Vol 13 No 8, August 2004
1009-1963/2004/13(08)/1330-04

Chinese Physics

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and IOP Publishing Ltd

Preparation of transparent conductive ZnO:Tb films and their photoluminescence properties*

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(Received 26 September 2003; revised manuscript received 16 January 2004)

Tb-doped Zinc oxide (ZnO:Tb) films were prepared by RF reactive magnetron sputtering of a Zn target with some Tb-chips attached. The results show that the appropriate Tb ions incorporated into ZnO films can improve the structural and electrical properties of ZnO films. Photoluminescence (PL) measurements show that the characteristic emission lines correspond to the intra-$4f^n$-shell transitions in Tb^{3+} ions at room temperature. Under the optimal conditions, the ZnO:Tb films were prepared with the lowest resistivity (ρ) of $9.34 \times 10^{-4}\Omega$cm, transmittance over 80% at the visible region and the strong blue emission.

Keywords: ZnO films, photoluminescence, RF reactive sputtering
PACC: 7155, 7855, 7360

1. Introduction

ZnO has been widely studied for its practical application in transparent electrodes for flat-panel displays, solar cells and various other optoelectronic devices.[1,2] Wurtzite ZnO is a wide band gap semiconductor, which is of interest for short wavelength (blue or ultraviolet) electro-optical devices such as light-emitting diodes and diode lasers.[3,4] Recently, a transparent oxidate light-emitting diodes have been demonstrated.[5] However, undoped ZnO typically exhibits weak n-type conductivity and weak spectral lines.[6,7] It is well known that rare earth (RE) ions are better candidates for luminescent centres because of their special 4f intrashell transition.[8,9] However, there have been few reports on RE-doped ZnO films. If RE ions are definitely doped in ZnO films, we think that the electrical and the optical properties of ZnO films are expected to be more informative.

In this study, we succeeded in synthesizing transparent conductive ZnO:Tb films by RF reactive magnetron sputtering of a Zn target with some Tb-chips attached. We found that the films prepared under the optimal conditions show strong blue band emission caused by the Tb^{3+} ions and various point defects in the ZnO:Tb films.

2. Experiment

ZnO films were prepared by RF magnetron reactive sputtering on Si (111) and common glass substrates. The sputtering target used was 100mm diameter Zn (purity 99.99%) target with some high purity Tb-chips (3mm×3mm) attached. The O_2/Ar pressure ratio was 1:9. Substrate temperatures were varied within a range from room temperature to 350°C. The sputtering power density, the gas pressure and the deposition time were 1.8×10^{-2} W/cm^2, 1.2Pa and 60min, respectively. The thickness of films were about 100nm. During the sputtering, the Si and common glass substrates with an area of 20mm × 30mm were placed parallel to the target surface at a distance of 45 mm. The ZnO films deposited on glass were used for optical transmittance measurements.

The x-ray diffraction (XRD) pattern and optical transmission spectra were obtained by the DMax/2400 x-ray diffractometer, and the Lambda-900 spectrometer, respectively. Electrical resistivity and Hall mobility were measured at room temperature by the Van der Pauw method. The photoluminescence spectra were measured at room temperature using the SHIMADZU spectrophotometer with an excitation wavelength at 369nm.

*Project supported by the National Natural Science Foundation of China (Grant No 50272027) and the Natural Science Foundation of Gansu Province, China (Grant No ZS011-050-C).
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3. Results and discussion

3.1. Structural properties

Figure 1 shows the XRD spectra of the ZnO:Tb films prepared at a substrate temperature of 250°C with different Tb/Zn area ratios on the sputtering target (the Tb content of the sputtering target). XRD patterns show that the orientation of the C axis (002) perpendicular to the substrate surface increased as the Tb content was increased up to approximately 4.1%. We suggest that Tb content doped into ZnO films inhibits the nucleation at the initial stage of the deposition and makes the doped films have large crystallite sizes, which improve the crystallinity of ZnO films. This phenomenon has been found in the experiments with copper-doped ZnO films.[10] However, when the Tb content is further increased, the orientation is strongly diminished in the Tb-doped ZnO films as shown in Fig.1, curve e. It is thought that the excess Tb incorporation led to the lattice aberrance of ZnO films; this was also observed in the fabrication of ZnO:Al films.[11] It can be concluded from the result shown in Fig.1 that the appropriate Tb incorporation in the ZnO films can improve the structural properties of the ZnO films. Curve f in Fig.1 shows the XRD patterns of ZnO:Tb films prepared with a Tb content of 4.1% at substrate temperature 350°C. We found that when the substrate temperature was above 250°C, the preferred orientation of ZnO:Tb films shows a marked decrease, which may be explained by the presence of the lattice aberrance in the films.

