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Effect of annealing temperature on surface morphology and work function of ZnO nanorod arrays

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ABSTRACT

A simple and effective method of fabricating nanomaterials and the understanding of their electronic structures are significant for designing novel nanodevices. In this study, ZnO nanorod arrays on ITO substrate were synthesized by electrochemical deposition, and the effect of annealing temperature on surface morphology and especially work function was investigated using various techniques. The results indicated that the formation of hexagonal ZnO nanorod arrays with (0001) orientation was strongly associated with the annealing temperature. The work function of well-aligned ZnO nanorod arrays is 4.84 eV, which shows an obvious dependence on the arrangement of ZnO nanorod arrays. These changes in work function of ZnO nanorod arrays (e.g., used as the photoanode of dye-sensitized solar cells) are important to understand the electron transport of related nanodevices.

1. Introduction

As a II–VI compound semiconductor with a wide band gap of 3.37 eV and a large exciton binding energy of 60 meV at room temperature, zinc oxide (ZnO) is regarded as one of the most promising functional materials owing to its attractive properties, such as good piezoelectric and optoelectronic characteristics, chemical stability as well as biocompatibility, and its potential applications in high-efficiency photonic devices, near-UV lasers and optoelectronic switches [1,2]. Especially, one-dimensional (1D) ZnO nanomaterials with a high surface to volume ratio have been intensively investigated for their underlying applications in sensing, photocatalysts, optoelectronics, field emission, new solar cells, and so on [3–7].

Nowadays, there are two main challenges for the realization of ZnO nanodevices. One is how to develop a simple and low-cost method of synthesizing ZnO nanomaterials [8,9]. In the past decades, various physical and chemical deposition techniques including pulsed laser deposition, molecular beam epitaxy, chemical vapor deposition, sol–gel method, hydrothermal synthesis and electrochemical deposition, have been employed to fabricate ordered ZnO nanomaterials [1,3–10]. For example, the ZnO nanorods were recently synthesized using successive ionic layer adsorption and reaction as well as chemical bath deposition approach [11], and the cadmium sulfide-decorated ZnO nanorod heterostructures were also grown by a combination of hydrothermal and pulsed laser deposition techniques [12]. To be indicated, among these techniques, it is found that the electrochemical deposition method has the merits of low temperature, large scale, and economical synthesis, being very suitable for the industrial mass production [13]. However, many details about the growth mechanisms and stability of ZnO nanocrystals grown by electrochemical deposition, such as the effect of annealing temperature, are not completely understood yet, and a further investigation of well-oriented ZnO nanorod arrays with a controllable size is also required [14,15].

Another challenge for ZnO nanodevice applications is how to understand their electronic structures such as charge transport and electron recombination in ZnO nanorods [16]. The electronic structures of a material are strongly dependent on its size, shape, defects and doping [1]. To be noticed, all the changes in electronic structures are associated with the movement of electrons relating with the Fermi level and work function (WF) [17]. In solid physics, the WF is defined as the minimum energy needed to remove an electron from the Fermi level of a solid to a point just outside the solid surface with zero kinetic energy [18,19]. As the escaped electron must move through the surface region, the WF obtained is affected by the chemical, magnetic, optical, electric, structural characteristics of the surface [20–22]. So the WF is an exceedingly sensitive indicator of the surface characters (such as absorbed layers, surface charging, surface defects, oxide layers, surface and bulk contamination, and so on). Therefore, the change in WF can be used to characterize the surface electronic structures of ZnO nanomaterials [23]. In fact, the size and shape of ZnO nanomaterials are easily affected by different growth conditions (such as growth and annealing temperature). These changes in ZnO microstructures readily alter the WF, thereby affecting the properties of

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related ZnO devices. However, few works have been focused on understanding the electronic structures of ZnO nanomaterials from the point of view of the WF.

In this study, ZnO nanorod arrays on ITO substrates were fabricated by electrochemical deposition method, and the influence of annealing temperature on their chemical composition, surface morphology and especially the WF was investigated using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Scanning electron microscopy (SEM), and Scanning Kelvin probe (SKP) techniques. The results illustrated that the well-oriented ZnO nanorod arrays were fabricated and the effect of annealing temperature on surface microstructures and WF was revealed.

2. Experimental details

Commercially available ITO-coated glass (10 Ω/cm) sheets with a size of 2×5 cm^2 were used as the substrates. These sheets were cleaned using a ultrasonic cleaner in purified water (18.6 MΩ/cm, for 20 min), reagent grade alcohol (for 10 min) and acetone (for 10 min), respectively, and then dried by blowing nitrogen gas. An equimolar (0.1 M) aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 98%, Aldrich) was used for the growth of ZnO nanorods. The measured electric resistance of the aqueous solution kept in 70 °C water bath was 2–3 MΩ/cm. The bias voltage of 1–10 V/cm dc and the deposition time of 30–120 min was tried. During growth ZnO was aggregated on the negative ITO electrode relative to the positive Pt electrode. After growth, the electrodeposited ZnO samples were rinsed, dried, and finally were annealed in vacuum drying oven at 300–500 °C for 2 h.

