International Journal of Electronics Engineering (ISSN: 0973-7383)
Volume 11 • Issue 1 pp. 977-985 Jan 2019-June 2019 www.csjournals.com

Optimization of Electrical and Optical Properties of Pulsed Laser Deposited Aluminum Doped Zinc Oxide Films

*Arun Vir Singh, S.K.Yadav

Department of Physics, Shivaji college (University of Delhi), New Delhi, India

Abstract Highly conductive and transparent aluminum-doped zinc oxide films have been deposited on corning and quartz glass by pulse laser deposition technique with XeCl laser (λ = 308 nm). The structural, optical and electrical properties of aluminum-doped zinc oxide films have been investigated to optimize laser fluence, target-substrate distance, and substrate temperature. Films deposited at optimized conditions show the lowest resistivity value of 1.432×10^{-4} Ω cm and have maximum transmittance $\approx$ 91%.

1. 1ntroduction:

The simultaneous occurrence of high optical transparency (more than 80%) in the visible region and high electrical conductivity (> 10^3 ohm^{-1} cm^{-1}) are the two basic requirements for a material to be used as transparent conducting electrode in photovoltaic devices [1].. The only way to obtain good transparent conductor is to create electron degeneracy in a wide band gap (greater than 3eV) oxide by controllably introducing non-stoichiometry and / or appropriate dopants. These conditions are very conveniently obtained in oxides of cadmium, tin, indium, zinc and their alloys in thin film form. In the fast few years ZnO has emerged as one of the most promising oxide materials owing to good optical and electrical properties together with their high chemical and mechanical stability [2]. ZnO is an n-type intrinsic semiconductor and its electrical conductivity is mainly due to zinc excess at inertial position [3]. Its electrical properties could be modified by thermal treatment with hydrogen [4] or by an appropriate doping process, either by cationic [5] or anionic substitution [6].

A variety of thin films deposition techniques have been employed to deposit transparent conducting oxides [TCO] such as evaporation [7] , chemical vapour deposition (CVD) [8] metal organic chemical vapour deposition (MOCVD) [2] (Hu and Gordan 1992), spray pyrolysis, [9] sol gel and dip coating [10], rf sputtering [11-13] and pulsed laser deposition (PLD) technique [14]. In comparison with other techniques PLD has many advantages such as (i) the composition of the films grown by PLD is quite close to that of the target; (ii) the surface of the films is very smooth; (ii) good quality films can be deposited at room temperature due to the high kinetic energies (> 1 eV) of atoms and ionized species in the laser-produced plasma[15].

A few studies exist for aluminum doped zinc oxide (AZO) thin films prepared by the PLD technique in oxygen ambient [16]. However, although several results have been reported on laser deposited AZO films, the majority of these results are centered on resistivity measurements. Other vital characteristics, such as the effect of effect of laser fluence, target-substrate distance target, in the deposition cell on the properties of AZO are barely documented. Hence, in this article we have examined the role of laser fluence, target-substrate distance target, substrate temperature, doping concentration to optimize the optical and electrical properties of AZO thin films to obtain device-quality films having high transmittance and low resistivity.

2. Materials and Methods:

AZO films were deposited on quartz and corning 7059 glass by focusing a XeCl (308 nm) laser onto a target rotating at 15-rpm. The ZnO targets (99.99% purity) were 2 in. in diameter and doped with 0.5- 4.0 wt% Al_2O_3 (99.99% purity). For all experiments, laser pulse repetition rate of 5 Hz and pulse duration was 20 ns were kept. To study the effect of laser fluence on the properties of AZO films laser energy was varied from 50 – 110 mJ/pluse while, keeping the area of focus constant.This corresponcd to laser energy density 1 to 2.5 J/cm^2. The distance between target and substrate was also varied from 10 to 30 mm. Films thickness is kept in the range of 3000-3500 Å. The deposition cell was initially evacuated to the pressure of the order of 6×10^{-6} Torr and film deposition was done in vacuum and in oxygen ambient (1 mTorr). The films were deposited in the substrate temperature range of room temperature (RT) to 400 ^{o}C. Film thickness was measured with a DEKTAK^3-ST profilometer. The crystal orientation of the films was evaluated by x-ray diffraction (XRD) using CuK α radiation (XRD Riggau).The transmission through the films, referenced to the quartz glass, was measured in the wavelengths from 200-800 nm spectrophotometer (HITACHI - 330). The electrical resistivity was measured by the van der Pauw method. Hall voltage measurements were carried out to calculate the carrier concentration and mobility.

