Available online at www.scholarsresearchlibrary.com

Scholars Research Library

Archives of Physics Research, 2013, 4 (4):20-27
(http://scholarsresearchlibrary.com/archive.html)

Archives of Physics Research
Scholars Research Library
ISSN : 0976-0970
CODEN (USA): APRRC7

Properties of Al doped ZnO thin films grown by spray pyrolysis

Shashidhara Bhat, Shrisha B. V, K. Gopalakrishna Naik*

Department of studies in Physics, Mangalore University, Mangalagangotri, India

---

ABSTRACT

In this work, the properties of aluminium doped ZnO thin films grown by spray pyrolysis are presented. The structural properties of the grown thin films were characterized by X-ray diffraction (XRD). The optical properties of the grown thin films were studied using UV-visible absorption and transmission spectroscopy. The crystalline quality of the grown thin films gets degraded as the Al doping is increased. With increase in Al atomic percentage in the spray solution from 0 to about 5 %, an increase in optical transmittance along with blue-shift of the absorption edge were observed for these Al doped ZnO thin films. With increasing the Al atomic percentage above 5 %, shows a decreasing trend in the optical transmittance. The improvement in transmittance may be due to the presence of Al_2O_3 or other Zn-O-Al phase in the thin films [1]. The decrease in transmittance for films grown from high atomic percentage of Al may be due to the degradation in the crystallinity of the thin films. Further, Al doping did not show any noticeable change in the carrier concentration in the ZnO films indicating that Al is not acting as a dopant in the grown thin films.

Keywords: Spray pyrolysis growth, thin films, Al doped ZnO, XRD.

INTRODUCTION

Zinc oxide (ZnO) is a II-VI direct band gap semiconductor with a room temperature band gap of 3.37 eV with large exciton binding energy of the order of 60 meV [2]. It has attracted considerable attention for applications in light emitters and detectors in UV and visible wavelength range, as a transparent conducting oxides and surface acoustic wave devices. ZnO is relatively cheap and abundant compared to the commonly used indium tin oxide (ITO) transparent conducting films. Even though ZnO shows high transparency in the visible wavelength region, the electrical properties of undoped ZnO thin films are not good enough for them to replace ITO [3]. To enhance the electrical properties of ZnO thin films, the elements in group III of the periodic table, such as Al, Ga, and In, are used as dopants into ZnO thin films. Among the above mentioned dopants, Al is very promising dopant for the enhancement of electrical properties of ZnO thin films. Furthermore, it has been observed that the band gap of the Al-doped ZnO thin films increases beyond the undoped ZnO band gap of 3.37 eV and this is advantageous for optical applications in the visible range. Various techniques such as molecular beam epitaxy (MBE), pulse laser deposition (PLD), magnetron sputtering, chemical vapor deposition (CVD), atomic layer deposition, electron beam evaporation, spray pyrolysis, and sol-gel process have been used to grow ZnO based thin films [4-10]. Among these methods, spray pyrolysis is simple and cheap method. In this study we attempt to grow Al doped ZnO thin films by spray pyrolysis. The grown thin films were characterized by XRD and UV-visible optical absorption techniques.

MATERIALS AND METHODS

Experimental

The ZnO and Al doped ZnO films were deposited by spray pyrolysis technique on glass substrates. The glass substrates were ultrasonically cleaned in acetone and methanol and double distilled water before the film deposition. The spray solution was prepared from a 0.1M solution of zinc acetate hexahydrate dissolved in mixture of 3:1 isopropyl alcohol and de-ionised water. A small amount of acetic acid was added to increase the solubility of zinc

acetate. The films were deposited by spraying 50 ml of the solution through a glass nozzle onto heated glass substrate kept at about 430º C. A PID temperature controller controlled planar heater was used to heat the glass substrates. Compressed air was used to spray the solution and the spray rate of solution was maintained at 5ml/minute. Results of three sets of samples are presented in this work. The first set of ZnO thin films were grown with 0, 1, 2, 3, 4, and 5 atomic percent of Al in the spray solution. The second set of ZnO thin films were grown with 0, 1, 2, 3, 3.5, 4 , 5 and 6 atomic percent of Al in the spray solution. The third set of ZnO thin films were grown with 0, 2, 4, 6, 10, 15 and 20 atomic percent of Al in the spray solution. The absorption and transmittance of the films were measured with a Shimadzu UV-1800 spectrophotometer. The film thicknesses were measured with an ellipsometer (Holmarc opto mechatronics, India) using DPSS laser (532 nm) beam. The structural characterization of the films was carried out using Rigaku MiniFlex 600 X-ray diffractometer using Cu-Kα. The van der Pauw geometry is used to measure resistivity and Hall measurement on the Al doped ZnO thin films. Silver paste was used to make electrical contacts to the films. Resistivity and Hall measurements were carried out using a Keithley 2400 source measure system and Keithley 2000 multimeter.

