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Influence of lead concentration on morphology and optical properties of Pb-doped ZnO nanowires

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Abstract

Undoped and Pb-doped ZnO nanowires with different lead concentrations were grown on Si(111) substrates using a thermal evaporation method. Scanning electron microscopy (SEM) results showed that, the undoped ZnO nanowires were well aligned with uniform diameters and lengths. On the other hand, the Pb-doped ZnO nanowires were tapered and not aligned in a unique direction. X-ray diffraction patterns and Raman measurements clearly indicated hexagonal structures for all of the products. In addition, the Raman results demonstrated that the Pb-doped ZnO nanowires had a lower crystalline quality than the undoped ZnO nanowires. Photoluminescence (PL) studies also confirmed the Raman results and showed a lower optical property for the Pb-doped ZnO nanowires compared to the undoped ZnO nanowires. Moreover, the PL results showed a smaller band-gap for the Pb-doped ZnO nanowires compared to the undoped ZnO.

Keywords: C. Optical properties; Pb-doped ZnO nanowires; Thermal evaporation

1. Introduction

Zinc oxide (ZnO) is an n-type metal oxide semiconductor with a wide band-gap (3.36 eV) and large exciton binding energy (60 meV). These characteristics make this material interesting for many applications such as solar cells [1], field emission materials [2], nano-electronic devices [3], antibacterial applications [4], and photocatalyst properties [5]. The key factors affecting these applications are the shape, size, impurities, doping, structures, and phases. To obtain the desired properties, many researchers in recent years have focused on the synthesis of doped and undoped nanocrystalline materials such as ZnO. Doping semiconductors with various elements is known to affect many of the basic physical properties of the semiconductor, including its electrical, optical, and magnetic properties, which are all crucial for most of the practical applications. In addition to ours, many other groups have also reported the synthesis of doped ZnO nanostructures with various morphologies using different methods [6–9].

Pb is also an important element with various applications in the semiconductor industry. Yet few studies [10–12] have investigated the properties of Pb-doped ZnO nanostructures. Thus, a detailed study of Pb-doping is still necessary to understand the role of Pb in ZnO nanostructures. Therefore, the effect of this element on the properties of the ZnO is very important. The main focus of the present work was an investigation of the effect of Pb-doping on the physical properties of ZnO nanowires. We believe that a high temperature can make it possible to obtain doped ZnO nanomaterials with high optical and structural quality. Accordingly, in the present work, a high temperature method was used to grow Pb-doped ZnO nanowires.

2. Experimental

The growth of undoped and Pb-doped ZnO nanowires was performed in a horizontal tube furnace. First, Si(111) substrates were ultrasonically cleaned using ethanol and de-ionized water.

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They were then lightly etched with an HF (43%) and deionized water mixture (1:10) for about 10 min to remove the native oxide layer. A mixture of lead oxide powder (99.99%), zinc oxide powder (99.99%), and commercial graphite powder in an x(1 and 3):10:10 weight ratio was used as the precursor material to grow the Pb-doped ZnO ($ZnPbO_1$ and $ZnPbO_2$). The precursor material was placed at the closed end of a small quartz tube and a Si(111) substrate was placed above of the precursor material, as shown in Fig. 1. The small tube was then inserted into the vacuum chamber so that the closed end was at the center of the furnace. The precursor materials and silicon substrate were heated to 1000 °C. High purity N_2 gas was fed at about 200 sccm into the furnace at one end, while the other end was connected to a rotary pump. The growth process was allowed to proceed for 1 h.

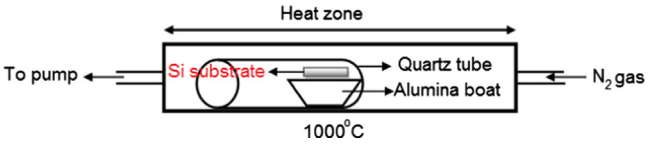

Fig. 1. Schematic of set-up used for growth of undoped and Pb-doped ZnO nanowires.

