Electrical and optical properties of Sb-doped ZnO thin films synthesized by sol–gel method*

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Sb-doped ZnO thin films with different values of Sb content (from 0 to 1.1 at.%) are deposited by the sol–gel dip-coating method under different sol concentrations. The effects of Sb-doping content, sol concentration, and annealing ambient on the structural, optical, and electrical properties of ZnO films are investigated. The results of the X-ray diffraction and ultraviolet-visible spectroscopy (UV-VIS) spectrophotometer indicate that each of all the films retains the wurtzite ZnO structure and possesses a preferred orientation along the *c* axis, with high transmittance ($> 90\%$) in the visible range. The Hall effect measurements show that the vacuum annealed thin films synthesized in the sol concentration of 0.75 mol/L each have an adjustable n-type electrical conductivity by varying Sb-doping density, and the photoluminescence (PL) spectra revealed that the defect emission (around 450 nm) is predominant. However, the thin films prepared by the sol with a concentration of 0.25 mol/L, despite their poor conductivity, have priority in ultraviolet emission, and the PL peak position shows first a blue-shift and then a red-shift with the increase of the Sb doping content.

Keywords: Sb-doped ZnO thin films, electrical and optical properties, sol concentrations, annealing ambient

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1. Introduction

In recent years, due to its wide band gap ($E_g = 3.37$ eV) and large excitation binding energy (60 meV),[1,2] ZnO has aroused increasing interest for its potential applications in several optoelectronic devices such as light emitting diodes (LEDs), field-effect transistors, and solar cells.[3–5] The electrical, optical, and other properties of ZnO could be modified by doping different elements.[6–13] For example, Ramakrishna Reddy *et al.*[6] prepared Mg-doped ZnO nanocrystalline films to modify the band gap of ZnO; Nahm *et al.*[7] derived Ga-doped ZnO thin films to improve the electrical properties of ZnO; Xian *et al.*[8] obtained Nd-doped ZnO thin films using the sol–gel method to modify the crystalline quality and the optical band gap of ZnO.

In addition, as is well known, the group-V elements (N, P, As, and Sb) are the most suitable dopants for p-type doping in ZnO.[14–16] Balasubramaniam *et al.*[17] reported on the fabrication of p-type ZnO thin films through co-doping of nitrogen (N) and aluminium (Al). Przeździecka *et al.*[14] obtained p-type Sb-doped ZnO films by thermal oxidation of the Zn–Sb starting material. However, Liu *et al.*[15] studied the effect of Sb-doping on the electrical behavior of ZnO, and pointed out that Sb predominantly occupied Zn positions and acted as a donor in its whole concentration range, which would lead to n-type conductive properties. Obviously, the electrical behavior of the Sb-doped ZnO is still under debate. Because PL is a powerful method to analyze the kinds and concentrations of defects, there might be some clues to the understanding of the origin of conductivity when the PL properties are investigated. However, the PL properties of Sb–ZnO films, especially at room temperature, are rarely examined.

Many techniques have been employed to prepare the doped ZnO, including nanoparticle assisted pulsed laser deposition (NAPLD),[18] pulsed laser deposition (PLD),[19] molecular beam epitaxy (MBE),[15,20] magnetron sputtering, metal–organic chemical vapor deposition (MOCVD),[21] and thermal oxidation,[14] which are limited due to the complex and expensive process. Compared with these methods, the sol–gel method is a relatively simple technique and can precisely control the chemical composition of doped ZnO films under low cost and low processing temperature. However, there also exist many variable factors to affect the physical properties of ZnO thin films prepared by the sol–gel method, such as pH value,[22] annealing temperature,[23] and sol concentration.[24] For sol concentration, the resistivity values of ZnO thin films decrease from 7.9×10^2 Ω·cm to 3.76×10^2 Ω·cm and the band gap values are between 3.266 eV and 3.281 eV with the sol concentrations increasing from 0.2 mol/L to 1.0 mol/L.[25] Therefore, this work focuses on the electrical and optical properties of Sb-doped ZnO films under different sol concentrations. Sb doping density is increased from 0.1 at.% to 1.1 at.% in steps of 0.2 at.% because of the low solubility limit.[15] Two

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sets of Sb-doped ZnO films with different representative sol concentrations (0.75 mol/L, 0.25 mol/L) are prepared to clarify the influence of sol concentration on the electrical and optical properties. Then Hall effect and PL measurements are used to investigate the optical and electrical properties.