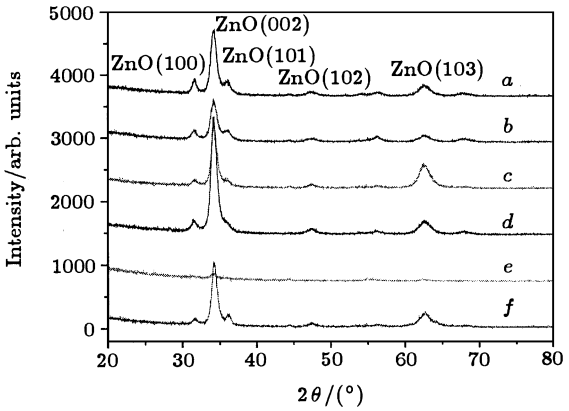


Fig.1. XRD patterns of ZnO:Tb films with the Tb content of (a)0, (b)1%, (c)2.6%, (d)4.1%, (e)5.3% (substrate temperature 250°C), (f) 4.1% (substrate temperature 350°C).

3.2. Electrical properties

Resistivity (ρ), Hall mobility (μ_{H}), and carrier concentration (n_{e}) as functions of the Tb content are shown in Fig.2 for ZnO:Tb thin films prepared at a substrate temperature of 250°C. n_{e} of the deposited ZnO:Tb thin films increases significantly as the Tb content increases, and reaches a maximum carrier concentration of $6.8 \times 10^{20}\mathrm{cm}^{-3}$ at Tb content of 4.1%; further increase in Tb content will result in decreasing n_{e}. This may suggest that a Tb atom doped into a ZnO lattice effectively acts as a donor by supplying a single free electron when it (as a Tb^{3+} ion) occupies the site of a Zn^{2+} ion. But the above behaviour of n_{e} suggests that all the Tb atoms in the films do not contribute to dopant. Choi and Im[12] found that, for Ga-doped ZnO films prepared by RF magnetron sputtering using a $ZnO+Ga_2O_3$ target, excess Ga atoms above a certain critical concentration in the ZnO films were segregated into the grain boundaries. Ma[13] reported that excess Al atoms above a certain critical concentration in the ZnO:Al films prepared by ultrasonic spray pyrolysis were segregated into the grain boundaries in the form of Al_2O_3. As shown in Fig.2, the decrease of n_{e} in the ZnO:Tb films prepared with a Tb content of 5.3% suggests that the excess Tb atoms may be segregated at grain boundaries in the form of Tb_2O_3. The Hall mobility of the ZnO:Tb films decreases as the impurity content increases. μ_{H} is expressed as[14]

$$\frac{1}{\mu_{\mathrm{H}}} = \frac{1}{\mu_{\mathrm{i}}} + \frac{1}{\mu_{\mathrm{g}}}, \tag{1}$$

where μ_{i} and μ_{g} are mobilities due to impurity scattering and grain boundary scattering, respectively. The gradual decrease of μ_{H} as the amount of Tb increasing to 4.1% is due to the increasing ionized impurity scattering. However, μ_{H} decreases with further increase of the amount of Tb, which means that the decrease of μ_{H} is mainly due to the increase of grain boundary scattering by the lattice aberrance of ZnO films. This result is consistent with that of XRD. ρ decreases from $6.42\times10^{-3}\Omega$cm for pure ZnO to a minimum value of $9.34\times10^{-4}\Omega$cm as the Tb content on the target increases to 4.1%; however, above 4.1%, ρ rapidly increases. The resistivity is determined by both n_{e} and μ_{H}. These results show that Tb^{3+} ions were successfully incorporated in ZnO films and the appropriate Tb incorporation in ZnO films may contribute to the decrease of resistivity for ZnO:Tb films.