RESULTS AND DISCUSSION

Structural properties:

The crystalline quality of the grown ZnO films was investigated by powder XRD. Fig.1-3 shows the XRD pattern of the three set of samples with different Al concentrations. The XRD spectra of the samples are in good agreement with diffraction standard (JCPDS) data belonging to hexagonal ZnO structure. The peaks corresponding to ZnO reflection planes (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0) and (1 0 3) are shown both in Fig. 1, 2, and 3. Apart from the ZnO characteristic peaks, a peak at ~25^o (indicates as X_1 in the XRD plot) is observed in all the samples. In addition to this, two more XRD peaks at about 38^o (X_2 in the XRD plot) and 44^o (X_3 in the XRD plot) were observed in some of the samples. The additional peaks, other than corresponding to ZnO, may be due Al_2O_3 or other Zn-O-Al phases in the grown films [1, 11]. The appearance of (0 0 2) peak with maximum intensity in undoped and Al-doped ZnO films indicates that the preferred orientation of the thin films is along the *c*-axis. The degradation in the crystalline quality of thin films was observed with increasing Al content, as shown Fig. 1, 2 and 3.

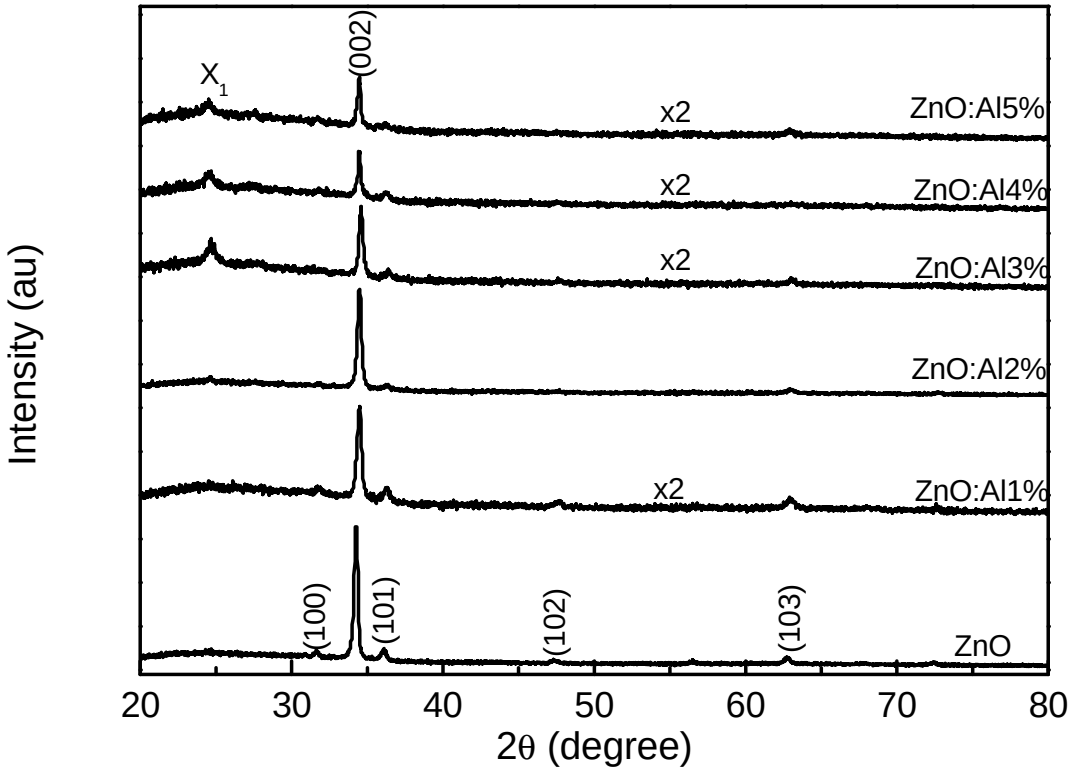

Fig. 1 XRD pattern of first set of ZnO and Al doped ZnO thin films.

