Effect of substrate temperature on the stability of transparent conducting cobalt doped ZnO thin films*

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Abstract: Transparent conducting Co doped ZnO thin films have been fabricated by Ultrasonic spray. The thin films were deposited at three different substrate temperatures of 300, 350 and 400 ℃. The obtained films had a hexagonal wurtzite structure with a strong (002) preferred orientation. The maximum crystallite size value of the film deposited at 350 ℃ is 55.46 nm. Spectrophotometer (UV-vis) of a Co doped ZnO film deposited at 350 ℃ shows an average transmittance of about 90%. The band gap energy increased from 3.351 to 3.362 eV when the substrate temperature increased from 300 to 350 ℃. The electrical conductivity of the films deposited at 300, 350 and 400 ℃ were 7.424, 7.547 and 6.743 $(\Omega\cdot cm)^{-1}$ respectively. The maximum activation energy value of the films at 350 ℃ was 1.28 eV, indicating that the films exhibit a n-type semiconducting nature.

Key words: ZnO:Co films; transparent conducting films; ultrasonic spray deposition; substrate temperature; band gap energy

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1. Introduction

Zinc oxide (ZnO) is a very interesting semiconducting material with a wide and direct band gap of 3.37 eV at room temperature and a high exciton binding energy of 60 meV[1]. Transparent conducting oxides (TCO) are widely used in microelectronic devices, light emitting diodes, thin film, antireflection coatings for transparent electrodes in solar cells[2], gas sensors in surface acoustic wave devices[3], varistors, spintronic devices, and lasers[4].

ZnO thin films can be produced by several techniques such as molecular beam epitaxy (MBE), chemical vapor deposition, electrochemical deposition[3], pulsed laser deposition (PLD), sol–gel process[4], reactive evaporation, magnetron sputtering technique and spray pyrolysis[5].

Cobalt doped ZnO thin films have various applications such as transparent conductives; ferromagnetism; semiconductors; piezoelectric and solar cells, as the films have low resistivity and good optical band gap energy at low temperatures, and are transparent in the visible region[6]. A ZnO:Co film is considered to be an important material due to its high conductivity, good transparency and low cost.

In this work, we have elaborated the conductive Co doped ZnO thin films on a glass substrate using an Ultrasonic spray. The films obtained have a concentration of 2 wt%. We have studied the effect of the substrate temperatures on the crystalline structure, optical and electrical properties of the semiconductors.

2. Experimental details

The spray solution was prepared by dissolving 0.1 M $(Zn(Zn(CH_3COO)_2, 2H_2O)$ in the solvent containing an equal volume of absolute ethanol solution, then a drop of NaOH solution was added as a stabilizer, after which 2% cobalt acetate tetrahydrate $(Co(CH_3COO)_2, 6H_2O)$ molar ratio was added to the solution, which had been stirred and heated at 80 ℃ for 1 h to yield a clear and transparent solution. The latter was sprayed on the heated glass substrates by an ultrasonic nebulizer system (Sonics) which transformed the liquid to a stream formed with uniform and fine droplets of 30 μm average diameter (given by the manufacturer). The deposition was performed at a different substrate temperatures of 300, 350 or 400 ℃ with a 120 s deposition time[7].

The crystalline structure of the films was confirmed by X-ray diffraction (XRD) analysis using CuKα radiation with a Bruker AXS-8D diffractometer. The optical properties of the films were measured by spectrophotometer (UV, Lambda 35) in the range of 300–800 nm, and the electrical properties of the films were measured in a coplanar structure obtained with evaporation of four golden stripes on film surface. All spectra were measured at room temperature (RT).

3. Results and discussion

3.1. Structural properties

Figure 1 shows the XRD patterns of Co doped ZnO thin films with different substrate temperatures. (002) and (101) diffraction peaks were observed; the films exhibit the hexagonal wurtzite polycrystalline structure from the spectra. Many authors investigated the structure of ZnO thin films obtained by different methods and deposited onto various substrates in the literature[1, 4, 8]. Where only a (002) diffraction peak is highest one, the film forming at 350 ℃ has a higher and sharper diffraction peak indicating an improvement in (002) peak in-

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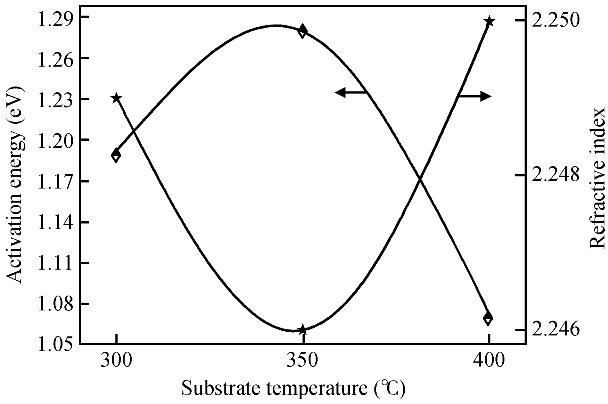

Fig. 7. Variation of the activation energy and the refractive index of Co doped ZnO thin films as a function of deposition temperature.

creases when the band gap energy E_g is increased. The Herve–Vandamme relationship[21] is:

$$n^2 = 1 + \left(\frac{A}{E_g + B}\right)^2, \tag{6}$$

where A and B are constants as $A \approx 13.6$ eV and $B \approx 3.4$ eV; E_g is the band gap energy and n is the refractive index of the films.

Figure 7 shows the variation of the activation energy E_a and the refractive index n as a function of the deposition temperature. The refractive index variation is in good agreement with the variation of the films disorder (Fig. 5), since it is well known that the refractive index is reduced in highly disordered films and reached its minimum value of 2.24 at the substrate temperature, however at this temperature the maximum value of the activation energy E_a was 1.28 eV, indicating that the transparent conducting ZnCoO exhibits an n-type semiconducting nature, where applied the relationship: $E_a < \frac{E_g}{2}$.

4. Conclusions

In conclusion, highly transparent conducting Co doped ZnO thin films have been fabricated on a glass substrate using an Ultrasonic spray. The structural, optical and electrical properties were investigated. All the films are polycrystalline structure wurtzite and (002) oriented. The average transmittance is about 62%–90%, in the visible region, and the band gap increased from 3.351 to 3.362 eV, which may be attributed to a similar ionic radius between Co^{2+} and Zn^{2+}. The decrease in Urbach energy is attributed to the decrease of defects. The increase in the conductivity of the samples has been explained by displacement of the electrons. From the measurement of the activation energy and optical gap, the samples are shown to be n-type in nature and exhibit semiconducting behavior in the ZnO thin films deposited at 350 ℃.

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