SYNTHESIS AND PHOTOLUMINESCENCE STUDIES ON ZINC OXIDE NANOWIRES

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ABSTRACT

Semiconductor single crystal ZnO nanowires have been successfully synthesized by a simple method based on thermal evaporation of ZnO powders mixed with graphite. Metallic catalysts, carrying gases, and vacuum conditions are not necessary. The x-ray diffraction (XRD) analysis shows that the ZnO nanowires are highly crystallized and have a typical wurtzite hexagonal structure with lattice constants $a = 0.3246$ nm and $c = 0.5203$ nm. The scanning electron microscopy (SEM) images of nanowires indicate that diameters of the ZnO nanowires normally range from 100 to 300 nm and their lengths are several tens of micrometers. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the nanowires were measured in the range of temperature from 15 K to the room temperature. Photoluminescence spectra at low temperatures exhibit a group of ultraviolet (UV) narrow peaks in the region 368 nm ~ 390 nm, and a blue-green very broad peak at 500 nm. Origin of the emission lines in PL spectra and the lines in PLE spectra is discussed.

Keywords: Semiconductors, nanostructures, photoluminescence, exciton, zinc oxide

1. INTRODUCTION

In recent years, one-dimensional (1D) semiconductor nanostructures including nanowires, nanorods, nanobelts and nanotubes have attracted much attention due to their importance in basic scientific research and potential technology applications. It is generally accepted that the 1D nanostructures are useful materials for investigating the dependence of electrical and thermal transport or mechanical properties on dimensionality and size reduction (or quantum confinement). They are also expected to play an important role as both interconnects and functional units in fabricating electronic, optoelectronic, electrochemical and electromechanical nanodevices [1]. In the past few years, much effort has been devoted to developing various 1D semiconductor nanostructures. Many methods have been used to synthesize various metal oxides, III-V and II-VI compound semiconductor nanostructures: vapor-phase transport [2, 3], laser ablation [4], chemical vapor deposition [5], metal-organic chemical vapor deposition [6, 7], and hydrothermal method [8].

Zinc oxide (ZnO) is recognized as a promising material for photonics because of its wide band-gap E_g of 3.37 eV and large exciton binding energy of 60 meV. Furthermore, ZnO is bio-safe and biocompatible, and may be used for biomedical applications without coating. Various kinds of ZnO nanostructures have been realized, such as nanowires, nanorods, nanobelts, nanotubes

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etc. [9]. Among the 1D nanostructures, ZnO nanowires and nanorods have been widely studied because of their easy nanomaterials formation and device applications.

In this paper, we present a metallic catalyst-free growth of ZnO nanowires using a simple method based on thermal evaporation of ZnO powders mixed with graphite. Photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the nanowires were measured in the range of temperature from 15 K to the room temperature. PL spectra are characterized by emissions from different mechanisms including free exciton (X), neutral donor-bound exciton (D^0X), recombination of an electron bound on a shallow donor with a free hole in the valence band (BF) [10], transition related to deep defects. It is found that the UV emission at room temperature is a mixture of emission due to free exciton and emission concerned with BF transition. Especially, the low temperature PLE spectra exhibit a fine structure related to the A and B exciton and other band edge transitions.

2. EXPERIMENTS DETAILS

Nanowires of ZnO were synthesized by thermal evaporation of a mixture of ZnO and graphite powders with molar ratio ranged from 1:2 to 1:4. The source material was placed at the closed end of a quartz tube. The other end of the quartz tube was open to the atmosphere. The quartz tube was inserted into a horizontal tube furnace, so that the source material was placed in the temperature region approximately 1050°C. The SiO₂/Si substrates were placed along the quartz tube in the temperature regions from 900°C to 650°C. After 45 min evaporation, the quartz tube was drawn out from the furnace and cooled down to room temperature. White color films were formed on the SiO₂/Si substrates. The crystal structure of the films was analyzed using a SIMENS D5005 X-ray diffractometer. The morphology of the films was characterized using a scanning electron microscope (JEOL 5410 LV). The composition of the films was determined by an energy dispersive X-ray (EDX) spectrometer (EDS, OXFORD ISIS 300) attached to the JEOL-JSM 5410 LV scanning electron microscope. PL and PLE spectra were measured at temperatures ranging from 15 K up to 300 K using a Fluorolog FL3-22 Jobin Yvon Spex USA spectrofluorometer with a xenon lamp of 450 W as an excitation source.

