Research Article

Photoluminescence of Hexagonal ZnO Nanorods Hydrothermally Grown on Zn Foils in KOH Solutions with Different Values of Basicity

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Aligned hexagonal ZnO nanorods on pure Zn foils were hydrothermally synthesized in 30 mL solutions containing 0.05–0.50 g KOH. The products were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and photoluminescence (PL) spectroscopy. In this research, wurtzite hexagonal ZnO nanorods grown along the [002] direction with green light emission at 541 nm caused by singly ionized oxygen vacancies inside were detected.

1. Introduction

One-dimensional (1D) semiconducting materials are able to be used for a number of potential applications in short wavelength optical, nanoelectronic, and optoelectronic devices due to their tunable electronic and optoelectronic properties controlled by morphologies and dimensions [1–3]. Compared to two-dimensional (2D), three-dimensional (3D), and zero-dimensional (0D) nanostructures, the 1D nanostructure has unique characteristic: large aspect ratio, single crystalline structure, and oriented growth [3]. Zinc oxide is an important low-cost II–VI basic semiconductor with 3.37 eV wide band gap and strong exciton binding energy of 60 meV at room temperature [4–7]. It possesses unique catalytic, electrical, optoelectronic, and photochemical properties—very interesting for a number of potential applications as room-temperature UV lasers, sensors, light-emitting diodes, optical switches, solar cells, and photocatalysis due to its low dielectric constant, high chemical stability, good photoelectric, and piezoelectric behaviors [4, 6, 8].

In the paper, hexagonal ZnO nanorods on Zn foils were hydrothermally synthesized in solutions containing 0.05–0.50 g KOH at 120°C. Their phase, morphology, and photoluminescence were investigated and discussed in more details.

2. Experimental Procedure

Reagents of the research were of analytical grade and used without further purification. The hexagonal prism ZnO nanorods were grown on Zn foils by the following. Several 10 × 10 mm square Zn foils with 0.25 mm thick were cleaned with deionized water and absolute alcohol in an ultrasound bath and put in 30 mL of 0.05, 0.10, 0.20, 0.30, 0.40, and 0.50 g KOH aqueous solutions, containing 1, 2, 4, 6, 8, and 10 times of KOH in sequence. All of the solutions and zinc foils were transferred into 50 mL Teflon-lined stainless steel autoclaves, which were tightly closed, heated at 120°C in a laboratory electric oven for 24 h, and naturally cooled to room temperature. In the end, the zinc foils were thoroughly rinsed by

FIGURE 1: (a) XRD patterns and (b) Raman spectra of the as-synthesized ZnO in 30 mL solutions containing 1 (0.05 g), 6 (0.30 g) and 10 times (0.50 g) of KOH.

deionized water several times and alcohol, and dried at 70°C in an electric oven for 12 h for further characterization.

X-ray diffraction (XRD) operated on Philips X'Pert MPD X-ray diffractometer with Cu K_{α} radiation in the 2θ of 20–70 deg with a scanning rate of 0.02 deg per step and Raman spectroscopy on T64000 HORIBA Jobin Yvon at 50 mW Ar Laser with 514.5 nm wavelength were used to determine phase, crystalline degree, purity, and vibration modes. Their morphologies were characterized by scanning electron microscopy (SEM, JEOL JSM-6335F) with an accelerating voltage of 15 kV across the LaB₆ cathode. Their nanostructures and growth direction were further investigated by transmission electronic microscopy (TEM) and selected area electronic diffraction (SAED) on a JEOL JEM-2010 TEM at 200 kV with LaB₆ gun. At the end, optical properties of the products were analyzed by a LS50B Perkin Elmer fluorescence spectrometer in the wavelength range of 450–700 nm.

3. Results and Discussion

Figure 1(a) exhibits typical XRD patterns of the as-grown ZnO on Zn foils, revealing that all diffraction peaks were explicable in term of wurtzite ZnO structure with $a = b = 3.251 \text{ \AA}$ and $c = 5.208 \text{ \AA}$ (JCPDS No. 36-1451) [9]. Sharp diffraction peaks indicate good crystalline degree of the as-synthesized crystals without other impurities detection.

Degree of c orientation of the as-synthesized ZnO samples was explained by the relative texture coefficient (TC) [10, 11] of the (002) peak calculated using the formula

$$TC_{002} = \frac{(I_{002}/I_{002}^0)}{[I_{002}/I_{002}^0 + I_{100}/I_{100}^0]} \quad (1)$$

TC_{002} is the relative texture coefficient of the (002) over (100) diffraction peaks. I_{002} and I_{100} are the measured diffraction intensities of the (002) and (100) peaks, including the corresponding I_{002}^0 and I_{100}^0 values of the randomly oriented standard powder, respectively. For randomly crystallographic orientation, the texture coefficient of ZnO is 0.5. In the solution containing 0.50 g KOH, calculated TC_{002} was 0.86, which supported the preferential orientation of the as-synthesized ZnO nanorods grown along the [002] direction on the Zn foil.