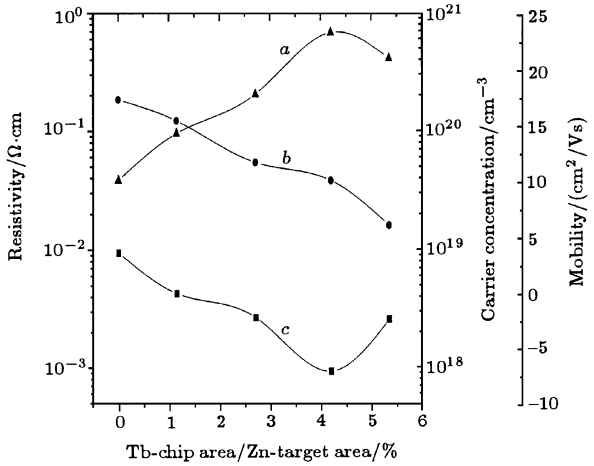


Fig.2. (*a*) Carrier concentration, (*b*) Hall mobility, and (*c*) resistivity as functions of Tb content for ZnO:Tb films prepared at 250°C.

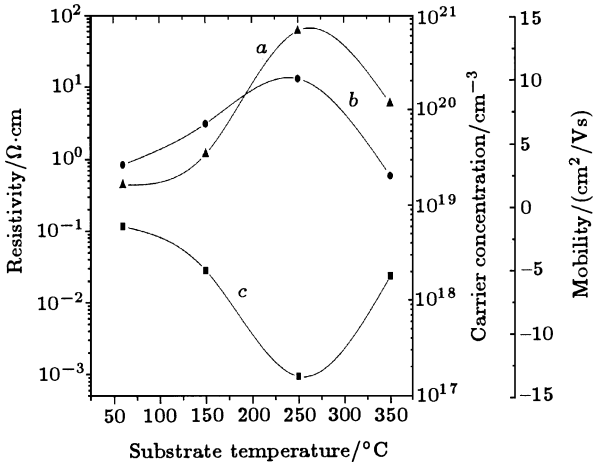


Fig.3. (*a*) Carrier concentration, (*b*) Hall mobility, and (*c*) resistivity as a function of substrate temperature for ZnO:Tb films prepared with the Tb content of 4.1%.

Figure 3 shows the substrate temperature (T_s)-dependence of ρ, μ_H, and n_e for ZnO:Tb films prepared with a Tb content of 4.1%. n_e increases sharply with increase in T_s up to 250°C. A further increase results in a sharp decrease in n_e. At temperature below 250°C, n_e of the ZnO:Tb films increases rapidly, possibly because of the increase of Tb^{3+} ions and decrease of Tb^{2+} ions. However, n_e of the ZnO:Tb films decreases rapidly due to segregation of Tb_2O_3 at grain boundaries in the films beyond a substrates temperature of 250°C. In other previous works, similar results have been reported.[15] Minami *et al*[16] ascribed that the increase of n_e with increasing temperature for substrate temperature above 250°C is due to the dramatic segregation of Al_2O_3 at grain boundaries in the Al doped ZnO films. μ_H increases at temperatures below 250°C. However, when the substrate temperature is further increased ($>250°C$), the rapid decrease of μ_H is probably due to the increased grain boundary scattering. ρ decreases rapidly at temperatures below 250° but increases above 350°C; this effect is due to the variation of both the carrier concentration and Hall mobility of donors. These results indicate that appropriate substrate temperature can decrease the resistance of ZnO:Tb films.

3.3. Optical properties

ZnO:Tb films are expected to have a high transmittance. Figure 4 shows the transmittance spectra of the ZnO:Tb films prepared with different Tb contents at a substrate temperature of 250°. The average transmittance of above 80% in the visible range was obtained in all the samples. The blue-shift of the absorption edge with increasing Tb content is mainly attributed to the Burstein–Moss shift,[17,18] which results from the increase of carrier concentration. From the results described above, it can be concluded that Tb is a good dopant for producing transparent and conductive ZnO films.

