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Growth kinetics and surface properties of single-crystalline aluminum-doped zinc oxide nanowires on silicon substrates

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Abstract

We present here the results from a systematic investigation on the growth kinetics and surface properties of Al-doped ZnO (AZO) nanowires synthesized on (0 0 1)Si substrates under different hydrothermal conditions. The as-synthesized vertical AZO nanowires exhibited a hydrophilic characteristic and their crystal structures were determined to be perfectly single crystalline with the axis of the wire parallel to the [0 0 0 1] direction. TEM and EDS results revealed that the as-synthesized AZO nanowires have tapered tips, and the Al-doped concentration in the AZO nanowires was about 1.6 at%. After a series of SEM examinations, the average length of AZO nanowires synthesized at each temperature studied was found to follow a linear relationship with the reaction time, indicating that the hydrothermal growth of AZO nanowires was a reaction-controlled process. The activation energy for linear growth of AZO nanowires on Si substrate, as obtained from an Arrhenius plot, was found to be about 46 kJ/mol. From UV–vis spectroscopic measurements, it was found that the Si substrate coated with vertically-aligned AZO nanowire arrays exhibited remarkably reduced reflectance (10–12%) over a wide range of visible wavelengths (400–800 nm) and angles of light incidence (8–60°). The good broadband and omnidirectional antireflection characteristics can be attributed to the light trapping effect and the graded refractive index resulting from the tapered AZO nanowire structures.

Keywords: Al-doped ZnO nanowires; Growth kinetic; Wettability; Activation energy; Antireflection

1. Introduction

Zinc oxide (ZnO) is a n-type semiconducting material with a wide direct band gap of about 3.2–3.4 eV at room temperature and has a hexagonal wurtzite crystal structure [1]. The synthesis and applications of one-dimensional ZnO-based nanostructures (e.g. nanowires, nanobelts) have drawn considerable interest in recent years because of their high surface-to-volume ratio and unique electrical, optical, and piezoelectric properties. It has also been found that the band gaps and properties of ZnO can be readily tuned and tailored by doping with small amounts of foreign elements such as Al, Co, Cu, and Ga [2–5]. Recent studies have shown that the electrical conductivity of ZnO nanowires was effectively improved by doping with aluminum without causing significant deterioration in crystal quality and optical transmission [2,6,7]. Thus, the Al-doped ZnO (AZO) nanowires have been considered as one of the most promising nanostructured materials for applications in advanced optoelectronics, nanogenerators, solar cells, and sensors for chemicals and gases [8–10].

Up to now, various synthetic techniques and routes, such as chemical vapor deposition, thermal evaporation, electroplating, and vapor–liquid–solid method have been applied to the synthesis of ZnO-based nanostructures on desired substrates [11–14]. However, the main limitations of these techniques are that they usually require the employment of complicated equipment and toxic precursors, need a high-temperature environment. Compared with these approaches, the hydrot

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hermal technique offers a relatively facile, low-temperature, and cost-effective synthetic method without the drawbacks mentioned above. In this technique, large-scale vertically-aligned AZO nanowires can be readily produced upon rigid or flexible substrates by immersing the substrates into hydrothermal aqueous solutions at low temperature (typically 60–95 °C) for appropriate reaction time [15–18]. Furthermore, studies have already been done demonstrating that the lengths of the ZnO-based nanowire arrays can be significantly affected by the hydrothermal conditions [16,19]. In 2009, Zhou and Deng reported the first study on the kinetics of randomly-distributed ZnO nanorods grown directly in the bulk of a hydrothermal solution [20]. Another study by Chen et al. also reported that the growth of ZnO nanorods in bulk solution was slightly retarded by the incorporation of Al dopants [21]. However, corresponding studies on the formation kinetics of vertically-aligned AZO nanowires grown on desired substrates are still absent. It is known that the kinetic data can provide crucial information leading to deeper understanding and better control of the hydrothermal process during AZO nanowires growth. Thus, systematic investigations of the growth kinetics of vertically-aligned AZO nanowires on solid substrates under different hydrothermal conditions are demanded. In addition, recent studies have also shown that the nanostructured ZnO materials can serve as antireflection coatings for Si-based solar cells due to their high transparency and appropriate refractive index ($n \sim 2$) match between Si substrates ($n \sim 4$) and air ($n = 1$) [22–24]. However, it is worth noting that most of these studies were carried out on pure (undoped) ZnO nanostructures. Studies investigating the optical reflection properties of Si substrates with AZO nanowire coatings and the corresponding incident angle-dependent antireflection characteristics are extremely rare.

