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ZnO nanorods/plates on Si substrate grown by low-temperature hydrothermal reaction

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ABSTRACT

The zinc oxide (ZnO) nanorods/plates are obtained via hydrothermal method assisted by etched porous Al film on Si substrate. The products consist of nanorods with average diameter of 100 nm and nanoplates with thickness of 200–300 nm, which are uniformly distributed widely and grown perpendicularly to the substrate. The ZnO nanoplates with thickness of 150–300 nm were grown on Si substrate coated with a thin continuous Al film (without etching) in the same aqueous solution. The growth mechanism and room temperature photoluminescence (PL) properties of ZnO nanorods/plates and nanoplates were investigated. It is found that the introduction of the etched Al film plays a key role in the formation of ZnO nanorods/plates. The annealing process is favorable to enhance the UV PL emissions of the ZnO nanorods/plates.

1. Introduction

Zinc oxide (ZnO) has a direct wide band gap of 3.37 eV and a large exciton binding energy of 60 meV, and has been widely applied [1], such as room-temperature and high-temperature ultraviolet (UV) lasers [2,3], field emission displays [4], surface acoustic wave devices [5], and gas sensors [6]. Recently, nanostructure materials have received growing interests due to their unique properties and various potential applications in the fabrication of the nanodevices. Therefore, fabricating suitable nanostructures become more important, and will offer a base for further building nanodevices. Over the past few years, many ZnO nanostructures with one-dimensional (1D) and two-dimensional (2D) morphologies have been successfully synthesized, such as nanobelts [7], nanowires [8], nanorods [9], nanotubes [10], nanoflowers [11], and nanoplates [12]. Once the 1D and 2D ZnO nanostructures are combined, a novel structure composed of nanorods and nanoplates (nanorods/plates) would lead to high-performance with advantages of both 1D nanorods and 2D nanoplates. However, ZnO nanorods/plates are generally prepared at high-temperature [13–15], which is detrimental to the fabrication and performance of nanodevices. How to fabricate the ZnO nanorods/plates on substrates at low-temperature is still a great challenging issue.

Many methods have been carried out on synthesizing ZnO nanostructures, such as chemical vapor deposition (CVD) [16], physical vapor deposition (PVD) [17], thermal evaporation [18], and electrochemical process [19]. However, the vacuum condition, high-temperature, sophisticated equipment, and other rigid experimental conditions are required in these methods, which may increase the cost and limit the choice of substrates [20]. Comparatively, the solution approach is more attractive for its simplicity, commercial feasibility, and good potential for a large-scale production. Hydrothermal synthesis, as an important method of solution synthesis, has been proven to be a versatile approach for ZnO preparation due to its convenience and simplicity in the fabrication.

Considering Si is low-cost and potential for integration with Si-based microelectronic devices, it is desirable to grow high-quality ZnO nanostructures on Si substrate. In this work, we present a simple hydrothermal route to the fabrication of ZnO thin films composed of nanorods and nanoplates on Si substrate at a low-temperature (95 °C), which shows a more promising prospect in the nanodevice fabrication. The structural characteristics, growth mechanism, and photoluminescence (PL) properties of the as-prepared nanostructure are investigated.

2. Experimental

The synthesis processes are described as follows:

First, the pure Al film was deposited on the (1 0 0) oriented n-type Si substrate by the RF (13.56 MHz) magnetron sputtering process. The substrate was ultrasonically cleaned with acetone and ethanol, rinsed in deionized water, and subsequently dried in a flowing nitrogen gas before deposition. Prior to sputtering, the background pressure of sputtering chamber was evacuated below

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2×10^{-3} Pa with a turbo molecular pump. The argon gas was introduced with the flow rate of 60 sccm (standard cubic centimeter per minute). The Al film deposition was performed at the sputtering pressure of 1.0 Pa and the power of 100 W.

Second, the Al-coated Si wafer was anodized in the 0.3 M oxalic solution at 40 V and 0 °C for about 30 min. Then the formed aluminum oxide layer was removed in an etching solution composed of 0.2 M chromic acid and 0.4 M phosphoric acid at 60 °C for about 30 min.

Finally, the reaction solution is prepared by adding 1 ml ammonia (25%) into a 30 ml zinc acetate solution (0.05 M) at the room temperature (RT). Those solutions were transferred into Teflon lined stainless steel autoclave of 40 ml in volume. The Si substrate with etched Al film was vertically immersed into the reaction solution. The autoclave was sealed and heated to a constant temperature of 95 °C for 2 h. Subsequently, the autoclave was allowed to cool down naturally. The obtained product on the Si substrate was thoroughly washed with distilled water to remove the residual salts and dried naturally in air for further characterization. For comparison, the Si substrate with Al film without etching was also applied for the same hydrothermal process.

The crystal structure and quality of the products were examined by X-ray diffraction (XRD) by a Rigaku D/max-RA diffractometer using Cu Kα radiation of 1.54056 Å. The scanning electron microscopic (SEM) morphologies of the products were observed with a JEOL JXA-8200 electron probe micro-analyzer. Transmission electron microscopy (TEM) and selected area electron-diffraction (SAED) studies were performed using HITACHI TEM H-8100IV operated at 200 kV. To prepare the TEM samples, the products were first scraped from the substrates, dispersed in ethanol and diluted, followed by placing a droplet of the solution onto a amorphous holey carbon film covered copper grid. RT PL spectra were observed by using HR800 LabRam Infinity spectrometer with a 325 nm Hd–Cd laser as the excitation source.

