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The effect of arsenic thermal diffusion on the morphology and photoluminescence properties of sub-micron ZnO rods

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ABSTRACT

As-doped sub-micron ZnO rods were realized by a simple thermal diffusion process using a GaAs wafer as an arsenic resource. The surface of the sub-micron ZnO rods became rough and the morphology of As-doped sub-micron ZnO rods changed markedly with increasing diffusion temperature. From the results of energy-dispersive X-ray spectroscopy, X-ray diffraction and photoluminescence, arsenic elements were confirmed to be introduced into the sub-micron ZnO rods. The acceptor ionization energy was deduced to be about 110 meV based on the temperature-dependent PL spectra.

1. Introduction

Zinc oxide is one of the most promising materials for applications in short wavelength optoelectronic devices due to its direct wide band gap (3.37 eV at room temperature) and large exciton binding energy (60 meV), which is larger than the thermal energy at room temperature ($K_BT = 26$ meV, $T = 300$ K)[1]. In recent years, ZnO nanostructures, including nanowires, nanorods, and nanobelts, have attracted much interest due to their potential applications in electronic and optoelectronic devices. These nanostructures have been synthesized by various methods, such as thermal evaporation, vapor transport, and hydrothermal methods, and so on [1–3].

Usually, ZnO shows n-type conductivity associated to its native detects, such as oxygen vacancies and zinc interstitials. By being doped with In, Ga, and Al [4–6], it is easy to enhance n-type conductivity of ZnO nanostructures. To realize ZnO-based electronic or photonic devices, a key and difficult point is to obtain a high quality and stable p-type ZnO material. It remains very difficult to obtain p-type ZnO nanostructures, as well as ZnO thin films. The cause is mainly due to the low dopant solubility, deep acceptor level, and self-compensation from native point defects [7]. In the past years, several research groups have obtained some success in preparing p-type ZnO by using the group V elements (N, P, As, and Sb) as dopants [8–12]. However, a few of the reports present the effect of diffusion process on the surface morphology and photoluminescence properties of the resulting films.

This article reports the realization of As-doped sub-micron ZnO rods using the arsenic as the dopant. It is known that photoluminescence (PL) is an invaluable tool in studying on the optical characteristics of ZnO-based structures. The effects of the thermal diffusion of arsenic on the morphology and photoluminescence properties of sub-micron ZnO rods were studied. While As-doped ZnO materials prepared by a similar method have already been reported previously [13–15], the study of the dependence of the morphology and photoluminescence of the structures on dopant diffusion temperature add valuable information on this system.

2. Experimental details

Firstly, the sub-micron ZnO rods were fabricated via a simple physical vapor deposition without any catalysts. A mixture of ZnO and Zn powders with a weight ratio of 1:1 was put into an alumina boat, which was placed into a quartz tube. Si (100) substrate was put in a definite distance (about 4 mm) above the source material. Before being loaded, the Si substrate was cleaned in an ultrasonic bath of organic solvent for about 5 min, etched by HF aid and washed with the deionized water. The furnace was heated up to 630 °C and kept for 1 h. During the synthesis process, a constant flow of nitrogen (300

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standard cubic centimeters) was introduced into the tube furnace. Finally, the substrate was naturally cooled down to room temperature (denoted as sample A).

Secondly, to realize As doping, the GaAs wafer was used as As source. The GaAs wafer was put rightly on the top of sub-micron ZnO rod arrays. Before being used, the GaAs wafer was cleaned in an ultrasonic bath of organic solvents (acetone and alcohol), then rinsed in HF acid for several minutes. Due to the GaAs wafer could decompose and release arsenic atoms above 600 °C [15], the diffusion temperature was chosen at 600 °C and 650 °C, respectively (the prepared samples under these two conditions were denoted as samples B and C, respectively). The annealing was carried out in argon gas for 4 h. The sample D was obtained by thermal-treating sample C at 800 °C for 1 h in the atmosphere. While part of as-grown sub-micron rods was annealed at 650 °C for 4 h without the GaAs wafer, Sampled E was obtained.