2. Experiment

All the reagents used for synthesis were analytical-grade purity without any further purification. The ZnO sol was obtained by dissolving a given amount of zinc acetate [$Zn(CH_3COO)_22H_2O$] in a 2-methoxyethanol ($C_3H_8O_2$) solution at room temperature. The concentration was set at 0.75 mol/L. Afterwards monoethanolamine (MEA, C_2H_7NO) was added into the solution, and the molar ratio of MEA to zinc acetate was kept at 1.0. Then the solution was stirred at 60 °C for 1 h. The antimony trichloride ($SbCl_3$) was added into the previous solution in an appropriate ratio and stirred at 60 °C for 1 h. After the solution was aged for 24 h at room temperature, finally transparent sol was obtained. Another group of ZnO sols was prepared using the previous process and the only difference was the sol concentration of 0.25 mol/L.

The Sail brand slice glass 7101 was used as the substrate for sol–gel dip-coating. The substrates were cleaned in distilled water, HCl, acetone, and ethanol step by step, in every step, the substrates were immersed for 1 h and then ultrasonically cleaned for 10 min. The substrates were dipped into the solution for 1 min, and then pulled out at the velocity of 4 cm/min. The samples were dried at 100 °C for 10 min and then preheated at 500 °C for 15 min. Such a process was repeated six times. Two similar pieces of films were prepared for each solution and then both were annealed in air at 550 °C for 1 h. After that, one of the two samples for each solution was treated by a post-annealing process (in a vacuum 5×10^{-3} Pa, at 550 °C for 1 hour) in order to improve the conductivity of the sample.

X-ray diffraction (XRD) patterns were measured from 20° to 80° by PANalytical X'pert MPD PRO with Cu Kα radiation. UV-vis absorption spectra were measured by a spectrophotometer (Jasco UV-4802). The electrical properties such as resistivity, carrier concentration, and Hall mobility were recorded by Hall effect measurements (ET-9000 system) using Van der Pauw configuration at room temperature. PL properties at room temperature were measured by using a PE-LS55 photoluminescence spectrophotometer at an excitation wavelength of 325 nm.

3. Results and discussion

Figure 1 shows the XRD patterns of undoped ZnO and $Zn_{1-x}Sb_xO$ (x = 0.1 at.%–1.1 at.% in steps of 0.2 at.%) thin films prepared with different sol concentrations: (a) 0.75 mol/L and (b) 0.25 mol/L. The diffraction patterns reveal that each of all the films has a single-phase wurtzite hexagonal ZnO structure. No traces of other impurities or any other secondary phases are found within the detection limit of the instrument. Each of the films shows that the intensity of the (002) peak is higher than those of other peaks, suggesting that each film possesses a preferred orientation along the c axis. The diffraction peaks for Sb-doped ZnO have no obvious shift compared with those of undoped ZnO, demonstrating that Sb atoms are more likely to occupy Zn sites (ionic radii are 0.76 Å for Sb^{3+} and 0.74 Å for Zn^{2+} versus 2.44 Å for Sb^{3-} and 1.38 Å for O^{2-}).[26] The peak intensity of the film prepared with the 0.75 mol/L sol is extremely higher than that of the film prepared with the 0.25 mol/L sol, which indicates that a higher sol concentration could improve the c-axis orientation of thin film based on ZnO due to the increase of film thickness value.[27]