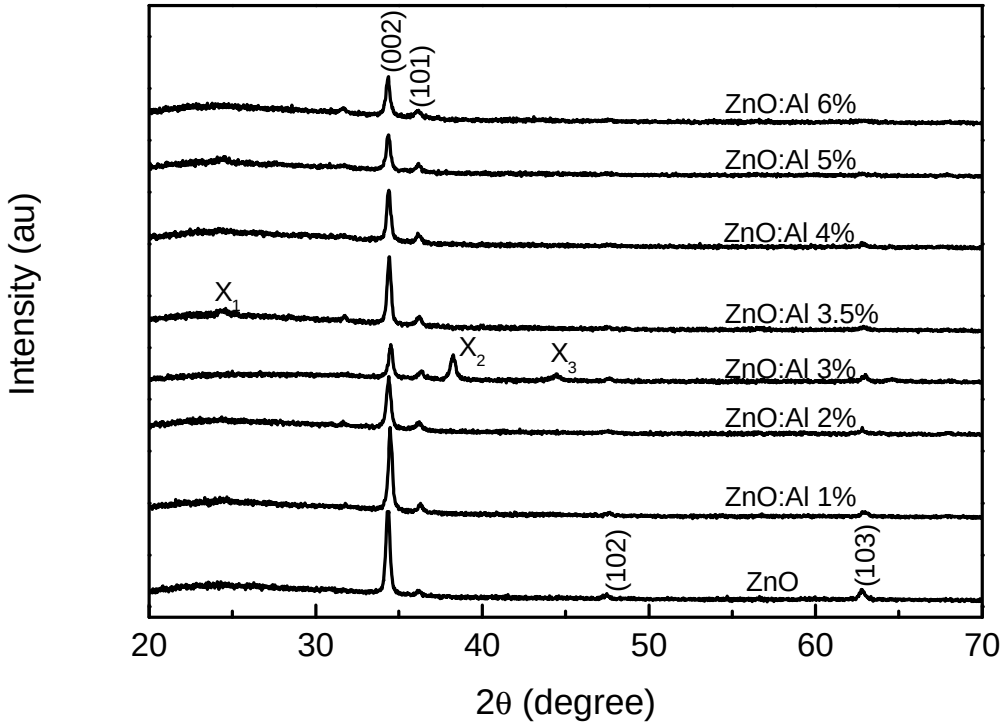

Fig. 2 XRD pattern of second set of ZnO and Al doped ZnO thin films.