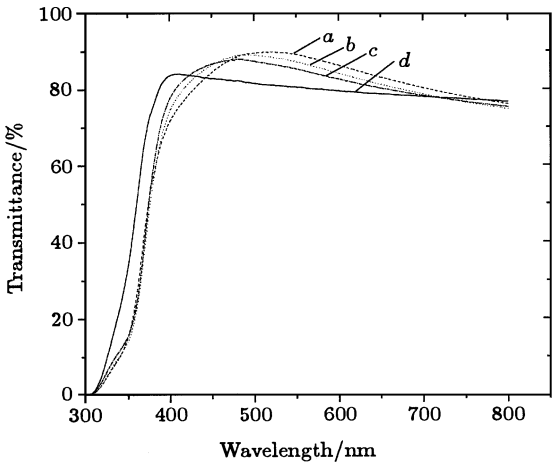


Fig.4. Transmission spectra for ZnO:Tb films prepared at 250°C with Tb content of (*a*) 0, (*b*) 1%, (*c*) 4.1%, (*d*) 5.3%.

The PL patterns for the undoped ZnO film and the ZnO:Tb film are shown in Fig.5, curves *a* and *b*. The ZnO:Tb film was prepared with the Tb content of 4.1% at a substrate temperature of 250°C. A blue band emission centred at 475nm was detected from the undoped ZnO films. Blue band emission of ZnO has been suggested to be mainly due to the presence of various point defects, either extrinsic or intrinsic,[19,20] which can easily form recombination centres. Curve *b* in Fig. 5 shows a stronger blue emission centred at 488nm, which is a characteristic emission wavelength

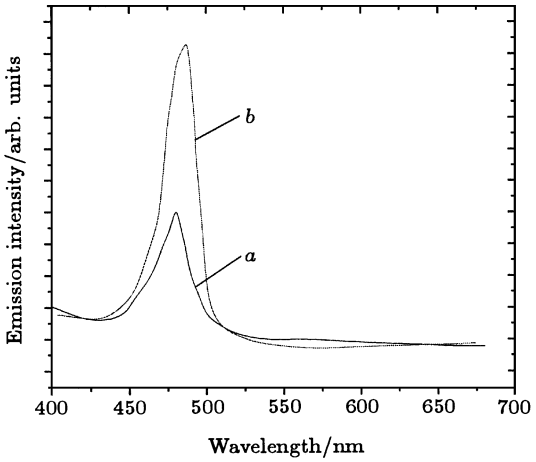


Fig.5. The PL spectra for (*a*) undoped ZnO films, (*b*) ZnO:Tb films with Tb content of 4.1%. The films deposited at 250°C.

of Tb^{3+} ions corresponding to the $^5D_4 \rightarrow ^7F_6$ transition. We noticed that the emission peak from Tb doped ZnO films is consistent with the strongest one from Tb doped amorphous AlN corresponding to $^5D_4 \rightarrow ^7F_6$ transition.[21] Thus, we suggest that the stronger blue luminescence intensity resulting from the superposition of both the blue band emissions is due to various point defects, and the characteristic emission originates from the intra-4f shell transition in Tb^{3+} ions of ZnO:Tb films.

4. Conclusion

Highly transparent conductive ZnO:Tb films have been prepared by RF reactive magnetron sputtering of a Zn target with some Tb-chips attached. It was found that Tb acts as effective donors in ZnO films; the optimal doping content of Tb is 4.1%. Deposited under optimum condition, the Tb-doped ZnO films exhibit attractive transmittance of above 80% in the visible range and the lowest resistivity of $9.34 \times 10^{-4}\Omega$cm. PL measurements show that the strong blue emission centred at 488nm is caused by various point defects together with the Tb^{3+} ions in the ZnO:Tb films. This is a new material, which has properties as those of the transparent conductive films comparable to ITO or ZnO:Al films. However, ZnO:Tb films have a strong blue emission, and may be widely used as transparent electrodes and luminescent material for light-emitting diode in the future.

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