3.Results And Discussion:

3.1.Deposition Rate

3.1.(a) Laser Fluence

Relationship between the deposition rate and laser fluence for the films deposited at room temperature in vacuum is shown in figure 1. The distance between the target and substrate 'h' was kept 30 mm. It is observed that with the increase in laser fluence, the deposition rate increases. The increase in the deposition rate is

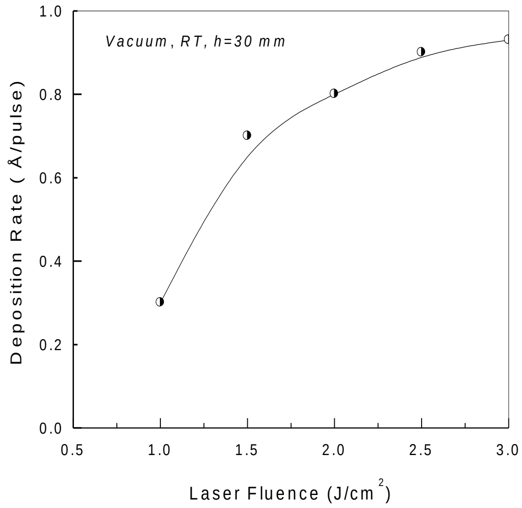

Figure. 1 Effect of laser fluence on the deposition rate for films deposited at room temperature in vacuum at h = 30 mm.

linear up to laser fluence1.5 J/cm^2 and for laser fluence > 1.5 J/cm^2 non-linear deposition rate showing saturating behavior has been observed. The saturation in the deposition rate is largely due to the saturation in the ablation processes[15]. This can be explained due to the decreases of etch depth (thickness of the ablated layer from the target) per pulse with increase in laser fluence [17] also reported the saturation in deposition rate with increase in laser fluence for ITO films.

3.1(b) Effect of Distance between Target and Substrate

Figure 2 shows the deposition rate at room temperature of the films deposited in vacuum and oxygen ambient at laser fluence of 1.5J/cm^2. The deposition rate increases 'h' increased from 20 - 30 mm. With further increase in 'h', (h > 30 mm) deposition rate decreases. The initial increase in the deposition rate can be explained due to the fact that, as 'h' increases, the velocity of various species in the laser plume reaching the substrate decreases which attributes to the decreases in the scattering of the incident flux with particles reflected and /or sputtered from the substrate decreases [15] . For the case of deposition in vacuum, the decrease in the deposition rate with increase of h (> 30 mm) follows the inverse square law .The dashed line shows

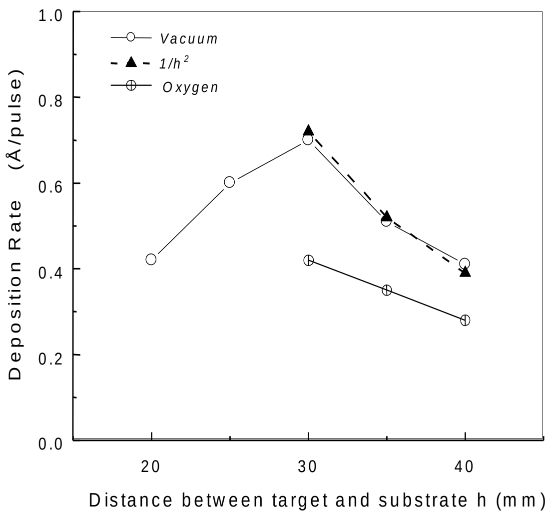

Figure.2. Dependence of deposition rate on the distance between the substrate and target 'h' at room temperature. The dashed line shows the 1/h^2 law

1/h^2 dependence for the films deposited in vacuum. For the films deposited in oxygen ambient (h > 30 mm), the deposition rate decreases slower than the 1/d^2 law, which is obeyed for point source evaporation in vacuum. This can be explained by the collision between the ablated atoms and ions and the oxygen ambient. Similar behavior observed by Zheng et.al.[18]

Maximum deposition rate was found to be 0.7 Å per pulse for the films deposited in vacuum and for the films deposited in oxygen ambient was about 0.42 Å per pulse.

Maximum value of deposition rate are obtained for the films deposited at optimum value of h, which is 30 mm in our case.