The morphologies and the compositions, of the samples (A–D) were characterized by the fielded emission scanning electron microscopy (FESEM) (model: Hitachis-4800) attach to energy-dispersive X-ray spectroscopy (EDX) (model: GENE SIS 2000 XMS 60S, EDAX, Inc.) operated at 15 kV. The structure of the samples (A–D) was determined by X-ray diffraction (XRD) (model:D/max-RA) using a CuKα radiation. Photoluminescence measurements were performed using a He–Cd laser line of 325 nm as the excitation source (model: LABRAM-UV Jobin Yvon). The bonding state of As in the As-diffused sub-micron ZnO rods was analyzed using a X-ray photoelectron spectroscopy (XPS) (model: Thermo ESCALAB 250). The position of the C1s peak was taken as a standard reference with a binding energy of 284.6 eV.

3. Results and discussion

Fig. 1 shows the SEM images of all the samples prepared. The as-grown sample (Sample A, Fig. 1a) is composed of hexagonal sub-micron rods with almost uniform size and flat top planes. This morphology changed considerably after As diffusion. The sub-micron rods become rougher for the sample prepared at 600 °C (Sample B, Fig. 1b), while the top planes remain hexagonal. The sub-micron rods' surface is much rougher with increasing the diffusion temperature to 650 °C (Sample C, Fig. 1c). The As content in these sub-micron rods as measured by EDX is shown in Table 1. The As dopant concentrations in samples B and C are 3 at.% and 7 at.%, respectively. The As atomic concentration drops to 0.2 at.%, which is around the detection limit of the apparatus, after annealing the sample prepared at 800 °C. Some small protuberances can be observed on the surface of this sample, as shown in Fig. 1d. However, the surface of the sub-micron rods of a control sample heated at 650 °C without any As source remains smooth (Sample E, Fig. 1e) retained the original hexagonal shape and flat top geometry. Since no change was observed on the surface morphology of sample E compared to the unheated sample, the morphology changes of the sub-micron rods after diffusion were induced by a chemical etching process. The As atoms decomposed from GaAs could diffuse into ZnO or react with oxygen on the surface of ZnO sub-micron rods at high temperature. For the former process the As atoms would be localized in the ZnO lattices, but for the later the As atoms could capture oxygen atoms and evaporate into the carrier gas, which may destroy the smoothness of the surface of the sub-micron rods.