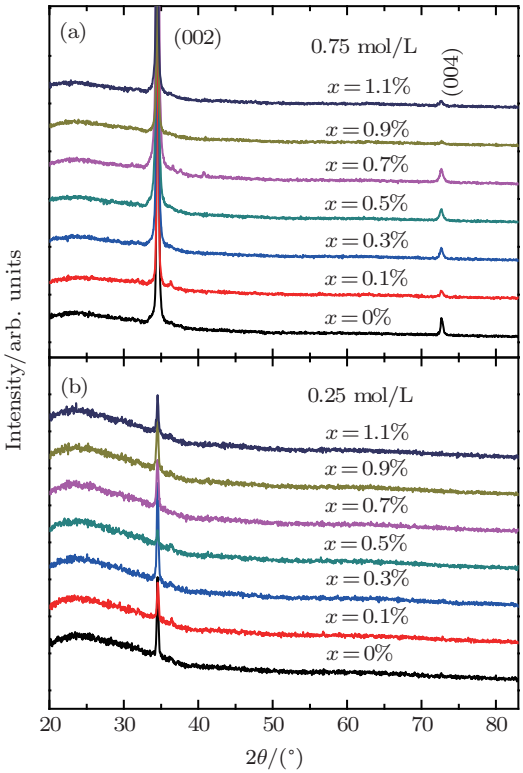


Fig. 1. (color online) XRD patterns of vacuum annealed undoped and Sb-doped ZnO (doping density x = 0.1 at.%–1.1 at.% in steps of 0.2 at.%) thin films prepared with (a) 0.75 mol/L and (b) 0.25 mol/L sol.

Transmittance spectra of Sb-doped ZnO films, which are annealed first in air and then in a vacuum, are shown in Fig. 2. The transmittances in the visible region (λ = 400 nm–800 nm) are distinctly above 90%, comparable to those of the traditional tin-doped indium oxide (ITO) materials.[28] The transmittances of the films prepared with 0.25 mol/L sol are significantly higher. Meanwhile, no obvious shift of band edges means that low (< 1 at.%) Sb doping has no significant effect on the optical band gap.

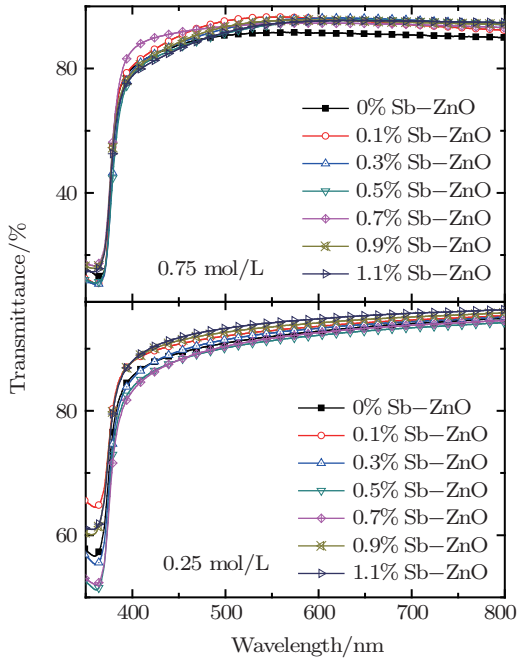


Fig. 2. (color online) Transmittance curves of vacuum annealed undoped and Sb-doped ZnO (doping density $x = 0.1$ at.%–1.1 at.% in steps of 0.2 at.%) thin films prepared with 0.75 mol/L and 0.25 mol/L sol.

Figures 3(a)–3(c) show the electrical properties of Sb-doped ZnO films prepared with 0.75 mol/L sol (doping density is in the range from 0 to 0.5 at.%, while the conductivity of the higher doping sample is quite low and exceeded the measuring range of our Hall effect instrument). The Hall effect measurements show all the Sb-doped ZnO films to have n-type conductivity, which is consistent with the results of ZnO:Sb layers grown by plasma-enhanced molecular beam epitaxy.[15] With the increase of Sb doping concentration, the resistivity [Fig. 3(c)] increases gradually, while the carrier concentration [Fig. 3(b)] decreases to that on the order of 10^{18} cm^{-3}. It might be due to the formation of Sb_{Zn}–$2V_{Zn}$ complexes as shallow acceptor levels compensate for parent defects.[29] In addition, some Sb atoms are probably incorporated onto the O sites as acceptors, leading to the decline of n-typed electrical conductivity.[15] The Hall mobility values of the films [Fig. 3(a)] range from 2.4 cm^2·V^{-1}·s^{-1} to 7.5 cm^2·V^{-1}·s^{-1}. The Hall mobility value increases as the doping content value rises from 0 to 0.1 at.%, and then decreases rapidly with the further increase of Sb doping content value, indicating that the electron scattering is enhanced due to the fact that more Sb ion defects are introduced. For the samples prepared with 0.25 mol/L sol, the minimum sheet resistance is about 3 MΩ/□, which is beyond the measuring range of our Hall effect measurement instrument. Compared with the films prepared with the 0.75 mol/L sol, the films prepared with 0.25 mol/L sol have obviously low electrical conductivity and carrier concentration, which would lead to a fairly weak internal photoelectric effect and then higher transmittance.[30] This result is in agreement with the transmittance test results mentioned above.

