OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 3, No. 12, December 2009, p. 1295 - 1298

Optoelectrical properties ZnO and W-doped In_2O_3 multilayer films grown by pulsed laser deposition

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Transparent and conducting thin films having structure of zinc oxide/tungsten doped indium oxide/zinc oxide (ZnO/IWO/ZnO) were deposited by pulsed laser technique. The effect of ZnO films thickness on structural, optical and electrical properties of multilayer films is studied. These films are highly oriented along (002) and (222) direction for ZnO and IWO respectively. The transparency of films is over 75 %. The conductivity, carrier concentration and mobility of films increase with increase in IWO film thickness. The low resistivity (1.24×10^{-4} Ω.cm), high mobility (198 $cm^2V^{-1}s^{-1}$) and high transmittance (> 80 %) suggest that these multilayer films could be used as highly conducting and transparent electrodes for optoelectronic applications.

(Received September 29, 2009; accepted November 23, 2009)

Keywords: Laser deposition, Multilayer thin films, Electrical conductivity, Optical materials, Oxides

1. Introduction

Zinc oxide (ZnO) is a wide band gap, II-VI compound with a wurtzite-type structure. It has a band gap of 3.37 eV [1]. Pure ZnO is n-type semiconductor with high conductivity [2]. The presence of Zn-interstitials and/or oxygen vacancy is responsible for its high conductivity. The conductivity and carrier concentration of ZnO can be improved by cationic substitution with a trivalent atom such as Al, Ga, and In [3]. Due to the unique properties of ZnO such as low resistivity, high optical transparency and wide bandgap, it is widely used for optoelectronic devices, sensors, spintronics and photovoltaic applications [4].

Many researchers are working to improve the structural, optical and electrical properties of ZnO by varying dopants, growth parameters and post treatment [5]. Also different methods are being used for deposition of thin films such as sol-gel [6], spray pyrolysis [7], chemical vapor deposition [8], sputtering [9], and pulsed laser deposition [10]. Recently multilayer systems based on semiconductor and metal such as ZnO/Ag/ZnO are used to improve the properties of ZnO films [11]. But the problem with metal as a middle layer is that, it reduces the transparency of the metal oxide and also the mobility of these films is not very high [12]. Tungsten doped indium oxide (IWO) is a promising material for optoelectronic and photovoltaic application due to its low electrical resistivity, high electron mobility and high transparency [13]. Here, we use IWO films as an intermediate layer. In this article, we report effect of IWO film thickness on optoelectrical properties of ZnO films.

2. Experimental details

The targets for the pulsed laser deposition were prepared by the standard solid-state reaction method using high purity of ZnO, In_2O_3 and WO_3. For IWO target, required amounts of In_2O_3 and WO_3 were taken by molecular weight to get two atomic weight percent of tungsten. The well-ground mixture was heated at 800 °C for 12 hours. The powder mixture was cold pressed at 6×10^6 N/m^2 load and sintered at 850 °C for 12 hours.

KrF excimer laser (Lambda Physik COMPex, λ = 248 nm and pulsed duration of 20 ns) is used for deposition of these films. The laser was operated at a pulse rate of 10 Hz, with an energy of 300 mJ/pulse. The laser beam was focused onto a rotating target at a 45° angle of incidence. ZnO/IWO/ZnO multilayers of various thicknesses (ZnO from 0 to 100 nm) were deposited at 500 °C under oxygen pressure of 1.0×10^{-3} mbar. The deposition chamber was initially evacuated to 1.2×10^{-6} mbar and then oxygen gas was introduced into the chamber during deposition. The growth rate for the films was ~3 nm/min.

The structural characterizations were performed using x-ray diffraction (XRD) and atomic force microscopy (AFM). The XRD spectra of all the films were recorded with Bruker AXS x-ray diffractometer using the 2θ-θ scan with CuK_α (λ = 1.5405 Å) radiation which operated at 40 kV and 40 mA. The AFM imaging was performed under ambient conditions using a Digital Instruments (Veeco) Dimension-3100 unit with Nanoscope® III controller, operating in tapping mode. The optical transmittance measurements were made using UV-visible spectrophotometer (Ocean Optics HR4000).

The resistivity and Hall coefficient measurements were carried out by a standard four-probe technique. The Hall effect was measured with the magnetic field applied perpendicular to film surface in the Van der Pauw configuration [14]. Carrier concentration and carrier mobility were calculated at room temperature using Hall coefficient and resistivity data [15].

3. Results and discussion

X-ray diffraction and atomic force microscopy is used for structural characterization of ZnO/IWO multilayer.