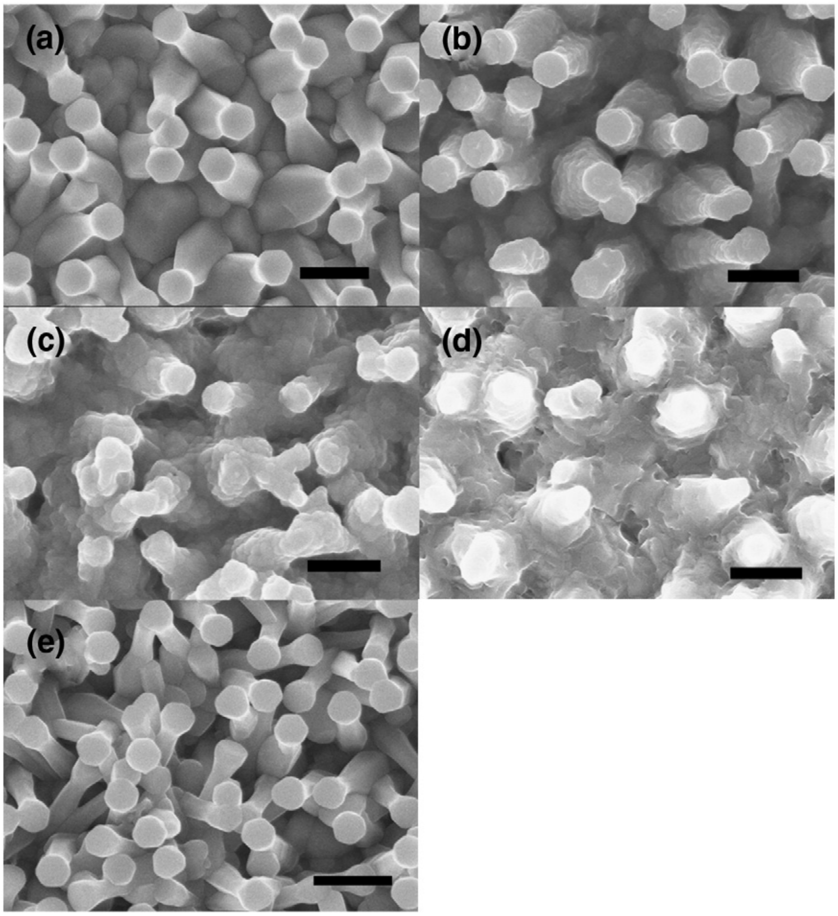

Fig. 1. SEM images of (a) as-grown sub-micron rods (sample A), (b, c) As-diffused ZnO rods under temperatures of 600 °C (b, sample B) and 650 °C (c, sample C), (d) thermally treated (800 °C) (sample D), and (e) sample annealed at 650 °C without GaAs wafer (sample E). The scale bar represents 1 μm.

Table 1
The arsenic content of undoped and As-doped sub-micron ZnO rods as measured by EDS.

Sample	Sample A	Sample B	Sample C	Sample D
Diffusion temperature (°C)	–	600	650	800
Arsenic content (at.%)	0	3	7	0.2

The XRD patterns of the pure and As-doped diffused sub-micron ZnO rods are displayed in Fig. 2. Fig. 2a shows the XRD spectrum of the pure sub-micron ZnO rods grown on Si (100) substrate, in which all the diffractive peaks could be indexed to ZnO wurtzite structure. For the As-doped sub-micron ZnO rods, the diffractive peaks shift to the low angle side slightly compared with the undoped one, which means the lattice constant of the As-doped ZnO crystal is increased. Because the ions radius of both zinc and oxygen is smaller than that of arsenic, the increase of the lattice constant could be attributed to the doping of As atoms into the ZnO crystal lattices. The As atoms could diffuse into ZnO, and the As atoms in ZnO may also escape from the lattice at high temperature, which is an equilibrium process. Although in EDX data the sample C has more As atomic percentages than that of the sample B in the EDX data, due to the escape speed which is high at 650 °C more As atoms are localized in ZnO lattices in sample B, which induces that the shift of the (002) peak position of the sample B is larger than that of the sample C. The excess As atoms in sample C may diffuse into the ZnO grain boundaries. After being annealed at a high temperature of 800 °C in atmosphere, the As atoms in the grain boundaries are released into the atmosphere, which results in the As concentration reduces rapidly.

In order to confirm the As doping into the ZnO lattices, low temperature PL measurements were performed. It is well known that PL is a sensitive technique to reflect the band structure of semiconductor. The low temperature PL spectrum of the sub-micron ZnO rods (84 K) is shown in the insert of Fig. 3a. The peak located at 3.363 eV is assigned to the radiative recombination of shallow donor-bound exciton (D^0X) [16]. At high energy side of D^0X (at 3.376 eV) a small shoulder could be observed, which is originated from the recombination of the free exciton (FX) [17]. The emission peaks located at 3.316 eV, 3.246 eV, and 3.176 eV are considered as the 1-LO (longitudinal optical), 2-LO, 3-LO phonon replicas of free exciton, respectively. The FX emission is almost disappeared with being doped with As (for samples B, C, and D) and the other emission peaks slightly shift to low energy side, especially for the sample D.

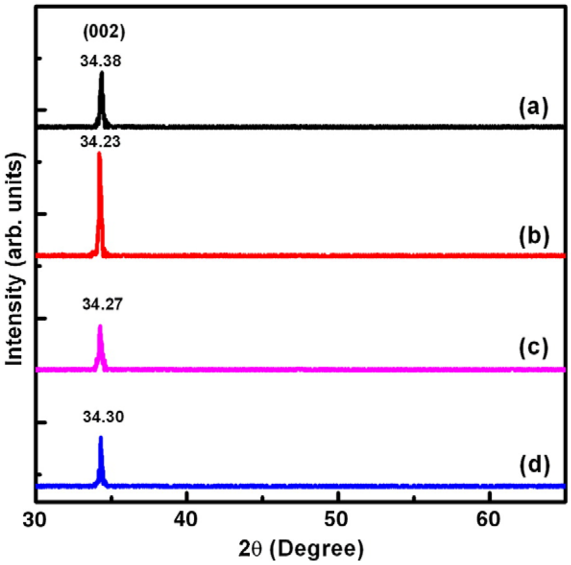

Fig. 2. XRD patterns of samples A–D.