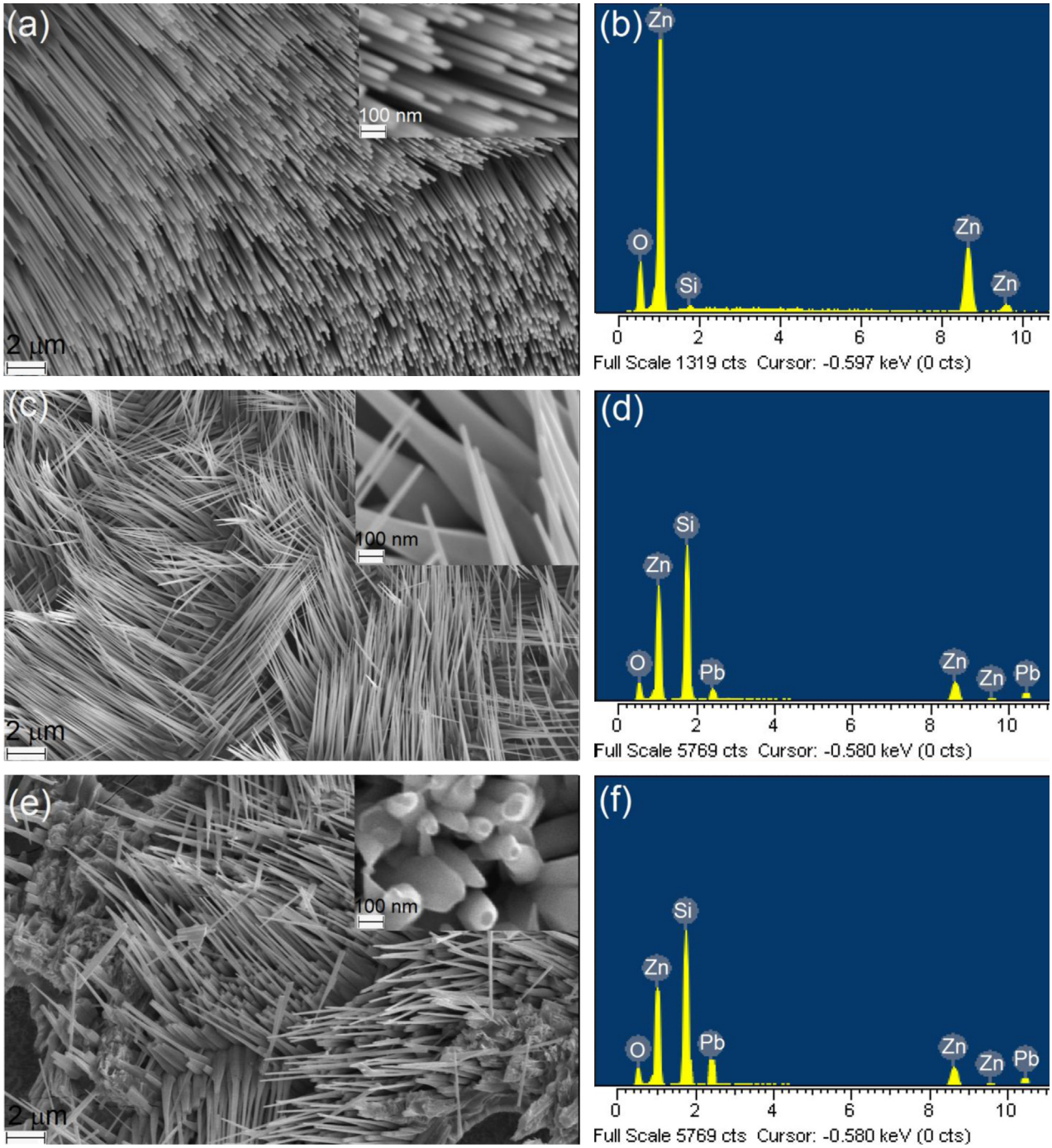

Fig. 2. (a,b) SEM images and EDX spectrum of the undoped ZnO nanowires. (c,d) SEM images and EDX spectrum of the Pb-doped ZnO nanowires (1:10, $ZnPbO_1$ nanowires). (e,f) SEM images and EDX spectrum of the Pb-doped ZnO nanowires (3:10, $ZnPbO_2$ nanowires).