Wurtzite ZnO structure belongs to C_{6v}^4 ($P6_3mc$) space group with two formula units per primitive cell, and all atoms occupy the C^{3v} sites. Group theory of wurtzite ZnO structure predicts eight sets of phonon modes: $A_1 + E_1 + 2E_2$ (Raman active), $2B_2$ (Raman silent), and $A_1 + E_1$ (IR active). Moreover, the A_1 and E_1 symmetry are split into longitudinal (L) and transverse (T) optical (O) components due to the macroscopic electric fields associated with the LO phonons. Figure 1(b) shows Raman spectra of the as-synthesized ZnO nanorods. They show a dominant peak of typical characteristic of the wurtzite ZnO structure at 439 cm^{-1} , assigned to be the optical phonon E_{2H} mode. The weak peak at 332 cm^{-1} was assigned to be the second-order Raman scattering arising from the zone/zero boundary phonons $E_{2H}-E_{2L}$ of multiphonon process, while the Raman peak at 379 cm^{-1} is attributed to A_1 symmetry with the TO mode. Furthermore, Raman spectra of ZnO samples at 567 cm^{-1} are a contribution of the E_1 (LO) mode which is directly associated with oxygen vacancies. The stronger E_1 (LO) mode indicates the presence of higher oxygen vacancies inside [5, 12–14].

SEM images as shown in Figure 2 were investigated on surfaces of Zn foils after hydrothermal treatment in 30 mL solutions containing 1 (0.05 g), 2 (0.10 g), 4 (0.20 g), 6 (0.30 g), 8 (0.40 g), and 10 times (0.50 g) of KOH. An interesting feature of the nanostructures grown on the bottom surfaces exhibited the presence of aligned nanorods of ZnO with the diameter ranging from 400 nm to 700 nm without the detection of other nanostructures. The lengths of the ZnO nanorods are in the range of several micrometers to even longer than 5–7 μm . These nanorods were enlarged and lengthened in sequence with an increase in the degree of basicity. The inset of Figure 2(f) demonstrates the hexagonal

FIGURE 2: SEM images of the as-synthesized ZnO samples in 30 mL solutions containing (a) 1 (0.05 g), (b) 2 (0.10 g), (c) 4 (0.20 g), (d) 6 (0.30 g), (e) 8 (0.40 g), and (f) 10 times (0.50 g) of KOH.

FIGURE 3: TEM image and SAED pattern of hexagonal ZnO nanorod in 30 mL solution containing 10 times (0.50 g) of KOH.

ZnO nanorod which was fully grown on Zn foil in the solution containing 0.50 g KOH.

The hexagonal ZnO nanorods were also characterized through TEM and SAED (Figure 3). TEM image reveals a single hexagonal ZnO nanorod with smooth surface and the preferred growth in the [002] direction. It shows the SAED pattern of bright spots corresponding to hexagonal wurtzite ZnO [9].

Based on the previous discussion, mechanism of the growth and morphology of ZnO nanostructure can be proposed as follows:

The formation of $\text{Zn}(\text{OH})_4^{2-}$ ions from Zn^{2+} and OH^- ions by a hydrothermal reaction is a key role in the formation of hexagonal wurtzite ZnO nanorods. The primary ZnO

nanoparticles began to nucleate on Zn foil by the dissolution of Zn atoms into the solution and the cause of concentration gradient of Zn^{2+} . The intrinsic electric fields of the polar ZnO lattice could be responsible for further growth of ZnO crystals, described as alternating planes of Zn^{2+} and O^{2-} , stacked along the c -axis. The oppositely charged ions produced positively charged and negatively charged surfaces, resulting in polarization along the c -axis. The preferred c -axis orientation of ZnO nanostructure is driven by electrostatic interaction between the polar charges to minimize surface energy. Finally, ZnO nanorods grew on Zn foil as substrate [15].

The main emission of ZnO nanorods can be assigned as the recombination of free excitons. Other peaks probably originated from position of band-edge emission of ZnO of relatively large dimensions with different concentration of native defects [16]. It is well known that visible photoluminescence mainly originates from defect states of Zn interstitials, zinc vacancies, and oxygen vacancies [17]. Photoluminescence (PL) of ZnO nanorods grown on Zn foils was investigated using excitation wavelength of 214 nm at room temperature as shown in Figure 4. PL spectrum of hexagonal ZnO nanorods using 0.50 g KOH shows the highest strong green light emission at 541 nm, due to the singly ionized oxygen vacancies of ZnO, in accordance with other reports [16–18].

4. Conclusions

In summary, densely aligned hexagonal ZnO nanorods on Zn foils were synthesized by a 120°C and 24 h hydrothermal reaction. The XRD, SEM, and TEM analyses showed that the

FIGURE 4: PL spectra of the as-synthesized ZnO in 30 mL solutions containing 1 (0.05 g), 6 (0.30 g), and 10 times (0.50 g) of KOH.

as-synthesized products were pure wurtzite ZnO nanorods with uniform hexagonal structure of 400–700 nm diameter and 5–7 μm long. Room temperature PL spectrum of the ZnO nanorods exhibited one strong green light emission at 541 nm due to the singly ionized oxygen vacancies inside.

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