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Synthesis of single-crystalline lanthanum hexaboride nanowires by Au catalyst

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Abstract

Lanthanum hexaboride (LaB_6) nanowires have been successfully fabricated by the facile catalytic reaction of lanthanum (La) powders, and gas mixture of boron trichloride (BCl_3), hydrogen and argon, where Au was used as the catalyst. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and selected-area electron diffraction (SAED) were used to characterize the composition, morphology and structure of the samples. Single crystal column-shape LaB_6 nanowires were obtained. It is expected that LaB_6 nanowires can provide thermionic emission, field-induced emission, and thermal field-induced emission of electrons for TEM, SEM, flat panel displays, as well as many electronic devices that require high-performance electron source.

Keywords: B. Electron microscopy; C. Electrical properties; D. Borides

1. Introduction

There is growing interest in pursuit of one-dimensional (1D) metal nanostructures such as nanorods, nanowires, and nanotubes for a variety of applications including plasmonics, nanoelectronics, chemical sensors, and biotechnology [1–3]. In particular, rare earth hexaboride RB_6 (R = rare earth element) nanowires are being explored as field-induced emission devices. In fact, the rare earth hexaborides have been investigated for years as the best thermionic electron sources due to their low work function, low volatility at high temperature, high conductivity, high chemical resistance, and high mechanical strength [4]. These properties are desirable for a wide range of applications, such as high-energy optical systems [5–7], sensors for high-resolution detectors [8], electrical coatings for resistors, and thermionic materials [4]. Because of their large surface area to volume ratio and possible quantum confinement effects, RB_6 nanostructures can be expected to be suitable for many novel device applications. LaB_6 whiskers with a sharp tip have been fabricated by Motojima et al. [9]. Givargizov et al. confirmed that oriented arrays of LaB_6 whiskers can be produced using the following chemical reaction [10,11]: $2LaCl_3(g)+12BCl_3(g)+21H_2(g)=2LaB_6(s)+42HCl(g)$, where Pt or Au were used as catalysts. Motivated by this experimental procedure, LaB_6 and CeB_6 single-crystal nanowires have been synthesized by Zhang et al. [12,13]. Unlike the vapor deposition growth of LaB_6 and CeB_6 nanowires, the synthesis of single crystalline lanthanum hexaboride nanowires and nanotubes in our previous work was carried out by the direct reaction of La powders and boron trichloride (BCl_3) gas under atmosphere of hydrogen and argon flow [14], where no catalyst was used throughout the whole growth process.

To the best of our knowledge, no information has hitherto been obtained about the LaB_6 nanowires prepared using Au as the catalyst. Here, we report the synthesis of single crystal column-shape LaB_6 nanowires with Au as the catalyst. The method employed to synthesize LaB_6 nanowires was carried out by the direct reaction of rare-earth

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metal with BCl_3 gas on gold-coated Si substrates. The experiment is based on the following chemical reaction: $La(s)+6BCl_3(g)+9H_2(g)=LaB_6(s)+18HCl(g)$.

2. Experimental

Unlike previously reported direct reaction growth of LaB_6 nanowires, the gold-coated Si substrate was used here. Commercial BCl_3 gas and high-purity metal La powders were used as raw materials. The La metal powder was loaded on the gold-coated Si substrate. The gold-coated Si substrate was located on the quartz boat and then the boat was pushed into a horizontal quartz tube furnace carefully. Before reaction, the atmosphere of a mixed gas of 30% H_2+70% Ar with a flow rate of 150 ml/min was kept. After the expected reaction temperature of 1070 °C was reached, a steady BCl_3 flow was started. After the above growth procedures, the quartz tube was cooled down to room temperature under flowing gas of 30% H_2+70% Ar at the flow rate of 30 ml/min. In order to remove the HBO_3 produced by the reaction of BCl_3 remaining on the substrate with water in air when the substrate was taken out of the furnace, the products obtained from the Si substrate were washed with distilled water. After drying in air at 80 °C for 40 min, the final product was obtained. The general morphology of the sample was characterized by a field-emission scanning electron microscope (SEM, Navo NanoSEM430). The phase identification of the sample was carried out by X-ray diffraction (XRD, TD 3500). A step scan mode was used with a scanning step of 0.02° and a sampling time of 2 s. The microstructure was studied with a field emission scanning electron microscope (SEM, LEO 1530 VP) and a transmission electron microscope (TEM, JEM-2010HR). For electron diffraction and microscopy observations, the sample was firstly dispersed in ethanol and then collected on a copper grid which was coated with a thin holey carbon film.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of as-prepared LaB_6 product at 1070 °C with the flow rate of 30 ml/min for BCl_3 and the reaction time of 50 min. No impurity phase can be detected under the resolution of our X-ray diffractometer. All reflections can be indexed as a cubic phase of LaB_6 (JCPDS Card no 65-1831) with the space group Pm3m and lattice parameter of $a=0.4156$ nm. Our X-ray diffraction result (not show here) reveals that LaB_6 phase cannot be observed when the reaction time is less than 10 min.