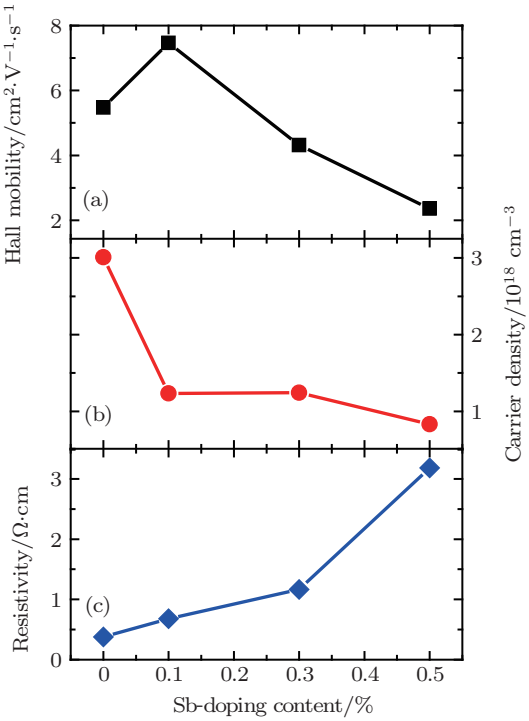


Fig. 3. (color online) Hall mobility carrier concentration (a), carrier concentration (b), and resistivity (c) versus Sb doping content of Sb-doped ZnO films prepared with 0.75 mol/L sol and annealed in a vacuum.

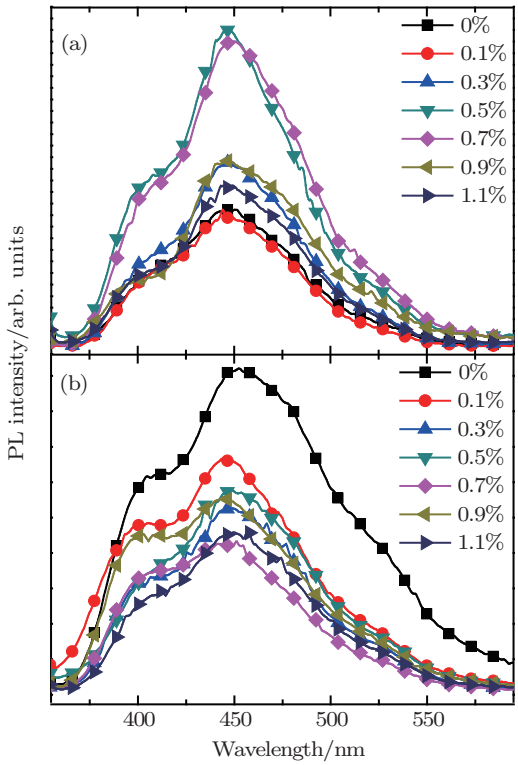


Fig. 4. (color online) Room temperature PL spectra of Sb-doped ZnO films prepared with 0.75 mol/L sol, annealed in air at 550 °C (a), and annealed in air at 550 °C first and then annealed in a vacuum of 5×10^{-3} Pa at 550 °C (b) at different doping content values.

Figure 4 shows the PL spectra of Sb-doped ZnO thin films prepared by 0.75 mol/L sol at different doping content values. For the films treated by air annealing (a), the PL spectrum shape does not change. While for the samples annealed

first in air and then in a vacuum (b), the PL spectrum peaks of Sb-doped ZnO show a little blue shift compared with those of undoped ZnO. However, both the films exhibit a strong broad peak in the range of 380 nm–530 nm. In addition, each of all the PL spectra shows that the highest peak is at $\sim$ 450 nm, which is related to the Zn vacancy (V_{Zn}).[31,32] The excitation emission from the conduction band to the valence band is weak. It might be due to the excess zinc and oxygen ions per unit volume because of the high sol concentration, leading to the formation of some native point defects such as Zn interstices, oxygen vacancies, etc. In such a case, it is the defect emission, not the ultraviolet emission, in the predominant part.

