig. 5, an array of narrow wires with diameter of about 3 nm can also form on the surface of K_2SO_4 nanowires.

The formation of ordering QDs were explained as follows. When the K_2SO_4 nanowires were under the electron radiation, the remnant H_2O molecules on the surface are heated and get rid off. This resulted in many vacancies appearing on the surface. The surface became instable. So it spontaneously formed K_2SO_4 crystallites of about 3.5 nm. Now, the heat radiation could only get rid off the remnant H_2O molecules around the crystallites of about 3.5 nm. These new vacancies then compressed the crystallites to form a compact arrange, the ordered dots. When the dots were dense enough to be conterminous with the neighboring dots in a line, instead of separate crystallites the residual K_2SO_4 formed narrow wires for the small crystallites being jointed with the neighboring ones. And the surface presented the narrow wires array.

The remnant H_2O molecules have been validated by the differential thermal analysis (DTA) measure on the fresh product.