A vacuum of 50 Torr was maintained inside the tube furnace during the deposition of the nanostructures. According to these conditions, two sets of the Pb-doped ZnO nanowires with different concentrations of the lead were grown. In addition, undoped ZnO nanowires were grown under the same conditions.

The morphology and crystal structure of the products were investigated using a scanning electron microscope (SEM, LAO 906E) and an x-ray diffractometer (XRD, SiemensD5000). Elemental analyses of the products were undertaken using energy dispersive X-ray (EDX, Quanta 200F). The room temperature photoluminescence (PL) and Raman (Jobin Yvon Horiba HR 800 UV) spectrometers were employed to study the optical properties and crystallinity of the Pb-doped ZnO nanowires. A He–Cd laser with an emission wavelength of 325 nm and an Ar ion laser with an emission wavelength of 514.5 nm were used for the PL and Raman measurements, respectively.

3. Results and discussion

Fig. 2(a–f) shows SEM images and EDX spectra of the undoped and Pb-doped ZnO nanowires. Fig. 2(a) shows an SEM image of the undoped ZnO nanowires. As can be observed in this SEM image, the undoped ZnO nanowires were grown in well-aligned arrays on the Si substrate, with a uniform diameter of ~70 nm (the inset) and length of several hundred micrometers. The EDX spectrum of the undoped ZnO nanowires in Fig. 2(b) reveals that, the nanowires were pure ZnO. Fig. 2(c) shows the Pb-doped ZnO nanowires, which were grown using a mixture of PbO:ZnO:C (1:10:10) ($ZnPbO_1$). As can be seen in the SEM images, the nanowires were completely straight, with non-aligned arrays, and were tapered with a tip diameter of $\sim 30 \pm 5$ nm and a base diameter of $\sim 180 \pm 5$ nm (the inset). The EDX spectrum of the $ZnPbO_1$ nanowires showed a Pb content of about 1.9% (atomic) (Fig. 2(d)). By increasing the lead concentration, most of the $ZnPbO_2$ nanowires were transformed into nanorods (Fig. 2(e)). In addition, tapering of the nanowires is seen in this sample (the inset). Fig. 2(f) reveals the EDX spectrum of the $ZnPbO_2$ nanowires. The EDX spectrum of the $ZnPbO_2$ nanowires shows a Pb content of about 4.5% (atomic). The tapering of the Pb-doped ZnO nanowires could be due to the big difference between the melting points of the ZnO (1980 °C) and PbO (890 °C). We did not use any metal as a catalyst on the substrate. Therefore, the growth had to begin at nucleation sites. These sites were most likely established by PbO particles because the melting temperature of PbO is smaller than that of ZnO. In addition, by etching with HF acid, the Si surface became very rough. Therefore, droplets of liquid PbO, were deposited on the surface, clustered, and served as ideal nucleation sites. PbO may in fact play a self-catalytic role in the growth of the Pb-doped ZnO nanowires. The EDX measurements (not shown here), which were used to investigate the longitudinal Pb distribution in a single nanowire, indicated a non-uniform distribution of the lead content along the nanowire. In fact, the Pb content decreased from the tip to the base of the Pb-doped ZnO nanowires. It could be concluded that, the PbO droplets were unstable during the nanowire growth process. Therefore, the Pb-doped nanowires were grown with a tapered shape. Our proof for this claim is the undoped ZnO nanowires, which were grown under the same conditions (Fig. 2(a)). According to these characterizations, the growth process for the Pb-doped ZnO nanowires can be explained by the following reactions:

$$2ZnO(s)+C(s) \rightarrow 2Zn(g)+CO_2(g) \quad (1)$$

$$2PbO(s)+C(s) \rightarrow 2Pb(g)+CO_2(g) \quad (2)$$

$$Zn(g)+Pb(g)+CO_2(g) \rightarrow \text{Pb-doped ZnO (nanowires)}+CO(g) \quad (3)$$