3.Structural Properties:

3.3.(a) Effect of Laser Fluence

Effect of laser fluence on the orientation and crystallinity of AZO films deposited at 300 ^{0}C in 1 mTorr of oxygen ambient keeping 'h' 30 mm is represented by the x-ray diffraction pattern in figure 3 . Only (002) and (004) x-ray diffraction peaks were seen. Intensity of (002) and (004) peak increases with the increase in the laser fluence 1–1.5 J/cm.^{2} A larger laser input power per pulse seems to favor growth with c-axis perpendicular to the substrate. This observed behavior could be explained on the basis of kinetic energy of the ablated atoms/ions, reaching at the substrate, with the increase in the laser energy per pulse. Increase in the kinetic energies of the ablated atoms/ions

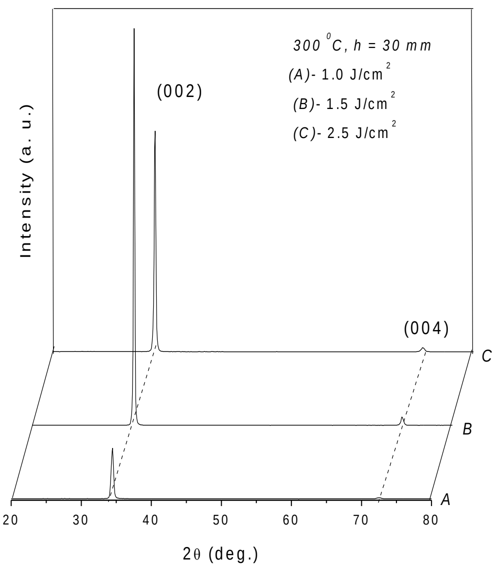

Figure. 3 Effect of laser fluence on X-rd spectrum of AZO films deposited at 300 °C in I mTorr of oxygen ambient.

enhance the surface migration of ablated particles, which arrives at the substrate surface, and crystallinity of the films. Whereas the films deposited with laser fluence of 2.5 J/cm^2 showed decrement in the ratio of intensity of (002) and (004) peaks. Decrease in the intensity of (002) and (004) peak may be due to the degradation of film quality due to the ablation of big size particulate from the target [19] .

The result of this experiment suggests that good quality films can be deposited by ablating the target with laser fluence of 1.5 J/cm^2.

3.3.(b) Effect of Distance between Target and Substrate

To study the effect of distance between target and substrate 'h'on structural properties, laser fluence was kept 1.5 J/cm^2. Figure 4 shows the effect of 'h' on the x-ray diffraction patterns of the films deposited at 300 °C in oxygen ambient of 1 mTorr. All the films showed (002) and (004) peaks. Sharp (002) peaks indicate a strong c-axis orientation to the substrate. Increase in 'h' (20–30 mm), enhances the intensity of (002) and (004) peaks. The films deposited at 'h'=35 mm show the broadening and decrease in intensity of (002) and (004) peaks.

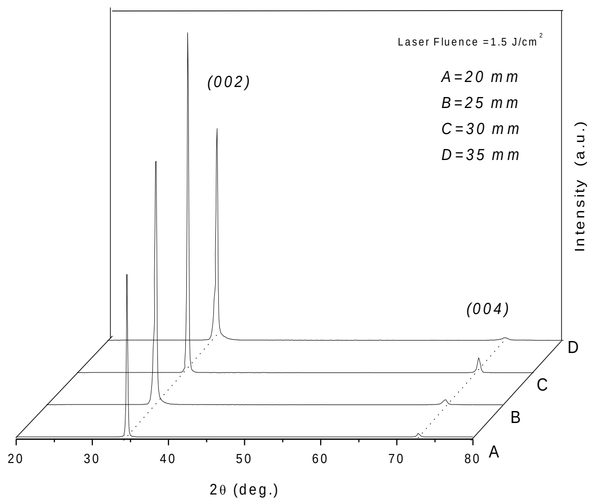

Figure. 4 X-ray diffraction pattern of AZO films deposited at 300°C for different values of 'h'(20–35 mm).

The increase in the orientation with c-axis perpendicular to the substrate can be explained by the reduction in the number of the of ions/atoms reflecting at the substrate [15] or by the increase in the film thickness as shown in figure 2, with the increase in 'h' up to 30 mm. The decrease in intensity and boarding of (002) and (004) x-ray diffraction peaks has been observed, this may be related to reduction in adhesion coefficient for the ablated ions /atom reaching at the substrate, for the films deposited at 'h'= 35 mm (Ryu et al., 2000). The broadening of (002) and (004) x-ray diffraction peaks may be related to reduction in the energies of the ablated ions /atom reaching at the substrate for the films deposited at a distance of 35 mm.

