Research Article

The Variation of Optical Band Gap for ZnO:In Films Prepared by Sol-Gel Technique

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ZnO:In films with different concentrations (0–5 at.%) are successfully synthesized on quartz substrates using sol-gel technique. The structure, morphology, and optical properties of ZnO:In films are investigated by X-ray diffraction, atomic force microscopy, and UV-visible spectrophotometer. It is found that all the films with columnar structural morphology grow along the preferred [001] orientation and the incorporation of indium can improve the crystallinity of ZnO films. The transmittance of the films is about 80% in the visible range. A change of the optical absorption edge from blue shift to red shift is observed for ZnO:In films as the doping concentration increases, which means that the optical band gap first increases and then decreases. The blue shift is due to the Burstein-Moss effect. The sharp jump of the absorption edge from blue-shift to red shift is ascribed to the band gap narrowing caused by the merging of the donor and conduction bands of ZnO:In at high doping concentration.

1. Introduction

Zinc oxide (ZnO) has been actively studied as a wide band gap oxide semiconductor ($E_g = 3.37$ eV) for transparent conducting oxide films, short wavelength light-emitting devices, and surface acoustic wave devices. Due to high exciton binding energy (60 meV) and similar structural and optical properties with GaN, ZnO has an advantage over GaN for excitonic device applications. For wide band gap semiconductors, addition of impurities often induces dramatic changes in their electrical and optical properties [1, 2], which is very important for their applications. Lu et al. [3] found that the optical energy gap first increased with the electron concentration and then suddenly decreased in Al-doped ZnO films; the variation was consistent with the Mott criterion for a semiconductor-metal transition. Based on spectroscopic ellipsometry, Kim [4] also found an abrupt jump of the optical absorption edge from blue shift to red shift for ZnO:In films prepared by RF magnetron sputtering. However, few researches reported on the jump of the optical band gap observed directly by UV-visible spectrophotometer for ZnO:In films prepared by sol-gel technique.

ZnO films have been prepared by various methods, such as pulsed laser deposition (PLD) [5], metal organic chemical vapor deposition (MOCVD) [6], physical vapor deposition [7], spray pyrolysis [8], and sol-gel technique [9]. Compared with others, sol-gel technique is simple, of low cost, and an advantage of large area deposition. Furthermore, the controllability of the dopant concentration is very easy using sol-gel technique.

In this work, we mainly focus on the variation of the structural and optical properties of ZnO:In films with increasing dopant concentration. The mechanism of the variation of optical band gap is discussed.

2. Experimental Procedure

ZnO:In films were prepared by sol-gel technique. As a starting material and a dopant, zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) and indium nitrate were dissolved in a mixture of 2-methoxyethanol (MOE) and monoethanolamine (MEA) solution. MOE and MEA were the solvent and the stabilizer, respectively. The molar ratio of MEA to zinc acetate was 1.0 and the concentration of zinc acetate

was 0.7 mol/L in the final solution. Indium concentration $[\text{In}^{3+}]/[\text{Zn}^{2+}]$ was varied from 0 to 5 at.%. The mixed solution was stirred vigorously at 60°C for 2 h with reflux to yield a clear and homogenous precursor solution, which served as the coating solution after cooling to room temperature. The solution was usually laid aside two days to increase its viscosity, and then the spin-coating was made. Quartz and Si substrates were employed to deposit ZnO:In films. Before the deposition, the substrates were ultrasonically cleaned by acetone and absolute alcohol in turn and then dried by blowing nitrogen gas. The solution was dropped onto the substrate, which was rotated at 3000 rpm for 20 s. Afterwards, the films were dried at 350°C for 10 min to evaporate the solvent and remove organic matter. The procedure from coating to drying was repeated three times. Finally, all the films were inserted into a furnace at the same time and annealed in air at 600°C for 1 h. ZnO:In films prepared were highly transparent and free from any cracks, voids, and so forth.

The crystalline structure of ZnO:In films was investigated by a DMax/2400 X-ray diffraction instrument (Cu K α radiation, $\lambda = 1.5406 \text{ \AA}$). The surface morphology was observed by an atomic force microscopy (SPM-9500). Optical transmittance was measured by the UV-visible spectrophotometer (Shimadzu UV-3101PC) in the wavelength range of 300–800 nm. The films prepared on Si substrates were used to measure the thickness and the refractive index using an ellipsometer (Gaertner Scientific Corporation L116E).