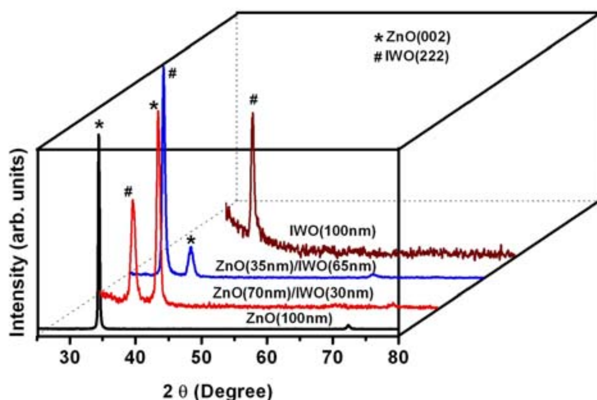

Fig. 1. XRD patterns of ZnO/IWO/ZnO films grown at 500 ˚C.

Fig. 1 shows x-ray diffraction patterns of ZnO/IWO multilayer films. It is evident for the XRD that all the films are highly oriented and crystalline in nature. It is observed that ZnO films are highly oriented along (002) direction while IWO films are highly oriented along (222) direction. It can be seen that with increase in thickness of middle layer i.e. IWO, the intensity of ZnO peak decreases.

Fig. 2 shows the AFM images of pure ZnO and ZnO(35nm)/IWO(65nm) multilayer film. It is clear from these figures that the films have very smooth surface. The root mean square (rms) roughness of the pure ZnO and ZnO/IWO multilayer films is calculated and found to be 1.99 nm and 1.65 nm respectively. This indicates that surface roughness of ZnO improves by fabricating multilayer. For any optoelectronic application not only rms roughness but peak to valley roughness is also a very important parameter [16]. It is reported that the leakage current of the device increases with increase in peak to valley roughness. The peak to valley roughness for ZnO and multilayer is 17.89 nm and 11.28 nm, respectively.

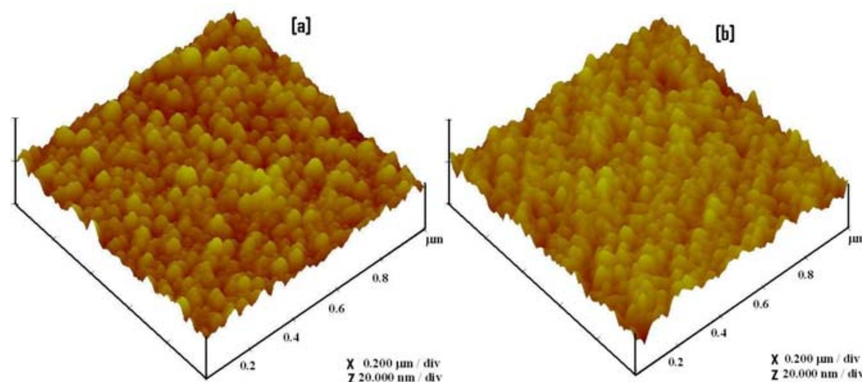

Fig. 2. AFM images of (a) ZnO (100 nm) and ZnO (35 nm)/IWO (65 nm) films.

The optical transmission spectrum of pure ZnO, IWO and multilayer were measured in the range of 250 nm-950 nm and is shown in Fig. 3. It is observed that all the films are highly transparent and transparencies of all the films are higher than 75 %. Saha *et al.* have deposited multilayers of ZnO and silver using rf-magnetron sputtering and observed that the transparency of multilayer films decreases drastically with increase in thickness of middle silver layer [11]. The decrease in the transparency of ZnO/Pt/ZnO multilayer films is also observed by Ramachandran *et al.* [12]. The transparency of the multilayer films decreases from ~ 60 % to ~ 25 % with increase in platinum layer thickness from 7 nm to 15 nm respectively. The advantage of all oxide based multilayer films is that the transparency of films is very high and almost independent of middle layer thickness.

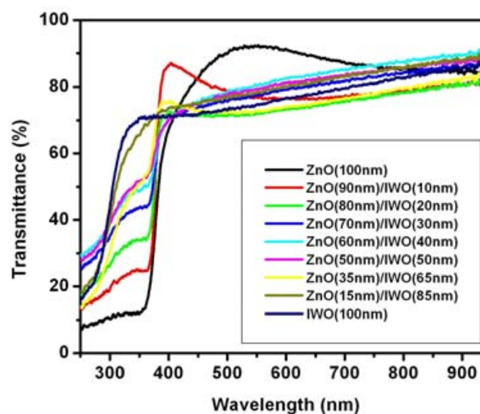

Fig. 3. Transmittance spectra of ZnO/IWO/ZnO films.