3. RESULTS AND DISCUSSION

Figure 1 shows typical scanning electron microscope (SEM) images of ZnO nanowires. The diameters of ZnO nanowires normally range from 100 to 300 nm and their lengths are several tens of micrometers.

Fig. 1. SEM images of ZnO nanowires

An X-ray diffraction (XRD) pattern of ZnO bulk nanowires is shown in Fig. 2. The XRD pattern clearly indicates that the ZnO nanowires possess a hexagonal wurtzite crystal structure with lattice constants of $a = 0.3246$ nm and $c = 0.5203$ nm. The (002) diffraction peak is dominant in the spectrum, which means that the nanowires have preferential growth direction along c -axis.

Fig. 2: XRD pattern of ZnO nanowires

EDX measurements were carried out in order to examine the elemental composition of the ZnO nanowires. A typical EDX spectrum of the ZnO nanowires is shown in Fig. 3. It can be seen from the figure, the nanowires are composed of zinc and oxygen.

Fig. 3: EDX spectrum of ZnO nanowires

PL spectrum of ZnO nanowires measured at 30 K using wavelength of 335 nm of a xenon lamp of 450 W as an excitation source is shown in Fig. 4. Photoluminescence spectra at low temperatures exhibit a group of ultraviolet (UV) narrow peaks in the region 368 nm ~ 390 nm (3.179 eV ~ 3.369 eV), and a blue-green very broad peak at 500 nm (2.480 eV).

This blue-green broad peak is found to have a distinct structure due to multi-phonon emission. The phonon energy on the average is about 70 meV, which is approximately equal to the energy of LO-phonon in ZnO (~72 meV). The blue-green broad peak is usually associated with deep defects such as singly ionized oxygen vacancies [11] or copper-related defects [12]. In this paper, we focus our attention only on the peak group in the UV region, concerning the origin of these emission peaks.

In order to investigate the origins of emission peaks, the PL spectra were measured in the temperature range from 15 K to 300 K. The PL spectrum at 15 K exhibits five emission peaks at

3.362, 3.314, 3.296, 3.240, and 3.223 eV (Fig. 5). The peak at 3.362 eV with full width at half-maximum value of 16 meV, as will be shown later, is attributed to neutral donor-bound exciton (D^0X), the peak at 3.314 eV is attributed to recombination of an electron bound on a shallow donor with a free hole in the valence band (BF). The peaks at 3.296 and 3.223 eV are interpreted as phonon replicas of D^0X with one and two LO-phonon energy of 72 meV (D^0X -1LO, D^0X -2LO), the peak at 3.240 eV is interpreted as a phonon replica of BF (BF-1LO).

Fig. 4: PL spectrum of ZnO nanowires measured at 30 K using wavelength of 335 nm of a xenon lamp of 450 W as an excitation source

Fig. 5: Low temperature PL spectra of ZnO nanowires measured at various temperatures. Here only UV peak group is shown

As it can be seen from Fig. 5 and Fig. 6, the intensity of the sharp peak at 3.362 eV (D^0X) is decreased rapidly and its position is shifted slightly to the low-energy side with increasing measuring temperature. At 120 K, this peak becomes much weaker than the BF peak at 3.314 eV.

From Fig. 6 it is also evident that beginning from 70 K a shoulder with an energy value of 3.377 eV appears at the high-energy side of the D^0X peak. The position of the shoulder is shifted to the low-energy side with increasing measuring temperature. This shoulder is still maintained up

to 250 K and is mixed to the BF peak at higher temperatures. This shoulder is interpreted to be the origin from the radiative recombination of free exciton (X_A). Indeed, as temperature is increased, the thermal activation energy is enough for the release of excitons from the neutral donor ($D^0X \rightarrow D^0 + X$), then, radiative transitions take place via states of the free excitons.

Fig. 6: PL spectra of ZnO nanowires at 70, 90, and 120 K. The spectra exhibit shoulders due to emission of free exciton A (X_A)

Fig. 7: The temperature dependence of the peak energies for X_A emission (solid triangle), D^0X emission (solid squares), and BF emission (solid circle)

Assuming that the peak position of free exciton and donor-bound exciton emission varies with temperature as the energy band gap, we tried to fit the observed temperature dependence to Varshni's semiempirical formula [13]:

$$E(T) = E(0) - \alpha T^2 / (T + \beta)$$

where $E(0)$, α and β are fitting parameters. As it can be seen in Fig. 7, the experimental values for the X_A peak and the D^0X peak fit rather well to the Varshni's curve (solid lines in the Fig. 7) with fitting parameters: $\alpha = -9.8 \times 10^{-4}$ eV/K, $\beta = -950$ K, and $E(0) = 3.384$ eV and 3.365 eV for X_A and D^0X peaks, respectively.