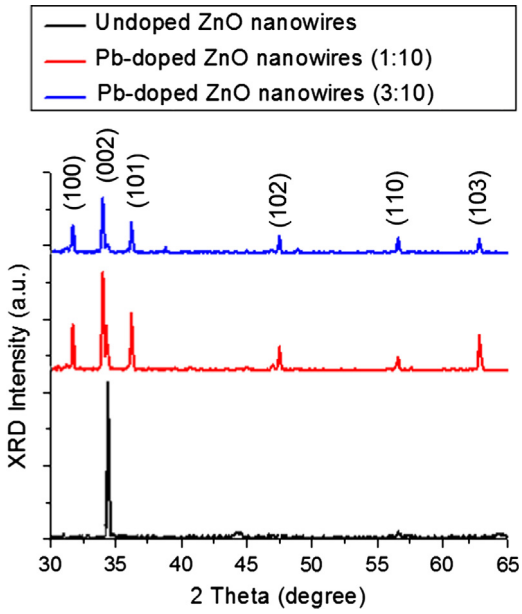

Fig. 3. XRD patterns of undoped and Pb-doped ZnO nanowires.

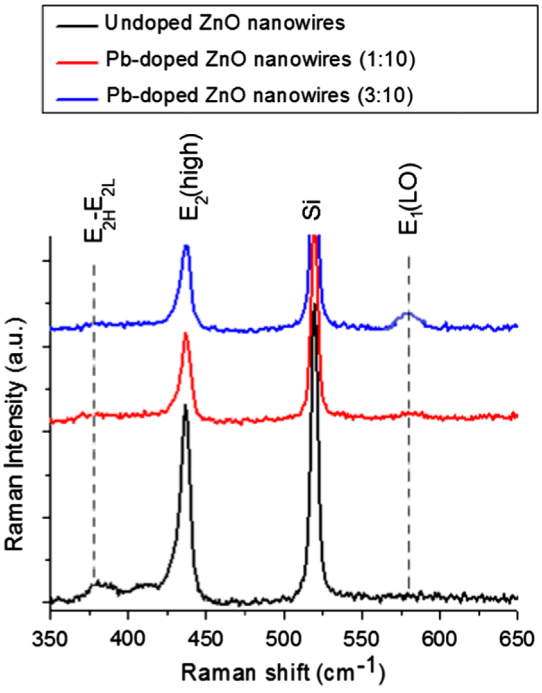

Fig. 4. Raman spectra of the undoped and Pb-doped ZnO nanowires.

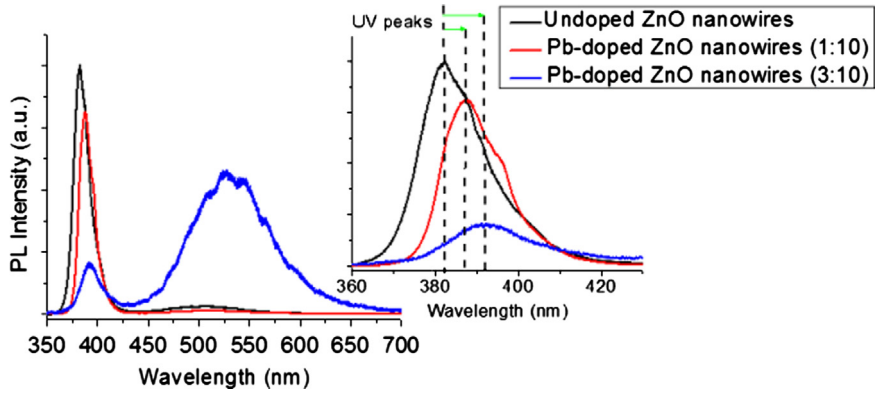

Fig. 5. PL spectra of the undoped and Pb-doped ZnO nanowires.

Fig. 3 shows the XRD patterns of the Pb-doped ZnO nanowires. The XRD patterns in Fig. 3 agree with the standard card for bulk ZnO with a hexagonal structure (JCPDS no. 800075). No peaks from Zn, Pb, PbO or other impurities are observed. The dominant peak of (002) for the well-aligned undoped ZnO nanowires indicates that in most of the ZnO nanowires, the [0001] direction is perpendicular to the substrate. The ionic radius of the substituted Pb^{2+} (1.19 Å) is larger than that of Zn^{2+} (0.74 Å). Thus, the Pb doping caused a slight shift in the XRD peaks toward lower diffraction angles by increasing the Pb concentration. This result provides an indirect evidence that Pb^{2+} was incorporated into the crystal structure, causing the ZnO crystal lattice to expand.