Fig. 4 shows the effect of ZnO films thickness on electrical resistivity, carrier concentration and mobility of ZnO/IWO/ZnO multilayer films. The electrical resistivity of films was determined by taking the product of sheet resistance and film thickness. The carrier concentration (n) is derived from the relation $n = 1/e.R_H$, where R_H is the Hall coefficient and e is the absolute value of the electron charge. The carrier mobility (μ) is determined using the relation $\mu = 1/ne\rho$, where ρ is resistivity. It is observed that the resistivity of the ZnO/IWO/ZnO multilayer films increases with increase in ZnO film thickness. The film resistivity increases from 1.04×10^{-4} Ω.cm to 8.19×10^{-3} Ω.cm to with increase in ZnO film thickness from 0 nm to 90 nm respectively. On the other hand, the carrier concentration and mobility is found to decrease with increase in ZnO film thickness. The electron mobility decreases from 231 $cm^2V^{-1}s^{-1}$ to 87 $cm^2V^{-1}s^{-1}$ with increase in ZnO film thickness from 0 nm to 90 nm, respectively.

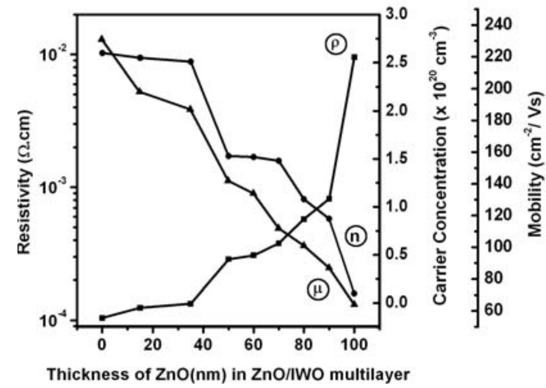

Fig. 4. Effect of ZnO thickness on resistivity (ρ), carrier concentration (n), and mobility (μ) of ZnO/IWO films.

Temperature dependent electrical resistivity of these multilayer films is studied in the range of 5-300 K (Fig. 5).