The binding energy of the exciton at neutral donor is estimated to be about 19 meV in accordance with the results in [14]. If we recognize a linear relation between the binding energy of the exciton at neutral donor $E_{bind.D^0X}$ and the binding energy of the donor E_D like in [14]:

$$E_{bind.D^0X} = A + B.E_D$$

with constants $A = -3.8$ meV and $B = 0.375$, we can estimate $E_D = 62.5$ meV.

For the origin of the BF emission peak at 3.314 eV, we believe that this peak probably corresponds to the recombination of a free carrier with a carrier bound on a defect. In our case, the sample is an n-type semiconductor, so it is more likely that an electron bound on a donor recombines with a free hole in the valence band (BF). In that case, the peak position of the BF emission should vary with temperature more slowly than the energy band gap does according to Varshni's model, as may be seen in Fig. 7. The experimental values of the BF peak position at various temperatures fit rather well to the curve (dotted line in the Fig. 7) calculated using the formula described the peak position of emission due to transitions from a donor to the valence band [15]:

$$h\nu = E_g - E_D + k_B T$$

where E_g is the band-gap energy, E_D as mentioned above, is the binding energy of the donor, T is temperature, k_B is Boltzmann constant. The free-to-bound radiative transitions have been observed in ZnO both at low temperatures and at room temperature by other authors [16, 17].

Fig. 8: The PLE (solid lines) and PL (dotted lines) spectra of ZnO nanowires measured at different temperatures. In the figure are shown the emission peaks related to the free exciton (X_A , X_B), the neutral donor-bound exciton (D^0X) and the bound-to-free transitions (BF)

Photoluminescence excitation (PLE) spectra for the broad emission peak at 495 nm (2.505 eV) were measured in the range of temperatures from 15 K to 300 K. The PLE spectra at low

temperatures exhibit fine structures (Fig. 8). The PLE spectrum at 15 K consists of a weak shoulder at 3.309 eV and six peaks at 3.361, 3.386, 3.411, 3.453, 3.499, and 3.538 eV. These peaks are shifted slightly to the low-energy side with increasing measuring temperature.

In order to find the origins of the PLE peaks, we compare the PLE spectra with the PL spectra measured at the same temperatures (Fig. 8). It is evident from Fig. 8 that the shoulder at 3.309 eV can be attributed to absorption transition from the valence band to a donor (BF). The peak at 3.361 eV is due to absorption transition of neutral donor-bound exciton (D^0X). The peak at 3.386 eV is attributed to absorption transition of the A-free exciton (X_A). The peaks at 3.411 and 3.453 eV are interpreted as absorption transitions to the ground ($n = 1$) and the first excited ($n = 2$) states of the B-free exciton (X_B), respectively.

The energy separation between the $n = 1$ and $n = 2$ states is 42 meV. Assuming the hydrogenic model based on the effective mass approximation is applicable, the binding energy of the B-exciton estimated from the separation of 42 meV is 56 meV in good accordance with the results in [18].

The peak at 3.499 and 3.538 eV can be attributed to absorption transitions to states $n = 1, 2$ of the B-exciton accompanied by an absorption of phonon ($X_B(n = 1) + \text{phonon}$, $X_B(n = 2) + \text{phonon}$), respectively.

4. CONCLUSIONS

The ZnO nanowires with diameters ranging from 100 to 300 nm and lengths of several tens of micrometers have been successfully prepared by thermal evaporation method without metallic catalyst. The ZnO nanowires possess a hexagonal wurtzite crystal structure with lattice constants of $a = 0.3246$ nm and $c = 0.5203$ nm. The A-free exciton (X_A), the neutral donor-bound exciton (D^0X) and the bound-to-free (BF) transition were observed both in low temperature PL spectra and in PLE spectra. Absorption transitions related to the ground and the first-excited states of the B-exciton (X_B) were observed in the PLE spectra measured at low temperatures. The room temperature PL in the UV region is a mixture of emission due to free excitation and emission concerned with transitions from a donor level to the valence band.

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