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Elaboration and characterisation of ZnO thin films

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Key words:
ZnO; thin film; dip-coating; annealing temperature

Abstract – Highly transparent ZnO thin films have been prepared on microscope glass substrate using dip-coating technique. The films were obtained at a concentration of sol-gel solution is 0.5 M. The structural and optical properties of the ZnO thin films were studied as a function of the annealing temperature varying between 450 to 600 °C. From the XRD analysis, the whole obtained films have a hexagonal wurtzite structure with a strong (002) preferred c-axis orientation. The grain size increased with annealing temperature indicating an improvement in the crystallinity of the films. The average transmittance of all the films is about 70–80% as measured by UV-vis analyzer. The band gap increased with the increase of temperature from 3.25 to 3.42 eV. The decrease of the strain of ZnO films is probably due to an improvement of the crystallinity of the films. The best result is achieved at 600 °C.

Mots-clés :
ZnO ; couche mince ; dip-coating ; température de recuit

Résumé – Elaboration et caractérisation des couches minces de ZnO. Les couches minces de ZnO plus transparents ont été préparées sur des substrats de verre par la méthode dip-coating. Les films ont été obtenus à une concentration de solution sol-gel de 0,5 M. Les propriétés structurales et optiques des couches minces de ZnO ont été étudiées en fonction de la température de recuit variant entre 450 à 600 °C. Par l'analyse DRX, les films obtenus ont une structure hexagonale Wurtzite avec une forte (002) préférée d'orientation à la c-axe. La taille des grains augmente avec l'augmentation de la température de recuit indiquant une amélioration de la cristallinité des films. La transmittance moyenne de tous les films est d'environ 70–80 %, mesurée par l'analyseur UV-vis. La bande interdite augmente avec l'augmentation de la température de 3,25 à 3,42 eV. La diminution de la tension de ZnO films est probablement due à une amélioration de la cristallinité des films. Le meilleur résultat est obtenu à 600 °C.

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Zinc oxide (ZnO) is a very interesting semiconducting material with a wide and direct band gap of 3.4 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 films, antireflection coatings transparent electrodes in solar cells [2], gas sensors 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].

The sol–gel process is an attractive method because of the following reasons: good homogeneity, ease of composition control, low processing temperature, large area coatings, low equipment cost and good optical properties. Many research groups have prepared ZnO thin films by sol–gel method and used them to fabricate optoelectronic devices. For example, Du et al. used the sol–gel derived ZnO/PVP nanocomposite thin film for superoxide radical sensor [6]; Ilican et al. utilized the sol–gel derived ZnO thin

films to fabricate thin film nanorod semiconductors [7]; Verma et al. applied the sol–gel derived Al doped zinc oxide for application as anti-reflection coating in terrestrial silicon solar cells [8]. Although the sol–gel process is especially efficient in producing thin, transparent, multi-component oxide layers of many compositions on various substrates, including glass, there are still many factors affecting the physical properties of ZnO thin films. These factors include ZnO sol concentration [9], preheating temperature [1], post-annealing temperature [11], annealing atmosphere [12], and film thickness [13]. Among these factors, the influence of annealing temperature on structural and optical properties of ZnO thin films (especially undoped ZnO thin films) derived from sol–gel method was less studied. The choice of temperature in range between 450 and 600 °C is important study with deposition the thin films on glass substrate. We observe that the glass substrate was brittle at a temperature higher than 600 °C.

In most cases, the metal alkoxides are used as raw materials for the sol–gel process. But the preparation of a stable sol is tiresome and reagents of the metal alkoxides are very costly. Also, diethyl zinc (DEZ) and dimethyl zinc (DMZ) are so reactive that there is a risk of explosion in air. Thus, some metal salts such as nitrate, acetate of metal are used to change the metal alkoxides for preparing the thin films. Zinc acetate (ZnAc), which is inexpensive, and easy to handle, has been used as raw material in many methods such as the spray pyrolysis, CVD, atomic epitaxy, etc., for example [11].

We report in the present study the deposition of ZnO thin films on glass substrate by dip-coating method using homogeneous and stable zinc acetate dihydrate with a concentration of 0.5 M. The effect of the annealing temperature on the crystal orientation, optical and mechanical properties of ZnO films was investigated.

