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Preparation of transparent conducting ZnO:Al films on glass substrates by ultrasonic spray technique

Abdelouahab Gahtar[1], Said Benramache[1, 2, †], Boubaker Benhaoua[1], and Foued Chabane[3]

[1]VTRS Laboratory, Institute of Technology, University of El-oued 39000, Algeria
[2]Material Sciences Department, Faculty of Science, University of Biskra 07000, Algeria
[3]Mechanics Department, Faculty of Technology, University of Biskra, Biskra 07000, Algeria

Abstract: Transparent conductive Al doped ZnO thin films were deposited by ultrasonic spray technique. Conditions of preparation have been optimized to get good quality. A set of aluminum (Al) doped ZnO (between 0 and 5 wt%) thin films were grown on glass substrate at 350 ℃. Nanocrystalline films with a hexagonal wurtzite structure show a strong (002) preferred orientation. The maximum value of grain size $G = 32.05$ nm is attained of Al doped ZnO film with 3 wt%. All the films have low absorbance in the visible region, thus the films are transparent in the visible region; the band gap energy increased from 3.10 to 3.26 eV when Al concentration increased from 0 to 3 wt%. The electrical conductivity of the films increased from 7.5 to 15.2 $(\Omega\cdot\text{cm})^{-1}$. So the best results are achieved in Al doped ZnO film with 3 wt%.

Key words: ZnO:Al; thin films; TCO; ultrasonic spray technique
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1. Introduction

ZnO is one of the most important semiconductor materials due to its wide band gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature[1]. Transparent conducting oxides (TCO) are widely used in microelectronic devices, light emitting diodes, thin film, antireflection coatings for transparent electrodes in solar cells, and in surface acousticwave gas sensors[2–5].

ZnO thin films can be produced by several techniques such as reactive evaporation, molecular beam epitaxy (MBE), magnetron sputtering technique, pulsed laser deposition (PLD), the sol–gel technique, chemical vapor deposition, electrochemical deposition[6–8] andspray pyrolysis[9]. Among these, we will focus more particularly in this paper on the spray technique that is a low cost method suitable for large-scale production. It has several advantages in producing nanocrystalline thin films, such as, relatively homogeneous composition, a simple and depositionon glass substrate because of the low substrate temperatures involved, easy control of film thickness, and fine and porous microstructure[10]. It is possible to alter the mechanical, electrical, optical and magnetic properties of ZnO nanostructures.

The Al doped ZnO thin films have various applications such as transparent conductive film, ferromagnetism, semiconductors, piezoelectric and solar cells. The films have low resistivity and good optical gap energy at low temperature, and are transparent in the visible region[11]. There are several reports on ZnO nanostructures doped with different elements, such as Fe, Ga, Li, N, Cu, P, and Co[10, 12–14]. The films (ZnO:Al) are considered to be a material of utmost importance due to their high conductivity, good transparency and lower cost.

In this paper, we have deposited Al doped ZnO thin films on a glass substrate through ultrasonic spray technique at a substrate temperature of 350 ℃, and the effect of the Al concentrations of the ZnO films has been studied. The main goal for this research is to find optimum Al doping concentration which gives highly semiconducting properties of Al doped ZnO thin films.

2. Experimental procedure

2.1. Preparation of spray solution

ZnO solution was prepared by dissolving 0.1M $(Zn(CH_3COO)_2\cdot 2H_2O)$ in the solvent containing equal volumes absolute ethanol solution (99.995%) purity, then adding drops of NaOH solution as a stabilizer, and stirring the mixture solution at 50 ℃ for 2 h to yield a clear and transparent solution.

ZnO:Al solution was prepared by adding to the precedent solution aluminum chloride, 6-methoxyethanol, such that theratio of Al/Zn. This Al content can be varied in the range of 0–5 wt%. The solution became clear and homogeneous after stirring for 2 h at 50 to 70 ℃.

The substrate was R217102 glass, $1 \times 1 \times 0.1$ cm^3 in size prior to pumping; the substrates were cleaned with alcohol in an ultrasonic bath and blow-dried with dry nitrogen gas.

2.2. Deposition of thin films

The resulting solutions were sprayed on the heated glass substrates by ultrasonic nebulizer system (Sonics) which transforms the liquid to a stream formed with uniform and fine droplets of 40 μm average diameter (given by the manufacturer). The deposition was performed at a substrate temperature of 350 ℃ with 2 min of deposition time[15, 16].

