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Catalyst-Free Growth of Magnesium Oxide Whiskers and Their Characteristics

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This study reports the production of magnesium oxide (MgO) whiskers on silicon (Si) substrates by the thermal heating of MgB₂ powders. We investigated the structural properties of the as-synthesized whiskers by using X-ray diffraction, transmission electron microscopy, selected area electron diffraction, and scanning electron microscopy. The product consisted of one-dimensional whiskers with a square cross-section. The whiskers had a single-crystalline cubic structure of MgO. The photoluminescence measurement with the Gaussian fitting exhibited visible light emission bands centered at 2.39 eV and 2.91 eV. We proposed the growth of MgO whiskers to follow the vapor–solid mechanism.

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1. Introduction

Low-dimensional materials such as one-dimensional (1D) nanoscale or sub-micron scale materials are currently being exploited as active components in a wide range of technological applications in various fields, due to their high surface-to-volume ratio and better material characteristics. Magnesium oxide (MgO) is a typical wide-band-gap insulator. It has found many important applications for use in catalysis, refractory material industry, paint, and superconductors. Furthermore, 1D MgO structures can display a unique capability to pin the magnetic flux lines within a high-temperature superconductor. In the present work, we have successfully fabricated MgO rod-like structures on Si substrates without using metal catalysts. The successful synthesis of whiskers on the conventional Si substrates without using metal catalysts will pave the way for integration of future devices with developed Si integrated circuit technology.

2. Experimental

The synthesis process was carried out in a quartz tube. The source material was pure MgB₂ powders. We employed standard polished *p*-type (100) Si

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substrates. The distance between the source material-containing boat and the substrate was approximately 10 mm. During the experiment, the furnace was maintained at a temperature of 900°C for 2 h with the ambient gas (Ar+O₂) at a constant total pressure of 2 Torr. The typical percentage of O₂ and Ar partial pressure, respectively, were set to approximately 2.7 and 97.3%. The apparatus to analyse the products was described in this issue (see paper written by Kim et al. [1]).

3. Results and discussion

The X-ray diffraction (XRD) pattern shown in Fig. 1 reveals the overall crystal structure of the product. The recognizable diffraction peaks correspond to the cubic MgO structure with lattice constants of $a = 0.421$ nm (JCPDS: 04-0829). No impurities, such as unreacted Mg or other magnesium oxides, were detected.

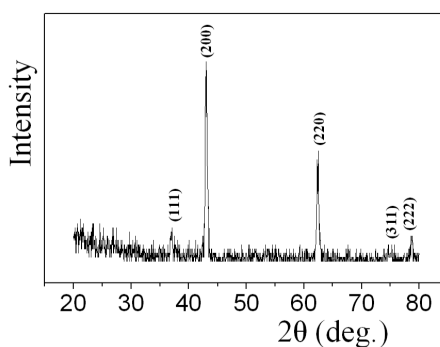


Fig. 1. (a) XRD pattern of the product.

Since the angle of the incident beam to the substrate surface was about 0.5° in the present XRD measurements, we conclude that the peaks originate mainly from the product. Figure 2a is a side-view scanning electron microscopy (SEM) image of the product on the substrate surface, exhibiting the random growth directions of the whiskers. The whiskers have a straight-line morphology along the length direction. Figure 2b is a top-view SEM image, showing the bare-Si substrate (dark region) as well as whiskers. Statistical analysis of many SEM images shows that the whiskers have diameters ranging from 270 to 540 nm. Close examination (Fig. 2c) reveals that the cross-section of the whiskers is close to square-shaped with no nanoparticle at their tips. We further examined the crystalline structure of the individual whisker by transmission electron microscopy (TEM). Figure 3a shows the lattice-resolved high resolution TEM (HRTEM) image taken near the side edge along a typical whisker. The interplanar spacing is about 0.21 nm, corresponding to the {200} plane of cubic MgO. The selected area electron diffraction (SAED) pattern shown in the inset can be indexed for the [001] zone axis of MgO, revealing the single-crystalline nature of the whiskers. The SAED pattern can be indexed (their hkl indices are given in inset) according to their cubic MgO structure.