1 Experimental details

1.1 Preparation of precursor sol

ZnO solution were prepared by dissolving (0.5 M) zinc acetate-dihydrate $Zn(CH_3COO)_2, 2H_2O$ in the solvent containing equal volumes absolute ethanol solution (99.995%) purity, then have added a drops of monoethanolamine solution as a stabilized, the mixture solution was stirred an heated at 50 °C for 6 h to yield a clear and transparency solution.

The substrate was R217102 glass in a size of 1 cm × 2 cm × 0.1 cm, prior to pumping, the substrate (R217102 glass) were cleaned with alcohol in an ultrasonic bath and blow-dried with dry nitrogen gas.

1.2 Deposition of thin films

The films were obtained by the dipping method on glass substrate at room temperature, 6 h after the preparation of the final solution. The withdrawal speed was 2.17 cm/min. The coating process was repeated for five times to obtain a thin film. It was found out that higher withdrawal rates resulted in films of lower quality. The preheat-treatment temperature of 100 °C is required for the complete evaporation of organics and the initiation of formation and crystallization of the ZnO film. After the deposition of the four layers, the resulting thin films were annealed at 450 °C, 500 °C, 550 °C and 600 °C in air for 1 h.

1.3 Characterization of thin films

The crystal phase and crystalline orientation of the thin films were determined by X-ray diffraction (XRD, Bruker D8 advanced X-ray diffractometer) with Cu Kα radiation (λ = 1.541 Å) The analysis the samples were scanned from 25° to 55°. A scanning electron microscopy (SEM, JSM–6700F) equipped with EDX was used to examine both morphology and elemental analysis of the samples. The optical transmission spectra of the films were measured in the range of 300–800 nm using a double-beam Lambda 35 UV/visible spectrophotometer. All spectra were measured at room temperature (RT) in air.

2 Results and discussion

The crystal structure of the undoped ZnO films has been examined using X-ray diffractometer. Figure 1 shows the XRD patterns

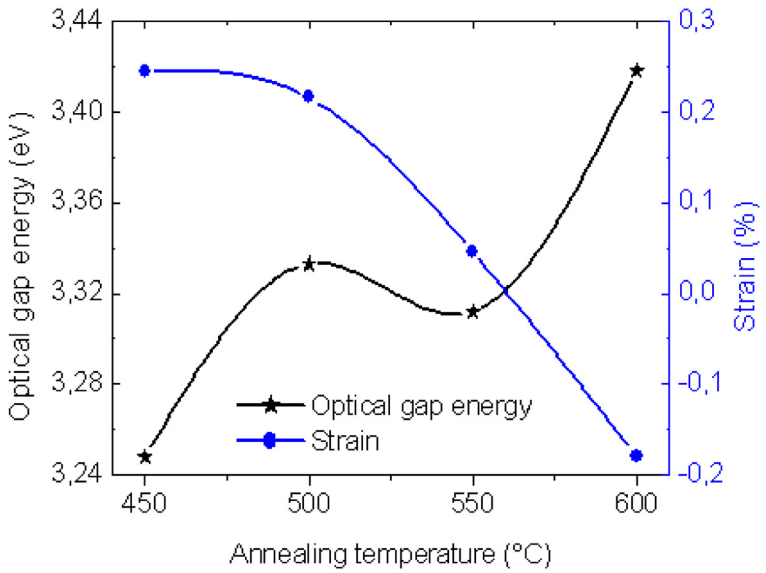

Fig. 7. Variation of the optical gap energy and the strain as a function of annealing temperature.
Fig. 7. Évolution du gap optique et coefficient de dilatation en fonction de la température de recuit.

ZnO thin film is compressive. The decreases of the strain of ZnO thin films are probably be due to an improvement of the crystallinity of the films, Mekhnache et al. [23] and Charpentier et al. [24]. We found that the decrease in the strain explained by decrease of the defects, which is related to the disorder in the film network, is expressed as [25]. Raoufi et al. [16] reported that the strain along the c-axis of ZnO thin film deposited on glass substrate at different annealing temperatures.

3 Conclusions

In conclusion, highly transparent ZnO thin films on microscope glass substrate have been deposited by dip-coating method. The structural, optical and mechanical properties were investigated. The whole obtained films have a polycrystalline wurtzite structure and are mainly (002) oriented. The grain size increased from 69 to 104 nm. The average transmittance is about 70–80% in the visible region, and the band gap energy increased from 3.25 to 3.42 eV, which may be attributed to the similar ionic radius between O^{2-} and Zn^{2+}. The increase of the strain is attributed to the decrease of the defects. In this study the ZnO thin films are annealed at 600 °C.

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