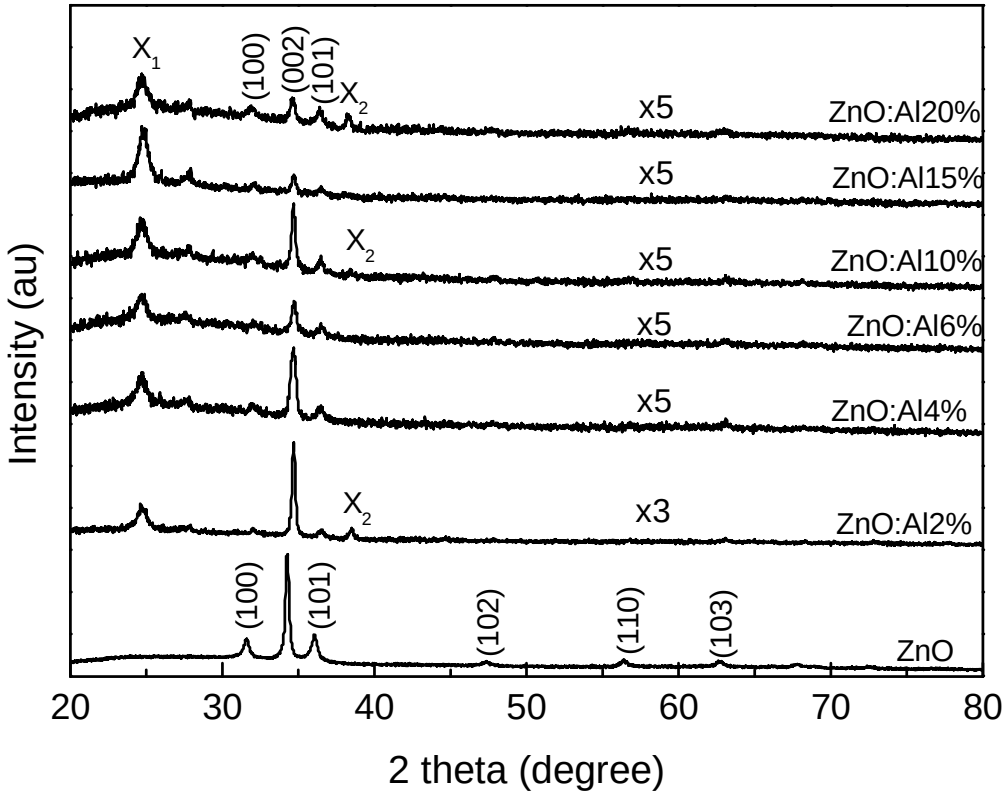

Fig. 3 XRD pattern of third set of ZnO and Al doped ZnO thin films.

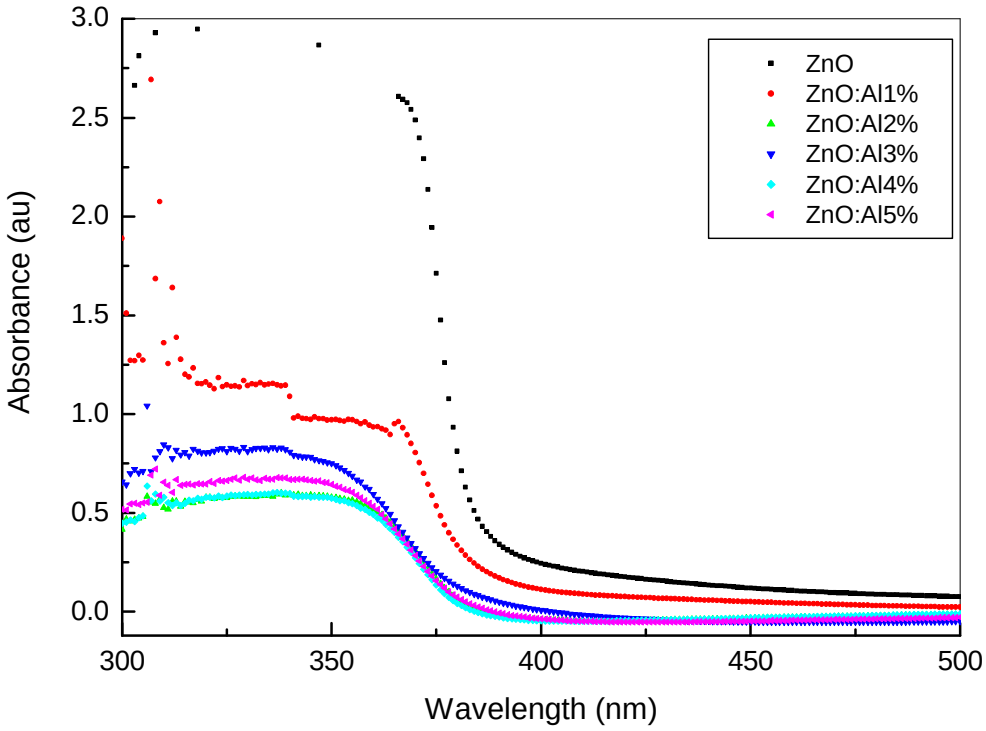

Fig. 4 Absorption spectra of first set of ZnO and Al doped ZnO thin films.