† Corresponding author. Email: saidzno2006@gmail.com
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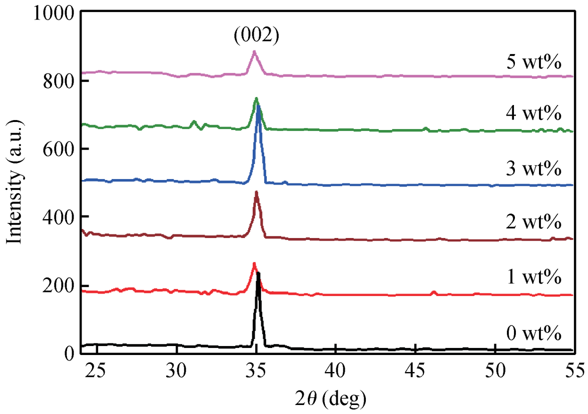

Fig. 6. X-ray diffraction patterns of Al doped ZnO thin films at different concentrations.

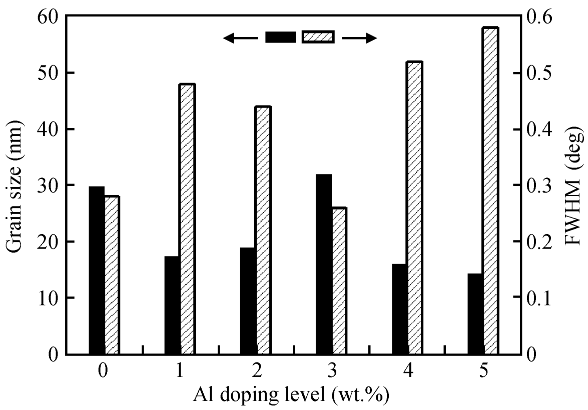

Fig. 7. The variation of the grain size and the FWHM of undoped and Al doped ZnO thin films.

where G is the grain size, λ is the X-ray wavelength (λ = 1.5406 Å), β is the full width at half-maximum (FWHM), and θ is Bragg angle of (002) peak.

In Fig. 7 we have reported the variation of grain size and FWHM as a function of doping level. As can be seen, the grain-size increased for Al doped ZnO thin films with 1 to 3 wt% and in this region the values of FWHM decreased. The increase of the grain size has been indicated by the enhancement of the crystallinity and c-axis orientation of ZnO thin films by Zhang[18]. The increase in the FWHM with decreasing the grain size for undoped and Al doped ZnO thin films indicates the deterioration in crystallinity of ZnO thin films due to Al doping.

4. Conclusions

In conclusion, highly transparent conductive thin films of Al doped ZnO have been deposited on glass substrate by ultrasonic spray at a substrate temperature of 350 ℃. The optical, electrical and structural properties were investigated. All the films are nanocrystalline structure wurtzite and (002) oriented, which is favorable to the diffusion of atoms absorbed on the substrate. The maximum value of crystallite size $G = 32.05$ nm is attained in ZnO:Al films with 3 wt%. All the films have low absorbance in the visible region, thus the films are transparent in the visible region. The band gap energy increases from E_g = 3.10 for undoped ZnO thin films to $E_g = 3.26$ eV for Al doped ZnO thin films at 3 wt%, which may be attributed to the similar ionic radius between Al^{3+} and Zn^{2+}. The increase in the conductivity of the samples has been explained by displacement of the electrons. The optimum amount of Al doping content is 3 wt% in ZnO thin films.

References

[1] Zhang Y, Wu C, Zheng Y, et al. Synthesis and efficient field emission characteristics of patterned ZnO nanowires. Journal of Semiconductors, 2012, 33(2): 023001

[2] Zhu X, Wu H, Wang S, et al. Optical and electrical properties of N-doped ZnO and fabrication of thin-film transistors. Journal of Semiconductors, 2009, 30(3): 033001

[3] Zhang H, Liu H, Lei C, et al. Low-temperature deposition of transparent conducting Mn–W co-doped ZnO thin films. Journal of Semiconductors, 2010, 31(8): 083005

[4] Ji Z, Mao Q, Ke W. Effects of oxygen partial pressure on resistive switching characteristics of ZnO thin films by DC reactive magnetron sputtering. Solid State Commun, 2010, 150(8): 1919