Raman spectroscopy is an effective technique for estimating the crystallinity of materials. According to the group theory, single crystalline ZnO belongs to the C_{6V}^4 space group, with two formula units per primitive cell and eight sets of optical phonon modes at the Γ point of the Brillouin zone, classified as $A_1+E_1+2E_2$ modes (Raman active), $2B_1$ modes (Raman silent) and A_1+E_1 modes (infrared active). The E_1 and A_1 modes are two polar modes and are split into the transverse optical (TO), and longitudinal optical (LO) branches. The Raman spectra of the undoped and Pb-doped ZnO nanowires are presented in Fig. 4. As shown in Fig. 4, the Raman spectra shows a sharp, strong, and dominant peak at 438 cm^{-1} for the nanowires, corresponding to the E_2(high) mode of the Raman active mode and a characteristic peak for the wurtzite hexagonal phase of ZnO. The strong peak appearing at 438 cm^{-1} and no detectable peak at 579 cm^{-1} in the Raman spectra for the undoped ZnO and $ZnPbO_1$ nanowires, are good evidence for this claim that the crystallinity of these samples was very high, because, the peak at 579 cm^{-1} belongs to E_1(LO) is associated with impurities and the formation of defects such as oxygen vacancies [13]. However, the E_1(LO) peak appears in the Raman spectrum of the $ZnPbO_2$ nanowires. Therefore, the crystalline quality of the $ZnPbO_2$ nanowires was lower than that of the other nanowires. In addition, Fig. 4 shows a peak at 330 cm^{-1}, assigned to the E_{2H}–E_{2L} (multi-phonon process) mode for the undoped ZnO nanowires. It is known that the E_{2H}–E_{2L} mode can only be found when the ZnO is a single crystal.

A PL study is a powerful method for investigating the effects of impurity doping on the optical properties of ZnO nanostructures, because doped ZnO nanostructures are expected to have different optical properties in comparison with undoped ZnO. Fig. 5 shows the room temperature PL spectra of the undoped and Pb-doped ZnO nanowires. The PL spectra of the undoped ZnO and $ZnPbO_1$ nanowires show a strong peak in the ultraviolet (UV) region at 381 and 388 nm, respectively, and a negligible green emission (deep-level emission (DLE)) peak in the visible region at around 480 nm. On the other hand, the PL spectrum of the $ZnPbO_2$ nanorods shows a stronger DLE peak than the UV peak (at 392 nm). In fact, Fig. 5 shows that the Pb-doped ZnO nanorods have very high concentrations of oxygen vacancies. Since lead has a larger ionic radius than zinc, the incorporation of Pb into the ZnO lattice will introduce lattice distortion. This effect influences the energy band structure of the ZnO nanostructures doped with lead, and as a result, new defects such as oxygen vacancies can be introduced by the new band structure deformation. Based on this reason, the DLE peak are dominant peak in the PL result for the as-grown Pb-doped ZnO nanowires with a higher concentration of Pb. In addition, compared with the undoped ZnO nanowires, the PL spectra of the Pb-doped ZnO nanowires show an obvious redshift in the UV emission. This redshift can be accounted for by the large difference between the E_g values of ZnO (3.36 eV) and PbO (1.9 eV).

4. Conclusion

The thermal evaporation method was used to grow undoped and Pb-doped ZnO nanowires. The SEM results showed well-aligned arrays of the undoped ZnO nanowires with a uniform diameter, while the Pb-doped ZnO nanowires were non-aligned arrays and tapered. In addition, increasing the lead content in the ZnO structures could cause a change in the morphology of the nanostructures from nanowire to nanorod. Furthermore, the PL and Raman results showed that the optical properties and crystallinity of the Pb-doped ZnO nanowires decreased with increasing Pb concentration. In addition, the UV peaks of the PL spectra were red-shifted for the doped

samples. This redshift could be accounted for by the large difference between the E_g values of ZnO and PbO.

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