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Germanium-catalyzed growth of zinc oxide nanorods by thermal evaporation for enhanced photonic efficiencies

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ABSTRACT

Germanium (Ge) doped zinc oxide (ZnO) nanorods were fabricated on silicon substrate using a simple thermal evaporation method at different contents Ge (0–30 at.%). High resolution transmission electron microscopy (HRTEM) images shows that prepared ZnO nanorods are structurally uniform and single crystalline. The diameters of the nanorods are in the range of 80–150 nm with typical length of 3 μm. The samples are evaluated by the determination of their photonic efficiencies for degradation of methylene blue. The photonic efficiency is increased with increasing the Ge content up to 13 at.% showing maximum photonic efficiency as 2.99% and it is found to be about 2 times higher than that of undoped ZnO nanorods because Zn_2GeO_4 is grown and decorated ZnO nanorods and make heterojunction between Zn_2GeO_4 and ZnO nanorods. This is the first report focusing on Ge-catalyzed growth of ZnO nanorods for enhanced photonic efficiencies.

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1. Introduction

ZnO is recognized as a promising photonic material in the blue-ultraviolet (UV) region due to its wide bandgap (3.37 eV) [1,2]. It has an exciton binding energy of 60 meV, which is much larger than the room-temperature thermal energy (25 meV) [3–5]. Equipped with these unique properties, ZnO has been extensively exploited, in both the thin film and nanostructure forms, for potential optical and photonic applications [6–10]. To improve the properties of electrical and optical devices, doping has been a necessary strategy. One-dimensional (1D) nanostructures have attracted considerable interest, because of their interesting electronic and optical properties associated with lower dimensionality that result in pronounced quantum confinement effects [11–15], ZnO in the form of nanowires, nanorods, and nanobelts, is attracting a great deal of attention from the research community. Several methods have been used to grow 1D ZnO nanostructures, such as vapor–liquid–solid (VLS) growth [16–18], physical vapor deposition [19–21], chemical vapor deposition (CVD) [22], metal organic vapor-phase epitaxy [23], metal organic CVD [24], template-assisted growth [25], and other methods [26,27]. Among these techniques, VLS growth has the advantage of allowing the controlled and patterned growth of ZnO nanowires [16–18], and yields nanowires from well-defined and/or patterned sites on surfaces that could facilitate the integration of ZnO nanowires for characterization and their use in devices. In order to generate desirable properties, 1D ZnO nanostructures have been doped with selected elements [28–31]. ZnO has been doped with different elements such as Al, Ag, Cr, Ga, Sn, Ni, In, etc. [32–39], but only few reports on Ge doped ZnO. Ge is an indirect band gap with smaller energy difference between the indirect gap and direct gap ($\Delta E = 0.12$ eV), and smaller effective masses for the electron and hole pairs. In addition, Ge is recognized as one of the elements used to enhance the optical transmission and electrical conductivity of ZnO [40–46]. Yu et al. [43] studied the structural and optical properties of Ge doped ZnO prepared by the solid state reaction method. They found that Zn_2GeO_4 phase was formed by the heavy doping of Ge atoms and ascribed the luminescence center to the inherent effects of ZnO and impurity effects of GeO_2 [43]. Zheng et al. [44] prepared Ge/ZnO multilayer films on quartz substrates by using rf magnetron

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sputtering system. They reported that Zn_2GeO_4has been formed with (2 2 0) texture and Zn deficiency from Ge/ZnO multilayer films in the process of annealing. However, lower Zn/Ge ratio can be improved with annealing temperature [44]. Su et al. [45] investigated the growth mechanism of aligned Zn_2GeO_4 coated ZnO nanorods and Ge doped ZnO nanocombs were prepared by a simple thermal evaporation method. Fan et al. [46] prepared Ge doped ZnO on silicon substrates by alternate radio frequency magnetron sputtering (ARFMS). They investigated the effects of doping and annealing on the structural and optical properties, and found that the crystalline quality of the film improved with annealing temperature [46]. In addition, Jiang et al. [47] deposited Ge doped ZnO on quartz substrates by RFMS technique. They reported that the X-ray diffraction patterns showed Zn_2GeO_4 phases formed in the films. In addition, the crystallization of Zn_2GeO_4 improved, and that ZnO phases turned worse with increasing the substrate temperatures [47]. Lv et al. [48] examined the structural, optical and electronic properties of Ge doped ZnO by density functional theory calculation. Their results showed that Ge atoms tend to cluster at high doping level leads to that Fermi level lies in the conduction band, which exhibits Ge doped ZnO is n-type character [48]. Structural, electrical, and optical properties of deposited Ge doped ZnO thin films on sapphire (0 0 1) substrates at different temperatures by using pulsed laser deposition technique were investigated by Shan et al. [49]. They reported that all of the GeZnO thin films had preferred (0 0 2) and (0 0 4) orientations, and the peak intensity of the (0 0 4) orientation increased with increasing growth temperature [49]. Moreover, GeZnO thin films have been deposited by atomic layer deposition [50]. The doping was controlled, by varying the ratio of deposition cycles for ZnO and GeO_2, at substrate temperature of 100–350 °C [50]. Compared to film and particulate counterparts, nanorods photocatalysts not only possess large specific surface area, which makes their surface active sites accessible for reactants more efficiently, but also have high length-to-diameter aspect ratio, which allows for the separation of photocatalyst more easily. In the present study, the fabrication of Ge/ZnO nanorods on a silicon substrate using a simple thermal evaporation of mixture of Ge and Zn powders is reported. Ge/ZnO nanorods were grown via VLS technique. Ge can be used for two reasons: (i) as an efficient catalyst for high-yield growth of very long (up to several micrometers), and (ii) for enhancing photonic efficiency of ZnO nonorods. The newly prepared photocatalyst Ge/ZnO at different Ge contents have been compared with undoped ZnO nanorods by the determination of their photonic efficiencies for the degradation of methylene blue. To our knowledge, this is the first report focusing on Ge-catalyzed growth of ZnO nanorods for enhanced photonic efficiencies. The measured photonic efficiency $\xi = 2.99\%$ is found to be the highest ξ-values reported up to now.