[5] Zuo C, Wen J, Zhong C. First-principles study of the electronic structures and optical properties of C–F–Be doped wurtzite ZnO. Journal of Semiconductors, 2012, 33(7): 072001

[6] Kumar P S, Raj A D, Mangalaraj D, et al. Growth of hierarchical based ZnO micro/nanostructured films and their tunable wettability behavior. Appl Surf Sci, 2011, 257(20): 6678

[7] Ye Z, Yuan G, Li B, et al. Fabrication and characteristics of ZnO thin films with Al/Si (100) substrates. Mater Chem Phys, 2005, 93(2): 170

[8] Zhang H, Yang S, Liu H, et al. Preparation and characterization of transparent conducting ZnO:W films by DC magnetron sputtering. Journal of Semiconductors, 2011, 32(4): 043002

[9] El Manouni A, Manjon F J, Perales M, et al. Effect of thermal annealing on ZnO:Al thin films grown by spray pyrolysis. Superlattices and Microstructures, 2007, 42(2): 134

[10] Rozati S M, Akesteh S. Characterization of ZnO:Al thin films obtained by spray pyrolysis technique. Materials Characterization, 2007, 58(4): 319

[11] Saleem M, Siddiqi S A, Atiq S, et al. Carriers-mediated ferromagnetic enhancement in Al-doped ZnMnO dilute magnetic semiconductors. Materials Characterization, 2011, 62(12): 1102

[12] Ma Q B, Ye Z Z, He H P, et al. Preparation and characterization of transparent conductive ZnO:Ga films by DC reactive magnetron sputtering. Materials Characterization, 2008, 59(2): 124

[13] Benramache S, Benhaoua B, Chabane F. Effect of substrate temperature on the stability of transparent conducting cobalt doped ZnO thin films. Journal of Semiconductors, 2012, 33(9): 093001

[14] Duclère J R, Novotny M, Meaney A, et al. Properties of Li-, P- and N-doped ZnO thin films prepared by pulsed laser deposition. Superlattices and Microstructures, 2005, 38(3): 397

[15] Hafdallah A, Yanineb F, Aida M S, et al. In doped ZnO thin films. Journal of Alloys and Compounds, 2011, 509(18): 7267

[16] Benramache S, Benhaoua B, Chabane F, et al. Influence of growth time on crystalline structure, conductivity and optical properties of ZnO thin films. Journal of Semiconductors, 2013, 34(2): 023001

[17] Venkatachalam S, Iida Y, Kanno Y. Preparation and characterization of Al doped ZnO thin films by PLD. Superlattices and Microstructures, 2008, 44(2): 127

[18] Zhu H, Hüpkes J, Bunte E, et al. Reactive sputtering of ZnO:Al thin films from rotatable dual metallic targets. Appl Surf Sci,

2012, 259(4): 582
[19] Zhu H, Hüpkes J, Bunte E, et al. Study of ZnO:Al films for silicon thin film solar cells. Appl Surf Sci, 2012, 261: 268
[20] Benramache S, Benhaoua B. Influence of substrate temperature and Cobalt concentration on structural and optical properties of ZnO thin films prepared by ultrasonic spray technique. Superlattices and Microstructures, 2012, 52(4): 807
[21] Benramache S, Benhaoua B. Influence of annealing temperature on structural and optical properties of ZnO: In thin films prepared by ultrasonic spray technique. Superlattices and Microstructures, 2012, 52(6): 1062
[22] Romero R, Ibanez R L, Dalchiele E A, et al. Compositional and physico-optical characterization of 0–5% Al-doped zinc oxide films prepared by chemical spray pyrolysis. J Phys D: Appl Phys, 2010, 43(9): 095303
[23] Mekhnache M, Drici A, Hamideche L S, et al. Properties of ZnO thin films deposited on (glass, ITO and ZnO:Al) substrates. Superlattices and Microstructures, 2011, 49(3): 510
[24] Mosbah A, Aida M S. Influence of deposition temperature on structural, optical and electrical properties of sputtered Al doped ZnO thin films. Journal of Alloys and Compounds, 2012, 515(1): 149
[25] Rahmane S, Djouadi M A, Aida M S, et al. Power and pressure effects upon magnetron sputtered aluminum doped ZnO films properties. Thin Solid Films, 2010, 519(1): 5
[26] Zhang C. High-quality oriented ZnO films grown by sol–gel process assisted with ZnO. Journal of Physics and Chemistry of Solids, 2010, 71(2): 364