3. Results and Discussion

Figure 1 shows X-ray diffraction (XRD) patterns of ZnO:In films with different dopant concentrations (In/Zn = 0, 1, 2, 3, and 5 at.%). A strong (002) diffraction peak and a weak (004) diffraction peak of wurtzite ZnO structure are clearly observed, which indicates that all the films exhibit preferential orientation growth along [001], that is, perpendicular to the substrate surface. It is also suggested that the surface energy of (001) plane is the lowest in ZnO crystal [10]. The intensity of the (002) peak sharply increases and then gradually decreases with increasing indium concentration. The film with 1 at.% indium impurity has the strongest (002) diffraction peak, which is consistent with the others [11]. When the dopant concentration is above 1 at.%, the crystallinity of ZnO:In films gradually deteriorates, which may be due to the internal stresses induced by the radius difference of In^{3+} (0.81 Å) and Zn^{2+} (0.74 Å). No new phases corresponding to indium oxide or other indium compounds are detected even if the concentration of indium increases up to 5 at.%, which means that the incorporation of impurity atoms does not change the wurtzite structure of ZnO. On the other hand, as can be seen from the inset in Figure 1, the (002) peak position of ZnO:In films (≥ 1 at.%) is obviously close to that of ZnO powder 34.426°, indicating that an appropriate amount of indium impurities can improve the structural properties of ZnO films. Figure 2 shows the atomic force microscopy (AFM) images of the doped ZnO film with 1 at.% indium. The images of other films are similar to them.

FIGURE 1: XRD patterns of ZnO:In films with different dopant concentrations (0–5 at.%). The inset is the plot of the (002) peak position as a function of indium doping concentration.

TABLE 1: Film thickness, refractive index, and band gap of ZnO:In films with different doping concentrations.

In concentration (at.%)	0	1	2	3	5
Film thickness (nm)	214	232	244	241	214
Refractive index	1.176	1.138	1.105	1.095	1.170
Band gap (eV)	3.157	3.216	3.202	3.197	3.151

As seen, the film shows a uniform columnar structure, which can be explained from the XRD pattern.

Figure 3 shows the optical transmission spectra of ZnO:In films with different doping concentrations. All the films exhibit good optical transmission properties (about 80%) in the visible light range. A jump of the ultraviolet absorption edge (around 380 nm) from blue shift to red shift can be clearly observed as the doping concentration increases. The absorption coefficients α of ZnO:In films are given by the transmittance T and the film thickness d using the following formula [12]:

$$\alpha = \frac{1}{d} \ln \left(\frac{1}{T} \right). \quad (1)$$

For the direct band gap semiconductor ZnO, α obeys the following relationship [13]:

$$(\alpha h\nu)^2 = A (h\nu - E_g), \quad (2)$$

where $h\nu$ is the incidence photon energy, E_g is the band gap energy, and A is a constant. A plot of $(\alpha h\nu)^2$ as a function of $h\nu$ is made to determine E_g using the linear fit. The detailed fitting process is shown in Figure 4. As shown in Table 1, the E_g , derived from the crosspoint at the $h\nu$ -axis with the tangent to $(\alpha h\nu)^2$, sharply increases and then gradually decreases with increasing indium concentration.

As a native n-type oxide semiconductor, ZnO is doped by indium impurities it is expected that the impurity acts as

FIGURE 2: Typical AFM images with different magnifications for ZnO:In thin film doped by 1 at.% impurity.

FIGURE 3: Optical transmittance spectra for ZnO:In films with different dopant concentrations (0–5 at.%).

the donor by substituting Zn. The excess electrons ionized by the impurities will fill up the conduction band minimum of ZnO. Due to low density of states near the conduction band minimum, electrons excited by the light from the valence band have to occupy the higher energy level. For ZnO:In films with low doping concentrations (0–1 at.%), the blue shift of the optical absorption edge is due to the above-depicted reason, which is the Burstein-Moss (BM) effect [14, 15]. For ZnO:In films with high doping concentrations, the carrier concentration is quite large (>1 at.%), and the donor level corresponding to In impurities in ZnO energy band gradually widens and merges with the conduction band. The merging leads to a sudden decrease of ZnO band gap. The optical absorption edge rapidly shifts to the large wavelength orientation. Therefore, the red shift of the optical absorption edge should be related to the band gap narrowing led by the semiconductor-metal transition accompanied by the merging of the donor and conduction bands.

4. Conclusions

ZnO:In films with different doping concentrations were deposited on quartz substrates by sol-gel technique. All

FIGURE 4: The plots of $(\alpha hv)^2$ versus hv of ZnO:In films with different dopant concentrations (0–5 at.%).

the films grow along the preferred [001] orientation and a proper indium doping can improve the structural property of ZnO films. The transmittance in the visible region is approximately 80%. The blue shift of the optical absorption edge of ZnO:In films is due to the BM effect. With the increase of doping concentration, the sharp change of the optical absorption edge from blue shift to red shift is ascribed to the semiconductor-metal transition accompanied by the merging of the donor and conduction bands.

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