3.2.(c) Effect of Substrate Temperature

All the samples deposited at room temperature showed amorphous nature. Films deposited at higher substrate temperature showed strong c-axis orientation perpendicular to the substrate.
Figure 5 shows the effect of the variation of the FWHM,$\Delta(2\theta)$ of the (002) diffraction peak of AZO films prepared at different substrate temperatures, in 1 mTorr of oxygen pressure. It was found that $\Delta(2\theta)$ decreases with increase in substrate temperature up to 300 °C. Since the value of $\Delta(2\theta)$ is inversely proportional to the grain size it implies that the grain size improves with the increase in film deposition temperature up to 300 °C. A

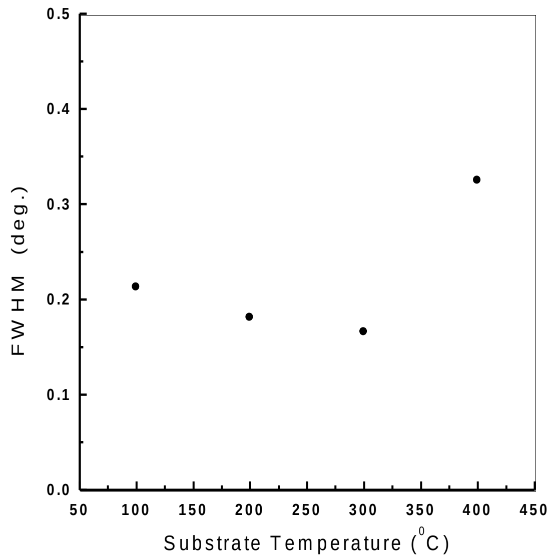

Figure. 5 Effect of the variation of the substrate temperature on FWHM, $\Delta(2\theta)$ of the (002) diffraction peak deposited in 1 mTorr oif oxygen ambient.

further increase of substrate temperature reduces the grain size. A slight increase in $\Delta(2\theta)$ of the films deposited at 400 °C was observed; this may be due to the degradation in the film quality.
This study reveals that substrate temperature during the nucleation process appears to be dominant factor in determine crystal orientation, and good quality films can be deposited at optimized substrate temperature which is 300 °C in our case.

3.3 Electrical Properties:

3.3(a).Effect of Distance between Target and Substrate

Variation of the resistivity 'ρ',carrier concentration 'n_e' and Hall mobility 'μ_H' as a function of 'h' for the films deposited by ablating the ZnO target having 0.5 wt% of Al_2O_3 content at 300 °C in 1 mTorr of oxygen pressure with laser fluence of 1.5 J/cm^2 is shown in figure 6. It can be seen from this figure that, electrical properties of AZO film are sensitive to 'h'.

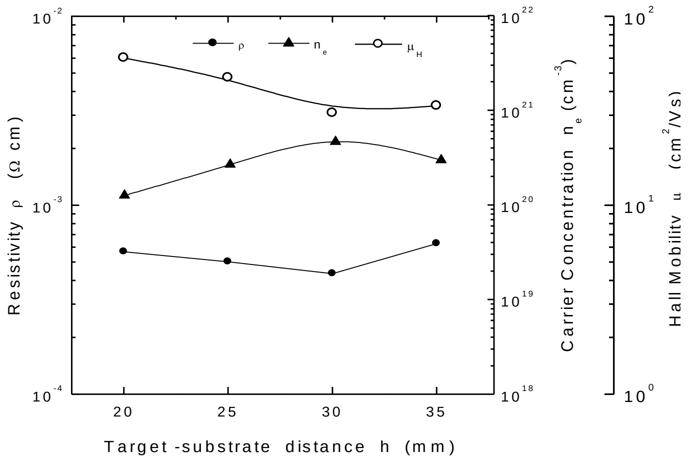

Figure.6 Resistivity resistivity 'ρ',carrier concentration 'n_e' and Hall mobility 'μ as a function 'h' for the films deposited at 300 ^oC in 1 mTorr of oxygen ambient.