The PL spectra for the undoped and Sb-doped ZnO thin films prepared with 0.25 mol/L sol are shown in Fig. 5. It is obvious that ultraviolet emission is dominant for all the films, which is unrelated to the annealing technique. The annealing technique is responsible only for the shift of the ultraviolet emission peak. As seen from Fig. 5(a), after being annealed in air, the sample has the peak position that does not change compared with undoped ZnO. However, after being annealed first in air and then in a vacuum, the sample has the peak position that is shifted, as shown in Fig. 5(b). These results imply that the desired properties could be obtained by varying the sol concentration and/or the treatment ambient.

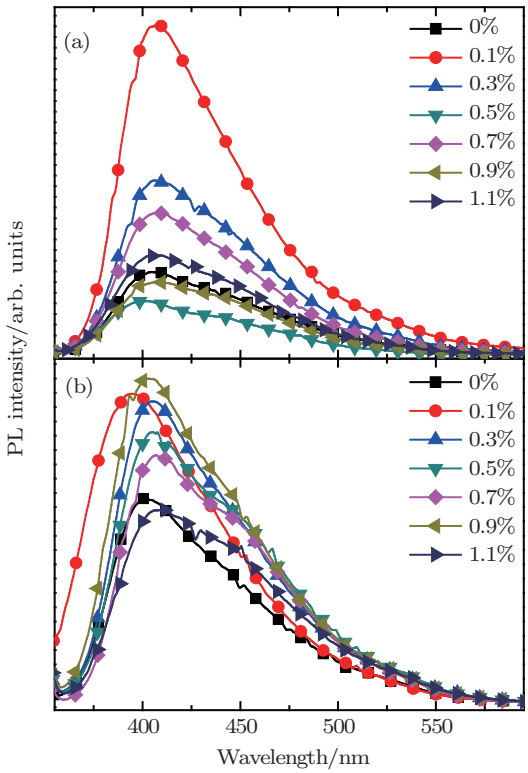


Fig. 5. (color online) Room temperature PL spectra of Sb-doped ZnO films prepared with 0.25 mol/L sol, annealed in air at 550 °C (a), annealed in air at 550 °C first and then annealed in a vacuum of 5×10^{-3} Pa at 550 °C (b), at different doping content values.

It is worth mentioning that the influences of the sol concentration on electrical and PL properties may not be ignored when fabricating Sb-doped ZnO thin films using the sol–gel method. The electrical conductivity of ZnO thin film increases with the increase of sol concentration[25] and/or film thickness value,[33] which is similar to that of our Sb-doped ZnO. Meanwhile, the PL properties manifest that the ZnO thin film prepared by lower sol concentration has a better ultraviolet emission performance, which was also observed by Gritskova *et al.*[34] and Xu *et al.*[27] Definitely, there is a trade-off between the conductivity property and ultraviolet emission. It can be explained as the fact that the intrinsic defects in ZnO thin films, which lead to defect emission, also made a significant contribution to the conductivity. So the film prepared with 0.75 mol/L sol, which presents a good n-type conductivity, shows that the strongest emission was the defect emission around 450 nm. From the above analysis, we can conclude that when using the sol–gel method to prepare Sb-doped ZnO thin films, a high sol concentration is conducive to electrical properties and defect emission while a low sol concentration is favorable to the ultraviolet emission.

4. Conclusion

Sb-doped ZnO thin films with the Sb content values in the range of 0 at.%–1.1 at.% are fabricated by the sol–gel dip-coating method. All the thin films retain the hexagonal wurtzite structure of ZnO and each possesses a preferred orientation along the c axis, with high ($> 90\%$) transmittance in the visible range. The electrical and PL properties of undoped and Sb-doped ZnO films prepared under different sol concentrations are discussed. When the sol concentration is 0.75 mol/L, the Hall effect measurements show n-type conductivity and the resistivity increases regularly with the increase of Sb-doping density, while the PL spectra each show a strong broad peak related to defects. When the sol concentration is 0.25 mol/L, despite their poor conductivity values, the PL spectra each show an absolute priority in ultraviolet emission.

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