2. Experimental details

2.1. Materials and nanorods synthesis

ZnO nanorods have been grown by the thermal-evaporation process, no metal catalysis was used. The weight ratio of 7:1, 0.5, 0.26, and 0.13 mixture of zinc and germanium metal powder (Zn and Ge metal powders were purchased from Sigma-Aldrich) was placed in an alumina boat inserted in a quartz tube inside a horizontal IR furnace. Si (1 0 0) substrates were used for the growth of the nanorods. The growth temperature was 1000 °C for 1 h. Nitrogen was used as a carrier gas and oxygen as a reaction gas, and flow rates were kept at 150 sccm and 12 sccm, respectively.

2.2. Characterization

Transmission electron microscopy (TEM) was conducted at 200 kV with a JEOL JEM-2100F-UHR field-emission instrument equipped with a Gatan GIF 2001 energy filter and a 1k-CCD camera in order to obtain EEL spectra. Field emission-secondary electron microscope (FE-SEM) images were carried out with a FE scanning electron microanalyzer (JEOL-6300F, 5 kV). X-ray diffraction (XRD) data were acquired on a PANalytical X' port diffractometer using Cu $K\alpha_{1/2}$, $\lambda\alpha_1 = 154.060$ pm, $\lambda\alpha_2 = 154.439$ pm radiation. Raman spectroscopy was carried out using a Perkin Elmer Raman Station 400. Reflectance spectrum of the undoped ZnO and Ge doped ZnO nanorods was taken at room temperature using a UV–visible spectrophotometer (lambda 950 Perkin Elmer) fitted with universal reflectance accessory in the range of 200–800 nm.

2.3. Photocatalytic testing

The photocatalytic tests were performed in an aqueous solution using methylene blue (Aldrich, $\lambda_{max} = 664$ nm) as the probe molecule. The samples were irradiated with 0.7 mW/cm^2 UV(A) light (160 W, Osram lamp). The Ge/ZnO nanorods on Si substrate (1.0 cm × 1.0 cm) were horizontally fixed in the middle of the beaker. Prior to irradiation, the dye solution (90 mL) was stirred and bubbled with oxygen for at least 30 min in the dark to allow equilibrium of the system so that loss of compound due to the adsorption can be taken into account. The samples were irradiated with light source placed horizontally above the beaker. The suspension was continuously stirred and purged with oxygen bubbling throughout the experiment. The photodegradation of the dye was followed by measuring the absorption spectra at regular interval (every 30 min) using a UV/vis spectrophotometer Lambda 950 (Perkin Elmer). The absorbance of MB (0.01 mM) was followed at 664 nm wavelength. The photonic efficiency, ζ, being defined as the ratio of the degradation rate and the incident photon flux was calculated for all tested films from these results.

$$\xi\ (\%) = \frac{\Delta c \times V}{\Delta t \times J_0 \times A} \times 100 \quad (1)$$

where Δc is the change of concentration in the time interval Δt, V represents the volume of the methylene blue solution, J_0 is the flux of UV(A) photons, and A is the irradiated surface area.

3. Results and discussion

XRD patterns of the synthesized samples of undoped ZnO and Ge doped ZnO nanorods at different Ge contents (1, 3, 13, and 30 at.%) are shown in Fig. 1. At undoped ZnO, all reflections (Fig. 1a) are assigned to the wurtzite structure of ZnO (JCPDS card no. 36-1451, space group $P6_3m$). It exhibits an (1 0 1) preferred orientation, with three secondary peaks, (1 0 0), (0 0 2) and (1 1 0) (Fig. 1a). The intensity of peaks decreased with increasing the Ge content in the ZnO nanorods (Fig. 1b–d). The decrease in ZnO intensity is attributed to Ge ions get a Zn lattice site, which reduces the crystallinity of the ZnO nanorods. Thus, it is suggested that the ZnO nanorods growth without catalyst have a preferential orientation along the *c*-axis. Fig. 1c at 13 at.% Ge doped ZnO, new peaks appear compared with those of the undoped ZnO. These peaks are formed from Zn_2GeO_4 compound and marked with a black square. It shows the reflection peaks including Zn_2GeO_4 at $2\theta = 21.53$, 24.92, 30.76 and 32.97, respectively, can be clearly indexed to rhombohedral crystal structure (JCPDS: PDF file no. 11-0687). They indicate that the sample mainly composed of ZnO mixed with Zn_2GeO_4 [42]. On the other hand, at 30 at.% Ge, Zn_2GeO_4 peaks disappeared and this can be explained by the formation of amorphous Ge coating ZnO nanorods.

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