. The resistivity and mobility decreases with the increase in h from 20 – 30 mm, however the resistivity and mobility increase with further increase in 'h' (from 30 – 35 mm.) Carrier concentration increases with the increase in 'h' from 20– 30 mm. With further increase in target–substrate distance carrier concentration decreases. The minimum resistivity was obtained for the films deposited at the optimal value of 'h' (30 mm). .Changes in the electrical properties may be attributed to structural changes as shown in figure. 5

3.3.(b) Effect of Laser Fluence

Figure 7 shows the variation of carrier concentration 'n_e', resistivity 'ρ', and Hall mobility 'μ_H'on the laser fluence. Resistivity decreases sharply with the increase in the laser fluence from 1-1.5 J/cm.^{2} However slight increase in the resistivity has been observed with further increase in the laser fluence from 1.5 - 2.5 J/cm^2. Carrier concentration increases continuously with the increase in the laser fluence from 1.5 - 2.5 J/cm^2. Mobility increases slightly with increase in the laser fluence from 1- 1.5 J/cm^2 and decreases

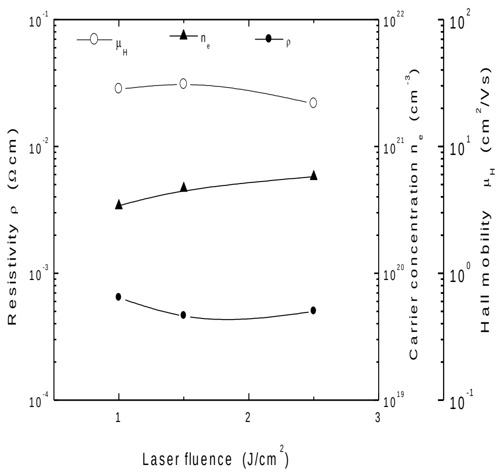

Figure.7 Effect of laser fluence on resistivity, carrier concentration and Hall mobility of AZO films deposited at, optimized target–substrate distance in 1 mTorr of oxygen ambient at room temperature.

rapidly with further increase in laser fluence from 1.5 - 2.5 J/cm^2. Initial decrease in the resistivity may be, due to the increase in carrier concentration or due to the improvement in the crystallinity of the films with the increase in the laser fluence (1.0-1.5 J/cm^2) as supported by x-rd data shown in figure 3. Slight increase in the resistivity may be due to the decrease in the mobility with the increase in laser fluence. Initial increase in the mobility is related with the improvement in the crystallinity with the increase in laser fluence from 1-1.5 J/cm^2 whereas; decrease in the mobility with increase in laser fluence (1.5-2.5 J/cm^2) is due to degradation of film quality as shown in figure 3.

3.4.Optical Properties:

3.4.(a) Effect of Distance between Target and Substrate 'h'.

Figure 8 shows the dependence of transmittance on 'h' in 300-800 nm range for the film deposited at 300 ^{o}C with laser fluence of 1.5 J/cm^2. Transmittance decreases with the increase in 'h'. All the films were highly transparent transmittance of these films varies between 80-90 %. The films deposited at minimum value of 'h' = 20 mm shows (maximum) average transmittance > 92%. Whereas for maximum value of 'h' =35mm showed minimum transmittance nearly 82 %. The decrease in the transmittance may be due to the increase in the film thickness for the films deposited for 'h' in the range 20 - 30 mm as shown in figure.1 The decrease in the transmittance for the films

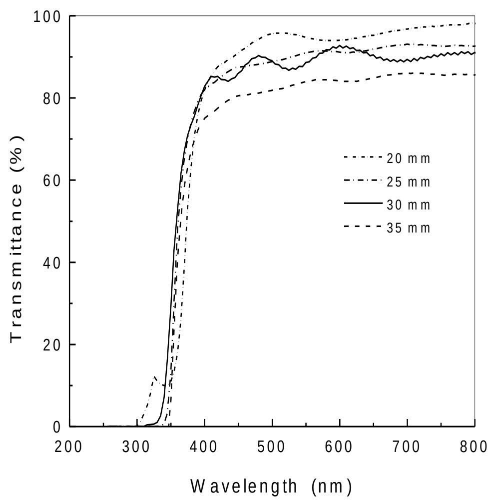

Figure. 8 Effect of distance between target and substrate 'h' on transmittance .

deposited h > 30 mm may be due to the degradation in the films quality caused by the reduction in the adhesion coefficient for source elements arriving at the substrate [20].This is supported by our XRD data as shown in figure 4.

3.4 (b) Effect of Laser Fluence

Dependence of transmittance (300-800 nm) on the laser fluence for the films deposited at 300 ^{o}C at h = 30 mm . All the films show high transmittance. Average transmittance was found to be in the range of 88-92%. Transmittance decreases as the laser fluence increases. The films deposited at low fluence showed highest transmittance and films deposited with highest laser fluence showed minimum transmittance.