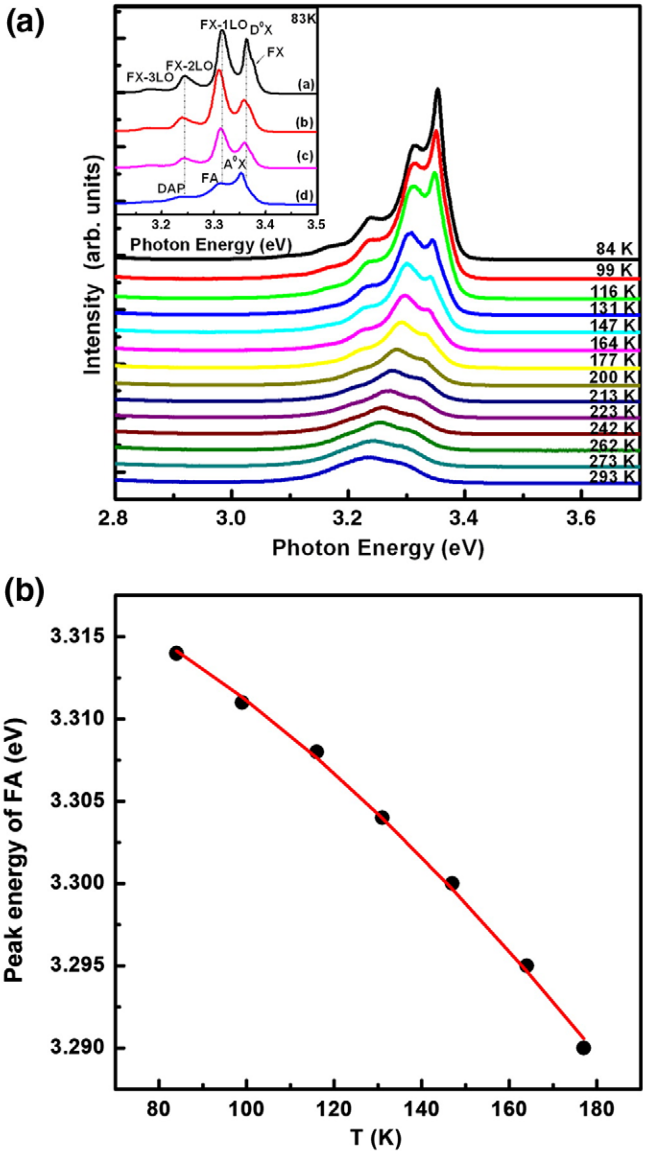

Fig. 3. (a) Temperature-dependent PL spectra of the annealed As-doped sub-micron ZnO rods (sample D), the inset shows the PL spectra of samples A–D at 83 K for comparison. (b) Temperature-dependent peak energy of FA and the fitting curve using Eq. (1) for sample D.

In order to clarify the origination of the emission peaks with As doping, the temperature-dependent PL spectra of annealed sub-micron ZnO rods (sample D) are shown in Fig. 3a. The emission peak located at 3.353 eV could be attributed to the acceptor-bound exciton radiative recombination (A^0X) induced by As doping [18]. Another peak located around 3.313 eV is broadened and shifts to low energy side compared with undoped sample. This emission peak is considered to be a mixture of free electron to acceptor (FA) transition related to the arsenic acceptor and the recombination of FX-1LO. But the FA transition is the dominant one. Furthermore, the FA emission peak around 3.310 eV also presents in N-doped [19] and P-doped ZnO [20]. In addition, the emission peak at 3.240 eV is ascribed to the donor–acceptor pair (DAP) transitions. The A^0X and DAP emissions are quenched quickly and gradually transforms into FA due to the thermal ionization of donors [21]. The step-like broad peak (at 3.168 eV) at the low energy side of DAP is 72 meV lower in energy