In the present study, we show the successful growth of vertically-aligned, single-crystalline AZO nanowire arrays on (0 0 1) Si substrates by using a low-temperature hydrothermal method. The results from a systematic investigation on the growth kinetic, surface morphology, crystallographic orientation, chemical composition, and broadband and omnidirectional antireflection properties of vertical AZO nanowire arrays synthesized under different hydrothermal conditions are reported.

2. Experimental procedures

Single-crystal, p-type (0 0 1)-oriented silicon wafers with a resistivity of 1–10 Ω-cm were cut into pieces of 1×1 cm^2 and used as the deposition substrates. All of the (0 0 1)Si substrates were cleaned chemically using a standard procedure and then dipped in a dilute HF solution to remove surface native oxide, prior to being loaded into a radio-frequency (RF) magnetron sputtering system. The base pressure in the sputtering chamber was better than 1×10^{-3} Pa. A thin layer of 2 wt% Al-doped ZnO film with a thickness of 200 nm was sputtered on the Si substrates at room temperature, followed by annealing in vacuum (< 2 Pa) at 400 °C for 1 h to improve its crystallinity and to serve as a seed layer for the subsequent hydrothermal process. For the hydrothermal synthesis of vertically-aligned AZO nanowires, the AZO seed layer-coated Si substrates were placed in a aqueous solution which was prepared by mixing 50 mM zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), 1 mM aluminum nitrate ($Al(NO_3)_3 \cdot 9H_2O$), and 50 mM hexamethylenetetramine (HMT, $C_6H_{12}N_4$). The hydrothermal process was performed at 65–80 °C for various time periods, and the pH value of the hydrothermal bath was adjusted and maintained at 10.6 by adding aqueous ammonia. Afterwards, all the synthesized nanowire samples were thoroughly washed with deionized water and then blown dry with N_2 gas.

The surface morphologies and growth rates of AZO nanowire arrays synthesized on (0 0 1)Si substrates at various hydrothermal reaction temperatures and time were examined using a scanning electron microscope (SEM). X-ray diffractometry (XRD), transmission electron microscopy (TEM), and selected-area electron diffraction (SAED) analysis were carried out for microstructure characterization and crystallographic orientation determination. A JEOL-JEM2100 high-resolution TEM (HR-TEM) in conjunction with a Link ISIS energy dispersion spectrometer (EDS) was utilized to determine the chemical composition. For TEM and EDS investigations, some of the as-synthesized AZO nanowires were scratched from the Si substrates and transferred onto carbon film-coated Cu mesh grids. The surface wettability of the produced AZO nanowire arrays was evaluated by water contact angle measurements. The volume of each DI water droplet was fixed at 3 μL. The antireflection properties of the Si substrates with AZO films and AZO nanowire arrays were characterized in the wavelength range of 400–800 nm using an ultraviolet–visible (UV–vis) spectrophotometer (PerkinElmer Lambda-35) equipped with an integrating sphere accessory.

3. Results and discussion

Fig. 1(a) is a representative cross-sectional SEM image of the AZO seed layer-coated Si substrate after the hydrothermal reaction, showing that dense and vertically-aligned AZO nanowires were successfully synthesized on the Si substrate. In addition, from the tilt-view SEM examination, the surface of as-synthesized AZO nanowire arrays was found to be clean and free of precipitated particles. An example is shown in Fig. 1(b). The chemical reactions and growth mechanism for the hydrothermal synthesis of AZO nanowires can be found elsewhere [19,25]. From the water contact angle measurements, as shown in Fig. 1(c), it is clear that the hydrothermally synthesized AZO nanowires exhibited a highly hydrophilic behavior with a low contact angle of approximately 8°. The hydrophilic characteristic of as-synthesized AZO nanowires could be attributed to the presence of surface hydroxyl (–OH) groups and oxygen related defects during the hydrothermal process, which were easily bound to water molecules [26]. The crystallographic structures of the AZO seed layer and AZO nanowire arrays were characterized by XRD analysis. Fig. 1(d) shows the typical wide-angle XRD spectra of the AZO seed layer-coated Si substrate before and after the hydrothermal reaction. The inset is the corresponding enlarged XRD patterns in the 2θ range of

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