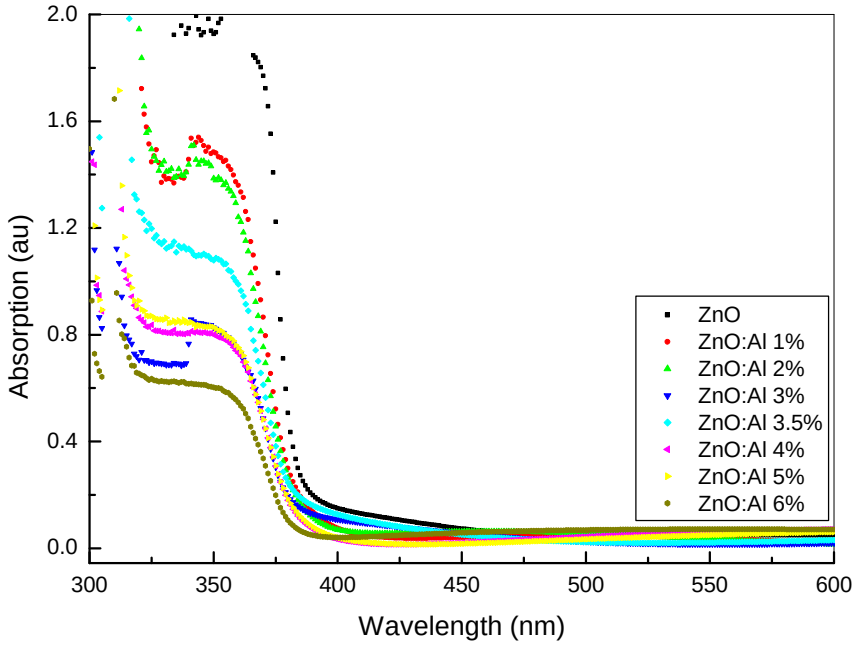

Fig. 5 Absorption spectra of second set of ZnO and Al doped ZnO thin films.

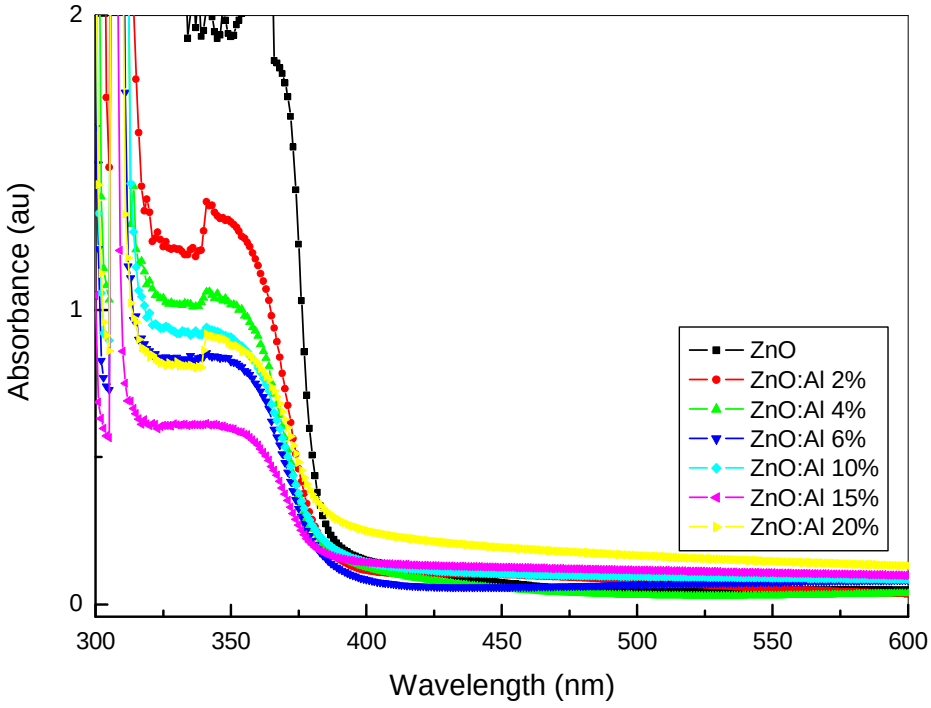

Fig. 6 Absorption spectra of third set of ZnO and Al doped ZnO thin films.