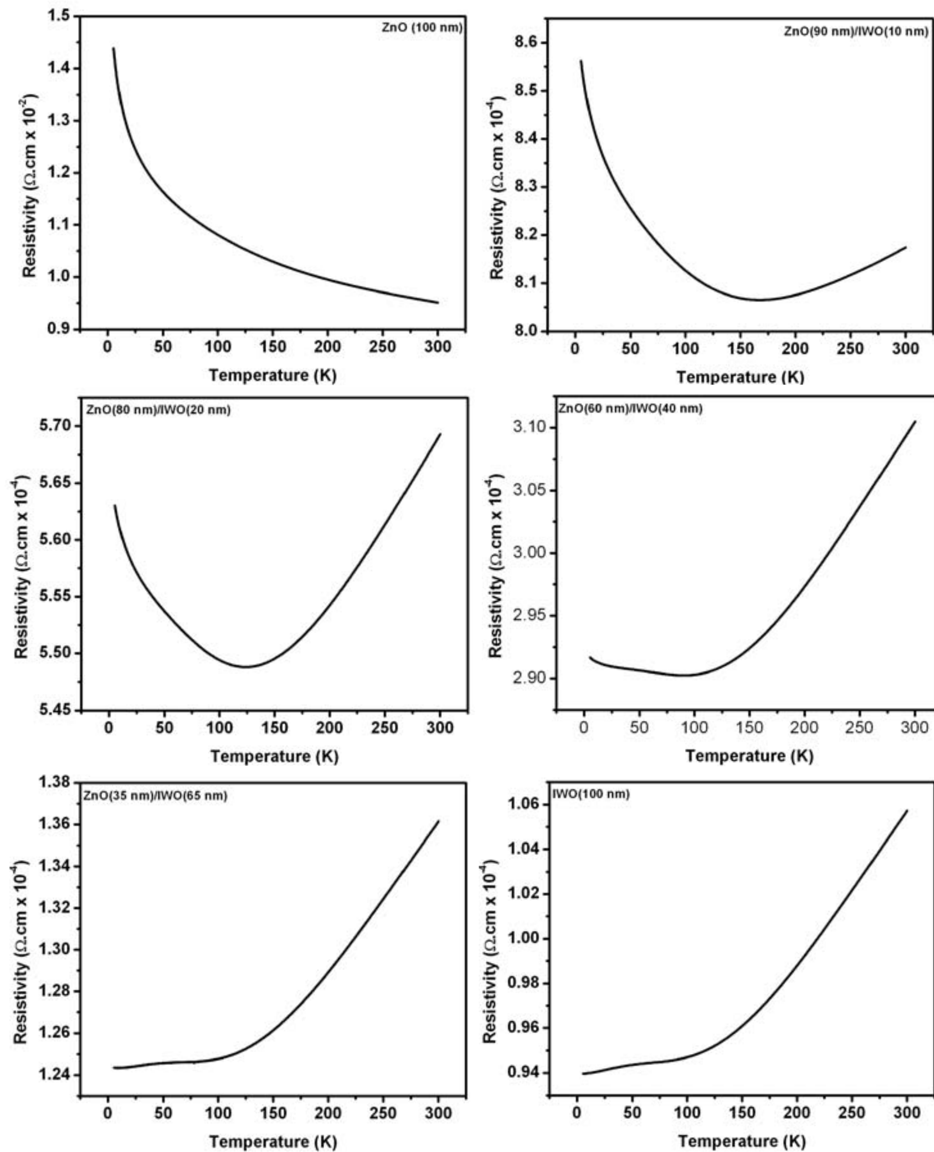

Fig. 5. Temperature dependent electrical resistivity of multilayer films having different thicknesses.

It is observed that the nature of multilayer film depends on film thickness of different layers. Pure ZnO film shows semiconducting behavior in the range of 5-300 K. The introduction of IWO film as a middle layer changes its behavior from semiconductor to metallic. Multilayer films having low thickness of IWO film show transition from semiconductor to metallic behavior. The negative temperature coefficient of resistance below the transition temperature and positive temperature coefficient of resistance above the transition temperature suggests that more than one competing mechanisms are operative. The negative temperature coefficient of resistance below the transition temperature could be due to localization of electrons [17, 18]. The positive temperature coefficient of resistance above the transition temperature shows delocalization of electrons. This delocalization of electrons leads to metallic conductivity, which is characteristic of a degenerate semiconductor [19].

4. Conclusions

The multilayer of ZnO/IWO/ZnO is grown by pulsed laser deposition. The effect of ZnO film thickness on structural, optical, and electrical properties of multilayer films was studied. These films are highly oriented along (002) and (222) direction for ZnO and IWO respectively. These films are highly transparent and conducting with high mobility. These high quality films could be used as transparent conducting electrodes for optoelectronic devices.

Acknowledgements

RKG thankfully acknowledges Missouri State University for the Research Assistant Professor position. The authors wish to acknowledge Dr. R. Mayanovic, Missouri State University, for providing XRD facility.

References

[1] M. Osada, T. Sakemi, T. Yamamoto, Thin Solid Films **494**, 38 (2006).
[2] V. R. Shinde, T. P. Gujar, C. D. Lokhande, R. S. Mane, S. H. Han, Mater. Chem. Phys. **96**, 326 (2006).
[3] H. Gomez, M. L. Olvera, Mater. Sci. Engg. B **134**, 20 (2006).
[4] X. Xiu, Z. Pang, M. Lv, Y. Dai, L. Ye, S. Han, Appl. Surf. Sci. **253**, 3345 (2007).
[5] S. H. Jeong, B. N. Park, S. B. Lee, J. H. Boo, Surf. Coat. Technol. **201**, 5318 (2007).
[6] C. S. Hong, H. H. Park, J. Moon, H. H. Park, Thin Solid Films **515**, 957 (2006).
[7] K. T. R. Reddy, H. Gopalaswamy, P. J. Reddy, R. W. Miles, J. Cryst. Growth **210**, 516 (2000).
[8] J. Hu, R. G. Gordon, J. Appl. Phys. **71**, 880 (1992).
[9] B. Y. Oh, M. C. Jeong, D. S. Kim, W. Lee, J. M. Myoung, J. Cryst. Growth **281**, 475 (2005).
[10] R. K. Gupta, K. Ghosh, S. R. Mishra, P. K. Kahol, Mater. Res. Soc. Symp. Proc. **1035E**, L11 (2007).
[11] D. R. Sahu, S. Y. Lin, J. L. Huang, Appl. Surf. Sci. **252**, 7509 (2006).
[12] S. Ramachandran, A. Chugh, A. Tiwari, J. Narayan, J. Cryst. Growth **291**, 212 (2006).
[13] R. K. Gupta, K. Ghosh, S. R. Mishra, P. K. Kahol, Appl. Surf. Sci. **254**, 1661 (2008).
[14] L. J. Van der Pauw, Philips Res. Rep. **13**, 1 (1958).
[15] I. Yasuhiro, K. Hirokazu, Appl. Surf. Sci. **169/170**, 508 (2001).
[16] Y.-H. Tak, K.-B. Kim, H.-G. Park, K.-H. Lee, J.-R. Lee, Thin Solid Films **411**, 12 (2002).
[17] K. Shimakawa, S. Narushima, H. Hosono, H. Kawazoe, Philos. Mag. Lett. **79**, 755 (1999).
[18] V. Bhosle, A. Tiwari, J. Narayan, J. Appl. Phys. **100**, 033713 (2006).
[19] C. Coutal, A. Azema, J.-C. Roustan, Thin Solid Films **288**, 248 (1996).

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