The crystal orientation of the samples was characterized by XRD (SMART APEX II) using Cu Ka radiation, and the chemical composition was measured using XPS (VG SCIENTA R3000) with the Mg Ka X-ray source ($h\nu$ = 1253.6 eV). The surface microstructures of the samples were observed using SEM (Quanta 200 and Nova NanoSEM 450). The WF was measured using SKP (RHC020, KP Technology Ltd.) system. The SKP system consisted of three sub-systems (digital oscillator, data acquisition, and sample translation), which was controlled by a host computer. A three-dimensional micro-stepper positioner permitted a high-resolution sample positioning (400 nm/step), and the space between the probe tip and the tested surface could be controlled within 40 nm. A gold Kelvin probe (2 mm diameter) was used and the shield was tied back to the ground. The oscillation frequency of the SKP probe was set to 84 Hz.

The WF could be measured using a point or plane scanning mode. An area of interest was scanned by the SKP and the WF measured was the average value over the scanned area. The machine gave the value of the WF relative to the probe tip rather than the absolute value. To determine the absolute WF of a sample, a tip calibration procedure should been done by measuring the WF difference relative to two reference samples such as Au and Al. If the WF difference of Au and Al measured was 1 eV, the WF of the probe tip could be obtained so that the absolute value of the WF of the sample surface was determined. All the measurements were performed at about 25 °C and at a relative humidity of 60%.

3. Results and discussion

3.1. Formation of ZnO nanorod arrays

After growing the ZnO samples by electrochemical deposition in 70 °C water bath, they are dried in air. Fig. 1 gives the SEM-EDS image of ZnO grown on ITO substrate without annealing. It is found from the SEM image that ordered ZnO nanorod arrays are not formed, instead, hexagonal rods and irregular particles at the sample surface. According to the EDS spectra, it is observed that the signal of Zn and O elements around the hexagonal rods is obviously stronger than that around the holes. Furthermore, the signal from the ITO substrate around the holes is not completely disappeared, which in turn indicates that the prominent rods and particles at the surface are from ZnO. Fig. 2a shows the corresponding XRD pattern of the sample. The weak diffraction peaks indicate that as-grown ZnO has a weak orientation. These results initially illustrate that ZnO has been grown on ITO substrate, but the regular structures are not formed at such a low growth temperature.

To obtain the well-aligned ZnO nanorod arrays, the samples are annealed at 300–500 °C for 2 h every time. Fig. 3 shows the surveyed XPS spectrum of the sample after annealing at 300 °C. Besides the peaks from Zn and O elements, no other peaks are observed. The values of binding energy (BE) of Zn $2p_{3/2}$ and O 1s core levels are 1021.5 eV and 530.1 eV, respectively, being characteristic of ZnO [22,24]. In addition, considering the difficulty to distinguish various chemical states of Zn-based materials by measuring Zn $2p_{3/2}$ line alone due to the similar BE values between Zn^{2+} and Zn^0 states, we calculate that the Auger parameter (α = BE(Zn $2p_{3/2}$) + KE(Zn LMM), KE = kinetic energy) value is 2010.5 eV, which strongly suggests the existence of Zn^{2+} [25,26], i.e. the formation of ZnO on ITO surface. Combining the EDS spectra with the XPS spectra before and after annealing, these results surely suggest that ZnO has been fabricated on ITO substrate by electrochemical deposition.

Fig. 4 shows face-on SEM images of the samples after annealing. Compared with the sample surface before annealing (Fig. 1), a high density of ZnO nanorods grown vertically on the substrate can be observed after annealing at 300–400 °C (Fig. 4a and b). Fig. 2 shows the corresponding XRD patterns of the samples after annealing. Compared with the diffraction peaks before annealing, these peaks are obviously stronger. Especially, the peaks of (002) at 34.4° is much stronger than other peaks, indicating that ZnO nanorods is

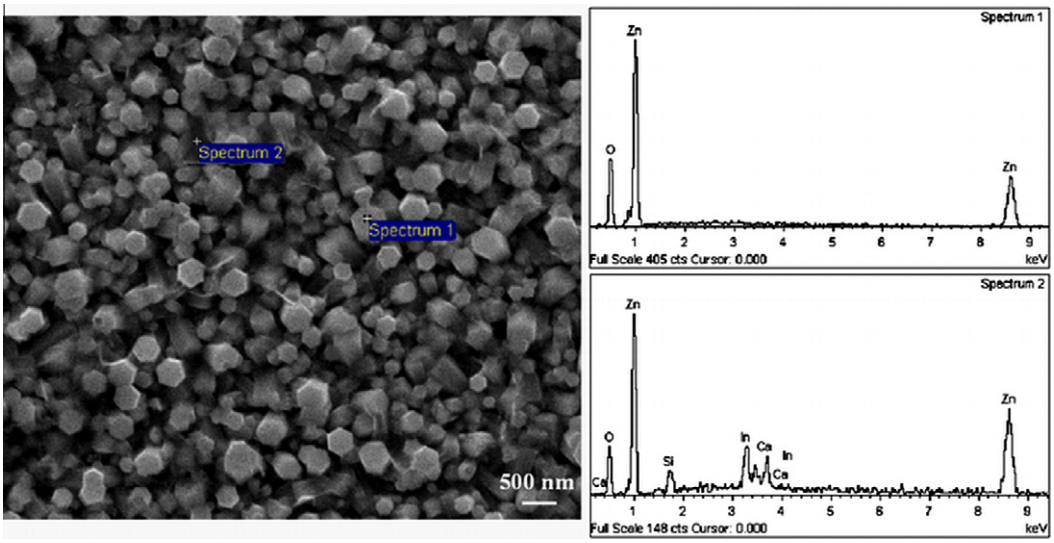

Fig. 1. SEM-EDS spectra of ZnO grown on ITO substrate before annealing. Spectra 1 and 2 are the selected points with and without ZnO nanorod, respectively.