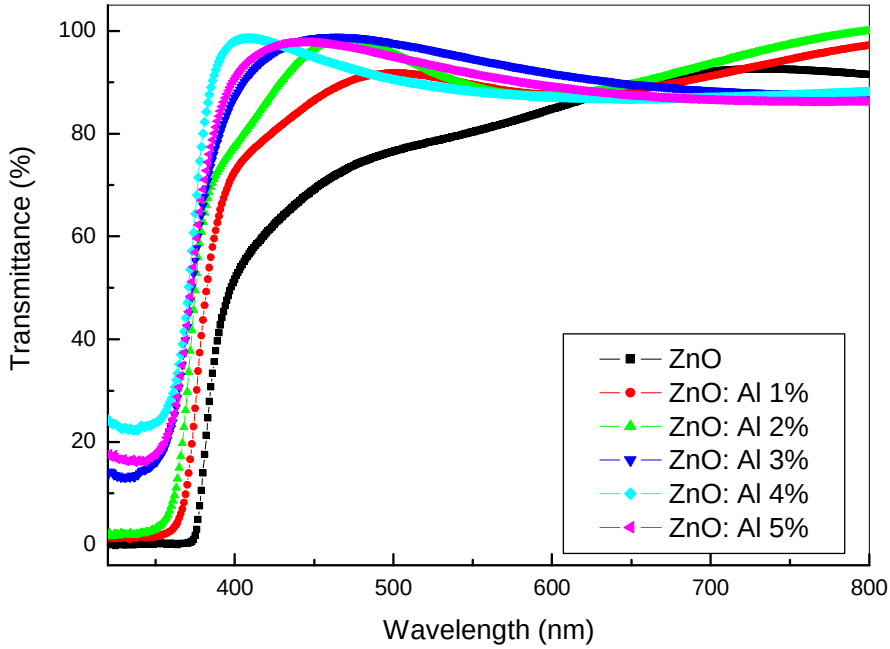

Fig. 7 Transmittance spectra of first set of ZnO and Al doped ZnO thin films.

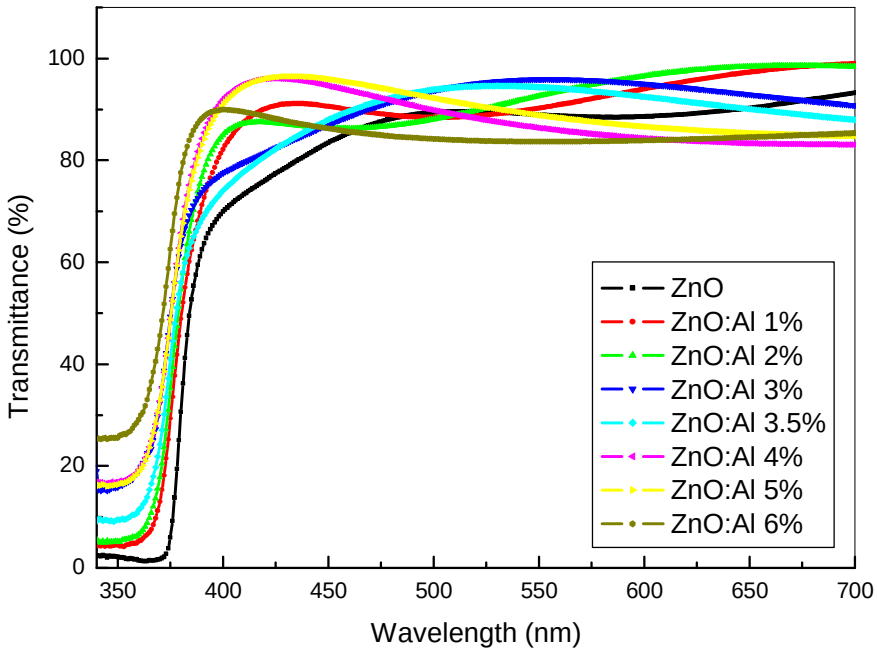

Fig. 8 Transmittance spectra of second set of ZnO and Al doped ZnO thin films.

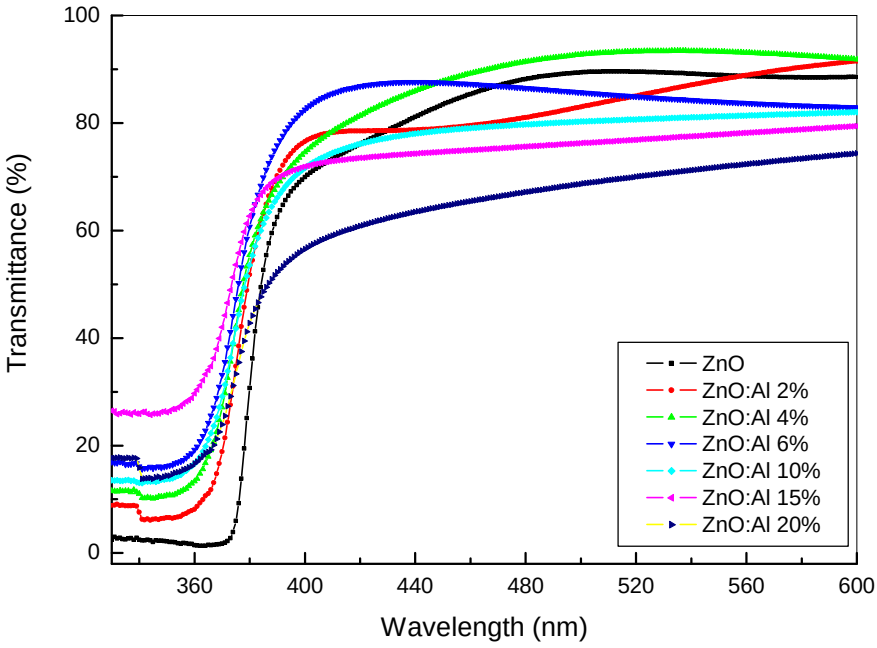

Fig. 9 Transmittance spectra of third set of ZnO and Al doped ZnO thin films.