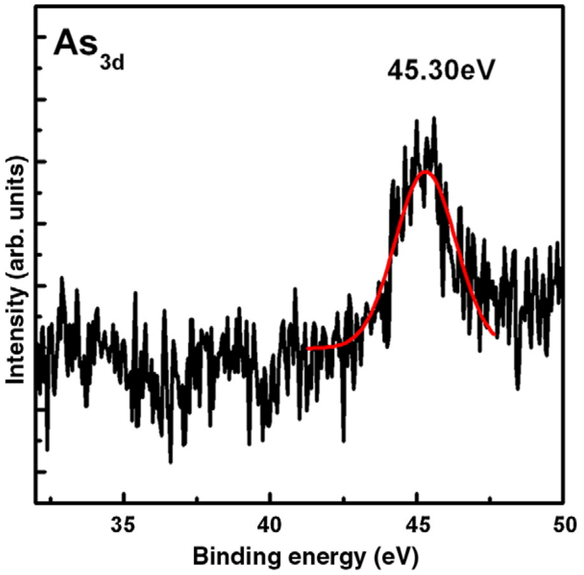

Fig. 4. XPS spectra of As 3d core level for sample D.

than DAP. The peak is ascribed to be the phonon replica of the DAP, because the difference is consistent with the longitudinal optical phonon energy.

The temperature-dependent peak position of the FA emission was analyzed, as shown in Fig. 3b. It can be seen that the FA transition energy shows a continuous red shift with increasing temperature. The acceptor binding energy of E_A in ZnO could be estimated by the following equation:

$$E_{FA}(T) = Eg(T) - E_A + \frac{1}{2}K_BT \qquad (1)$$

where Eg(T) and $E_{FA}(T)$ are the temperature-dependent band gap energy and free electron to acceptor energy, respectively, K_B is the Boltzmann constant. Here, Eg(T) is a function of temperature, which is fitted well with the formula: $\mathrm{Eg}(T) = \mathrm{Eg}(0) - \alpha T^2/(\beta + T)$, where α and β are constants. Eg(0) is the band gap energy at $T = 0$ K. Based on the above equations, the acceptor energy level could be calculated to be about 110 meV. The E_A value obtained from Eq. (1) was in good agreement with those reported by Ryu and Lee [18]. The fitting curve, which matches well with the experiment data, verifies our assignment of FA transition.

In order to further understand the As chemical surrounding in ZnO lattice, XPS analysis was also carried out by an X-ray photoelectron spectroscopy with AlKα ($h\nu = 1486.6$ eV) line as the irradiation source. The C 1s peak with binding energy of 284.6 eV was used for a standard reference. The typical XPS spectrum of the sample D is shown in Fig. 4. The As 3d core level with the photon emission peak located at 45.3 eV could be ascribed to the oxidized states of As (As–O) by Gaussian-fitting [22]. The theoretic calculations have showed As_O has very high acceptor ionization energy (about 930 meV above the valence band maximum), but an As_{Zn}–$2V_{Zn}$ complex has shallow accepter level (about 150 meV) [23]. Based on our experimental data it is assumed that during the thermal diffusion process, substituted As atoms form much more complex structure, namely As_{Zn}–$2V_{Zn}$, in which the As atoms prefer to substitute the Zn sites and to release two Zn-vacancy in ZnO.

4. Conclusion

In a conclusion, As-doped sub-micron ZnO rods were realized by the thermal diffusion process. With increasing diffusion temperature the surface of sub-micron ZnO rods became rough and the morphology of As-doped sub-micron ZnO rods changed considerably. The EDX and XPS analysis gave evidences that the arsenic atoms have been introduced into the ZnO crystal lattices. The neutral acceptor-bound exciton (A^0X), free electron to acceptor (FA) and donor–acceptor pair (DAP) emission peaks could be observed for the As-doped sub-micron ZnO rods in the low temperature PL spectra. And the As_{Zn}–$2V_{Zn}$ complex was considered as the origination of the acceptors.

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