Fig. 2 shows the scanning electron microscope images of the LaB_6 products. Fig. 2(a) and (b) shows the images of nanowires with the reaction time of 50 min and the flow rate of 30 ml/min for BCl_3. In a low-magnification image shown in Fig. 2(a), the nanowires with the uniform column-like shape can be observed. These LaB_6 nanowires

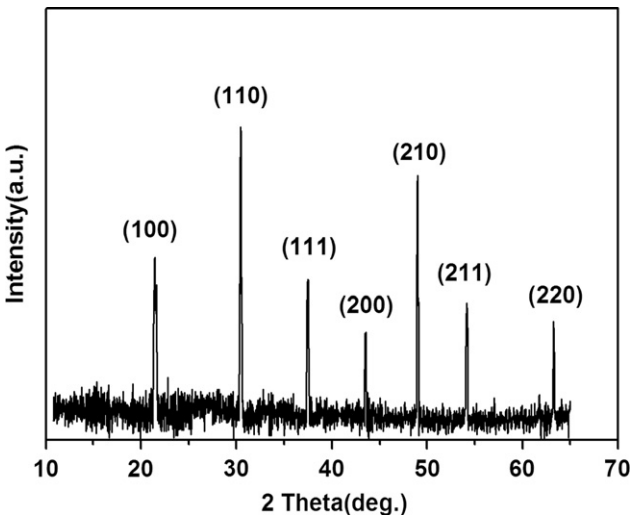

Fig. 1. X-ray diffraction patterns of the LaB_6 obtained from Si substrate.

are approximately 400 nm in diameter and more than 10 μm in length. The enlarged image of Fig. 2(a) provides more details of the morphology of the products, as shown in Fig. 2(b). From Fig. 2(b) it can be seen that the surfaces of nanowires obtained under the experimental conditions in this work are smooth and the width and length of nanowires are uniform. It also can be seen that some catalyst particles on the tips of a few nanowires (marked by circle in Fig. 2(b)), which suggests that LaB_6 nanowires synthesized here are dominated by the conventional vapor–liquid–solid (VLS) growing process proposed for nanofibers grown by a catalyst-assisted process [15]. In order to see how the reaction parameter (such as time or gas flow) changes influence the structure (diameter and length of nanowires), Fig. 2(c) and (d) shows SEM images of the LaB_6 products prepared with different reaction times or BCl_3 gas flow rates at 1070 °C. As shown in Fig. 2(c), no nanowires formation was initiated when the reaction time is less than 10 min, which agrees with our X-ray diffraction result. As a result, nonuniform nanowires with a small diameter were produced when the reaction time increases to 30 min, as shown in the inset of Fig. 2(c). The image of influence of gas flow on the structure is shown in Fig. 2(d), where the nanowires with quite nonuniform morphology in shape can be observed with the gas flow rate of 10 ml/min. These results clearly indicate the importance of both the reaction time and gas flow during the LaB_6 nanowires synthesis process. The best results in terms of uniformity of the generated LaB_6 nanowires was observed for the reaction time of 50 min and the flow rate of 30 ml/min for BCl_3 if the reaction temperature of 1070 °C was adopted.

To seek insight into the growth mechanism of LaB_6 nanowires, the morphology and microstructure of the product were further characterized by transmission electron microscopy (TEM) and the selected area electron diffraction (SAED). Fig. 3(a) shows a typical TEM image of an individual LaB_6 nanowire (shown in Fig. 2(a)) at a