Optical properties:

The UV-visible absorption spectra of the Al doped ZnO thin films are shown in Fig. 4 – 6 and transmittance spectra are shown in Fig. 7 - 9. A blue shift in the optical band edge was observed both in optical absorption as well as in transmittance spectra, with Al doping. As shown in Fig 7- 9, the optical transmittance of the films initially increases with increasing Al doping up to 4-5 at% and transmittance increases more than 80 % in the visible region. Further increase in Al doping leads to decrease in transmittance. The improvement of transmittance and blue shift in the optical spectra of Al doped ZnO thin films may be due to the presence of Al_2O_3 and Zn-O-Al phases in the thin

films, and/or formation of nano-structured films due to Al doping [1]. The decrease in transmittance of the films grown from high atomic percentage of Al may be due to the degradation in the crystallinity of the thin films.

Electrical properties:

Table.1 Resistivity and carrier concentration values of first set of samples.

Sample	Resistivity (Ω-cm)	Carrier concentration n (cm^{-3})
ZnO	0.1602	1.01×10^{17}
ZnO:Al 1%	0.1793	1.38×10^{18}
ZnO:Al 2%	0.1560	6.58×10^{17}
ZnO:Al 3%	0.1764	1.44×10^{17}
ZnO:Al 4%	0.1728	1.06×10^{17}
ZnO:Al 5%	0.2115	7.57×10^{17}

Table. 2 Resistivity and carrier concentration values of second set of samples.

Sample	Resistivity (Ω- cm)	Carrier concentration n (cm^{-3})
ZnO	0.5306	0.77×10^{17}
ZnO: Al1%	0.6478	1.02×10^{17}
ZnO:Al 2%	0.6412	0.80×10^{17}
ZnO:Al 3%	0.6217	1.11×10^{17}
ZnO:Al 3.5%	0.4258	1.01×10^{17}
ZnO:Al 4%	0.4145	1.28×10^{17}
ZnO:Al 5%	0.3160	1.80×10^{17}
ZnO:Al 6%	0.3520	0.26×10^{17}

Table. 3 Resistivity and carrier concentration values of third set of samples.

Sample	Resistivity (Ω- cm)	Carrier concentration n (cm^{-3})
ZnO	0.5306	0.77×10^{17}
ZnO: 2 % Al	0.4582	2.52×10^{17}
ZnO: 4% Al	0.5538	3.69×10^{17}
ZnO: 6% Al	0.4086	1.46×10^{17}
ZnO: 10 % Al	0.4436	0.49×10^{17}
ZnO: 15 % Al	0.3729	0.50×10^{17}
ZnO: 20 % Al	0.5003	0.12×10^{17}

The van der Pauw geometry was used for resistivity and Hall measurements [12, 13] on the Al doped ZnO thin films. Silver paste was used to make electrical contacts to the films. The van der Pauw method involves applying current and measuring voltages (V_1 to V_8) using four small contacts on the circumference of thin film. Once all the voltage measurements are taken, resistivity ρ_a and ρ_b are derived as follows:

$$\rho_a = \frac{\pi}{\ln 2} f_a t \left(\frac{V_1 - V_2 + V_3 - V_4}{4I} \right) \quad \text{and} \quad \rho_b = \frac{\pi}{\ln 2} f_b t \left(\frac{V_5 - V_6 + V_7 - V_8}{4I} \right)$$

where 't' is the thickness of the thin film in cm, the values of 'f_a and f_b ' can be found from the standard plot of f_a verses (R_{1234}/R_{2341}) and f_b versus (R_{5678}/R_{6781}) [13].