3. Results and discussion

3.1. Structure and morphology

Fig. 1 shows the XRD pattern of ZnO nanorods/plates deposited on the Si substrate with etched Al film. Evidently, the diffraction peaks can be indexed to a hexagonal wurtzite phase of ZnO and the (0 0 2) peak dominates the spectrum, which suggests that the samples are well crystallized and preferentially oriented in the *c*-axis direction. Expect to the ZnO-related diffraction peaks, the peaks at $2\theta = 38.83^\circ$ and 45.01° are well assigned to Al (1 1 1) and Al (2 0 0), respectively. Furthermore, Si (4 0 0) peak appears at 69.45°. No other uncertain diffraction peaks are represented, suggesting that high-purity ZnO products have been synthesized.

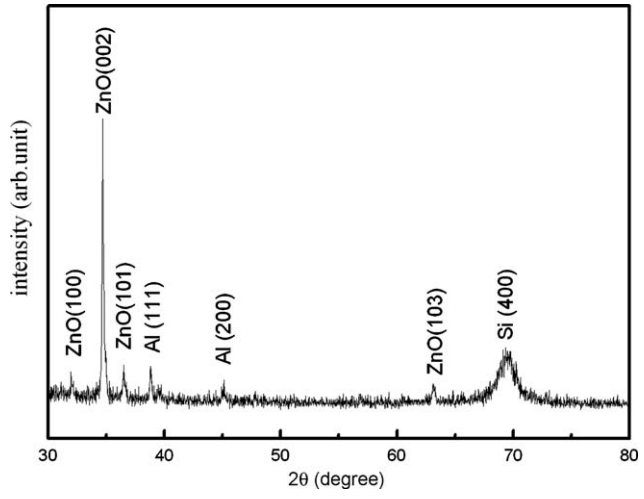

Fig. 1. XRD pattern of the nanorods/plates grown on Si substrate with etched Al film.

A typical surface morphology of the Si substrate coated with the etched Al film is shown in Fig. 2a. It shows that the Al film has almost the same arrangement of pits with an average diameter about 60 nm and an interspace about 120 nm (inset of Fig. 2a). After hydrothermal reaction, the very thin homogenous film coats on the surface of Si substrate coated with etched Al film. The SEM images of the as-prepared products are shown in Fig. 2b and c. It is found that a large number of sheet-like nanocrystals are uniformly grown on the substrate. Observed from the enlarged image of Fig. 2c, one can see the homogenous film consist of nanorods/plates. The nanoplates have smooth surface and the thickness ranges from 200 to 300 nm. The average diameter of the nanorods is about 100 nm.

TEM and SAED were employed to investigate the morphology and the structure of the as-prepared products. The representative TEM image of ZnO nanorod is shown in Fig. 3a. The inset of Fig. 3a is the corresponding SAED pattern, which confirms the single crystal nature of the nanorods and growth along the [0 0 0 1] direction [21]. Fig. 3b is the result from ZnO nanoplates, observed from the image contrast, the thickness of the ZnO nanoplate are nearly homogeneous. The SAED pattern taken along the [0 0 0 1] zone axis demonstrates that the crystalline nature of the ZnO nanoplates is dominated by (0 0 0 1) facets. The doping is believed to be related to the growth process, where the $Al(OH)_4^-$ species play a significant role in the formation of the (0 0 0 1) surface dominated nanoplates [22,23].

As comparison, Fig. 4a and b show the morphology of ZnO nanostructures grown on Si substrate with Al film without etching. An overview SEM image of the films is presented in Fig. 4a, from which one can see that a large amount of flake-like ZnO nanocrystals are produced on the whole substrate. High magnification observation (Fig. 4b) shows that these ZnO nanostructures consist of smooth nanoplates (with 150–300 nm in thickness) and no nanorods appear, which is in contrast to the observations in Fig. 1 mentioned above. This is similar to the previously reported results [22,23], where ZnO nanoplates are synthesized on the Al substrate. Fig. 4c shows the XRD patterns of the corresponding ZnO nanoplates. Evidently, the diffraction pattern can be indexed as hexagonal wurtzite ZnO. Interestingly, the intensity of the (1 0 1) peak is stronger than the (0 0 2) peak, significantly different from that of the ZnO nanorods/plates arrays (Fig. 1). Other peaks can be well assigned to (1 1 1), (2 0 0), (2 2 0), (2 2 2) peaks of Al and (4 0 0) of Si, as labeled in Fig. 4c.

3.2. Growth process and mechanism

The major reactions involved in the formation of ZnO nanorods/plates and nanoplates can be summarized as the following [24]:

$$NH_3 \cdot H_2O \leftrightarrow NH_4^+ + OH^- \quad (1)$$

$$Zn^{2+} + 4NH_3 \cdot H_2O \leftrightarrow Zn(NH_3)_4^{2+} + 4H_2O \quad (2)$$

$$Zn(NH_3)_4^{2+} + 2OH^- \leftrightarrow ZnO + 4NH_3 + H_2O \quad (3)$$

In the synthesis systems, ammonia serves as a alkaline buffer to release OH^- (Eq. (1)). The complexion $Zn(NH_3)_4^{2+}$ is formed by mixing ammonia and zinc acetate solution (Eq. (2)), and finally the ZnO is formed by the reaction between $Zn(NH_3)_4^{2+}$ and OH^- under thermal treatment conditions (Eq. (3)).

Based on the above experimental results, a possible formation route of the present ZnO nanostructures can be schematically summarized in Fig. 5. As known, Al is an amphoteric metal, which can be dissolved into the solution under alkaline conditions in the