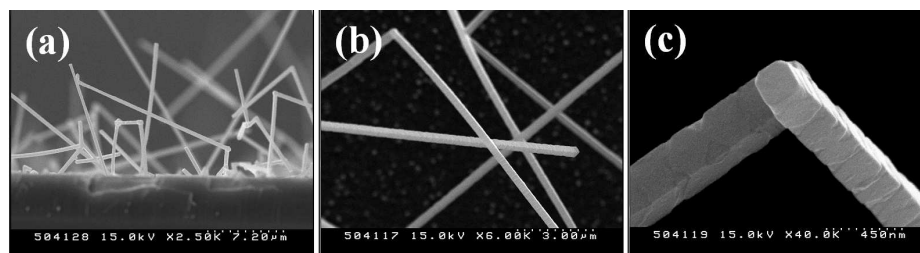


Fig. 2. (a) Side-view SEM image, (b) top-view SEM image, and (c) high magnification SEM image of the product.

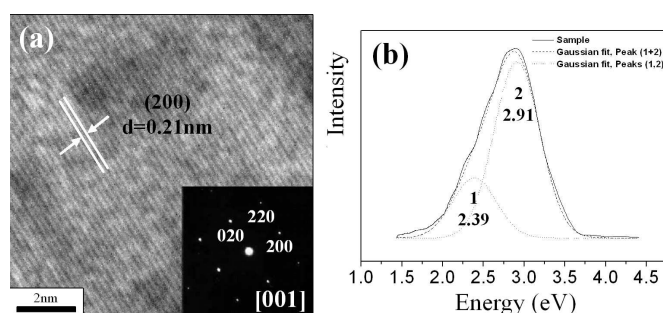


Fig. 3. (a) HRTEM image (inset: associated SAED pattern recorded along the [001] zone axis). (b) Photoluminescence spectrum from the product.

Figure 3b shows the photoluminescence (PL) spectrum measured at room temperature. After multi-peak Gaussian fitting to two major peaks of the PL spectrum, we found that the Gaussian curves fit the original curves almost perfectly. Therefore, the PL spectrum mainly consists of two bands, peaking at approximately 2.91 eV in blue region and 2.39 eV in blue-green region, respectively. The similar blue emission has been previously observed in PL spectra of MgO nanowires [2] and MgO nanoplates [3], whereas the blue-green emission was found from MgO nanobelts [4]. Both blue and blue-green emissions may originate from defects in MgO, such as oxygen vacancies [3–5]. In the present high-temperature evaporation process, oxygen vacancies should be generated [6].

No metal catalyst was used in the present study, and no particle was observed at the ends of the whiskers in our SEM observations (Fig. 2). Therefore, the growth mechanism of the whiskers can be understood on the basis of a self-catalytic process with the characteristics of vapor–solid (VS) growth process, corresponding to a diffusion-limited process in a supersaturated environment [7]. Brief scheme on the formation of MgO whiskers is shown in Fig. 4. Mg vapor may combine with O_2 gas, rapidly generating MgO vapor. The MgO vapor directly deposits on the substrate and grows into 1D whiskers. Two-dimensional square island nucleation is a usual phenomenon in the MgO film deposition process [8]. The square cross-

section of whiskers reveals that the MgO whiskers have been elongated from the square nuclei (Fig. 2c). From Figs. 2a and 2b we observed that MgO whiskers have been generated on Si substrates, without forming the predeposited MgO layers. According to the VS mechanism, under low enough supersaturation in the present study, we conclude that the square islands on substrate will elongate and preferentially form the 1D whiskers.

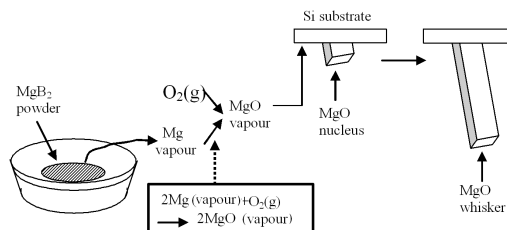


Fig. 4. Schematic illustration of MgO whiskers via the VS mechanism.

In conclusion, we successfully synthesized the MgO whiskers on bare Si substrate via a heating MgB₂ powders at 900°C. SEM images indicate that the MgO whiskers have average diameters in the range of 270–540 nm. No catalytic particle is observed on the ends of the as-synthesized whiskers. XRD and energy-dispersive X-ray (EDX) analyses coincidentally show that the MgO structures are of single crystalline cubic structure. A growth mechanism based on the VS process is proposed for the formation of MgO whiskers. The PL spectrum shows prominent visible emission bands peaked at 2.91 eV in the blue region and 2.39 eV in the blue-green region, extending the potential application of MgO whiskers in optoelectronic sub-micron devices.

Acknowledgments

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