The resistivity ρ in ohm.cm is given by

$$\rho = \left(\frac{\rho_a + \rho_b}{2} \right)$$

From the Hall voltage measurements, the average Hall coefficient R_H can be calculated as follows:

$$R_{HC} = t \left(\frac{V_{4-2+} - V_{2-4+} + V_{2-4-} - V_{4-2-}}{4BI} \right)$$

$$R_{HD} = t\left(\frac{V_{3-1+} - V_{1-3+} + V_{1-3-} - V_{3-1-}}{4BI}\right)$$

$$R_H = \left(\frac{R_{HC} + R_{HD}}{2}\right)$$

where R_{HC} and R_{HD} are hall coefficients in cm^3/C, 't' is the thickness in cm, 'I' is the current through the sample in amperes, B is the magnetic flux in Vs/ cm^2 (1 Vs/ $cm^2=10^8$ gauss). The value of carrier concentration 'n' can be calculated using the equation

$$n = \left(\frac{1}{R_H q}\right)$$

where 'q' is the electron charge.

Table 1, 2 and 3 shows the resistivity and carrier concentration of the Al doped ZnO thin films. No noticeable change in resistivity and carrier concentrations with Al doping of ZnO thin films was observed. The electrical data indicates that Al^{3+} ions did not get substituted into Zn^{2+} sites in the films, the Al atoms may be segregated into grain boundaries. These segregated Al atoms did not act as dopant, therefore, no changes in electrical properties were observed.

CONCLUSION

Aluminium doped ZnO thin films with hexagonal wurtzite type polycrystalline structure and good optical quality have been prepared on glass substrates by spray pyrolysis. The crystalline quality of the grown thin films gets degraded as the Al doping is increased. The transmittance of the films prepared from spray solutions with Al atomic percentage up to around 5% was improved from that of undoped ZnO films. The improvement of transmittance and blue shift in the optical spectra of Al doped ZnO thin films were due to the presence of Al_2O_3 and Zn-O-Al phases in the thin films, and/or formation of nano-structured films due to Al doping.

Acknowledgements

The authors acknowledge the financial support of DST-PURSE Project (MU/CHEM/PURSE PIG/2012) of the Mangalore University, the use of Rikagu MiniFlex600 powder XRD of the department of physics, Mangalore University set up under DST FIST grant. The authors also thank the Chairman, department of applied botany, Mangalore University for allowing to use Shimadzu 1800 UV-visible spectrophotometer.

REFERENCES

[1] D. C. Altamirano-Juárez, G. Torres-Delgado, R. Castanedo-Pérez, O. Jiménez-Sandoval J. Márquez-Marín and S. Jiménez-Sandoval, *Superficies y Vacío*, **2001**, 13, 66-68.
[2] J. G. Lu, Z. Z. Ye, Y. J. Zeng, L. P. Zhu, L. Wang, J. Yuan, B. H. Zhao, Q. L. Liang, *J. Appl. Phys*, **2006**, 100, 073714.
[3] J. H. Lee, Jae-Won Lee, S. Hwang, S. Y. Kim, H. K. Cho, J. Y. Lee and Jin-Seong Park, *J. Nanosci and Nanotech*, **2012**, 12, 5598–5603.
[4] Y. W. Heo, D. P. Norton, and S. Pearton, *J. Appl. Phys*, **2005**, 98, 073502.
[5] H. Kim, M. Osofsky, S. M. Prokes, O. J. Glembocki, and A. Pique, *Appl. Phys. Lett*, **2013**, 102, 171103.
[6] T. Minami, Y. Ohtani, T. Miyata, and T. Kuboi, *J. Vac. Sci. Technol, A* , **2007,** 25, 1172.
[7] I. Volintiru, M. Creatore, and M. C. M. van de Sanden, *J. Appl. Phys*, **2008**, 103, 033704.
[8] P. Banerjee, Won-Jae Lee, Ki-Ryeol Bae, Sang Bok Lee, and Gary W. Rubloff, J. Appl. Phys, **2010**, 108, 043504.
[9] M. Shahjahan, M. K. R. Khan, M. F. Hossain, S. Biswas, and T. Takahashi, *J. Vac. Sci. Technol A* **2009**, 27, 885.
[10] Jen-Po Lin and Jenn-Ming Wua, *Appl. Phys. Lett*, **2008**, 92, 134103.
[11] M. M. Rahman, M. K. R. Khan, M. Raqul Islam, M. A. Halim, M. Shahjahan, M. A. Hakim, D. K. Saha and J. U. Khan, *J. Mater. Sci. Technol*, **2012**, 28(4), 329-335.
[12] Kiethley application note series No.2475.
[13] Van der Pauw L J 1958 *Philips Res. Rep*, **1958**, 13, 1-9