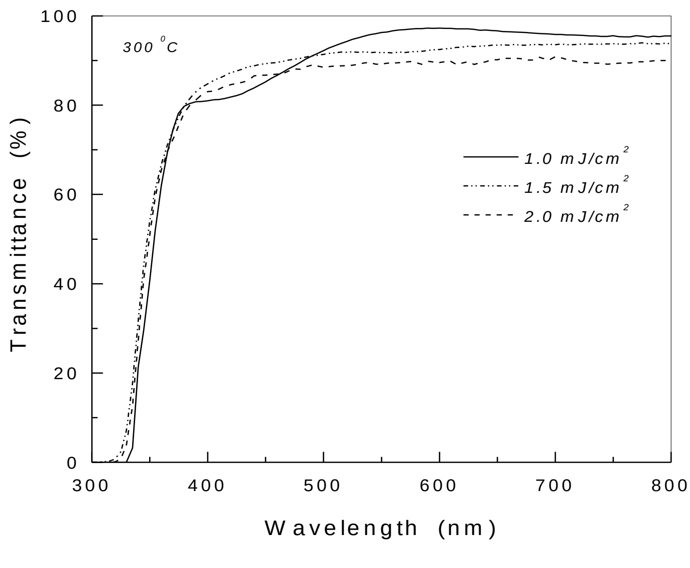

Figure. 9 Dependence of transmittance (300-800nm) on the laser fluence.

The decrease in the transmittance may be due to (i) the difference in the thickness of the films or (ii). increase in the film roughness. .

4. Effect of doping on Resistivity and Transmittance

Figure 10 shows the relationship between resistivity and transmittance as a function of

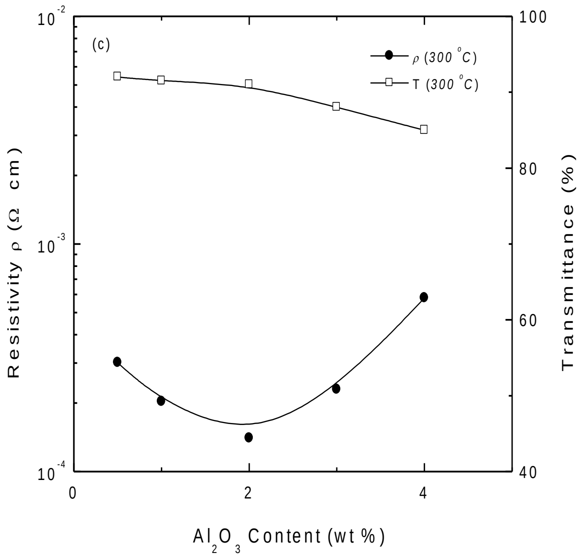

Figure. 10 Relationship between resistivity and transmittance as a function of dopant concentration

dopant (Al_2O_3) concentration for the films deposited at optimized values of 'h' = 30mm, laser fluence (1.5 J/cm^2) and film deposition temperature (300 ^oC)used in the present study.

It is observed that transmittance decreases continuously with the increase in dopant concentration whereas, resistivity decreases only upto 2wt % of dopant concentration and with further increase in dopant concentration increase in resistivity has been observed. Continuous decrease in transmittance and increase in the resistivity for Al_2O_3 concentration greater than 2 wt% is due to the degradation of films caused by the addition of Al_2O_3 impurity (Minami, 1990). Minimum resistivity (1.43×10^{-4} Ωcm) is found for the films doped with 2 wt% of Al_2O_3 .

Conclusions:

In this study we found that laser fluence , target –substrate distance and film deposition temperature strongly affects optical, electrical, and structural properties of AZO films significantly. Good quality highly conducting and transparent AZO thin films can be prepared at target–substrate distance value of 30mm and laser fluence value of 1.5 J/cm^2. An average transmittance about 90% in the visible range and a minimum resistivity of 1.43×10^{-4} Ωcm was obtained for AZO 2 wt% films prepared in 1 mTorr of oxygen pressure at 300 °C.

Acknowledgment

The author gratefully acknowledges the financial support of AIEJ, Japan and Professor R.M.Mehra (U.D.S.C) New Delhi for use full discussion for the present work.

.**References:**

1. K. L. Chopra, S. Major, D. K Pandya, D. Thin Solid Films .,102 , (1983) 1-183.
2. J. Hu., R. G Gordan,. J. Appl. Phys, 71, (1992) 880.
3. G. Newman,. phys. stat. sol. (b), (1981) 105.
4 G. Heiland, Z. Phys., 148 (1957) 15.
5. S.Major., A. Banerjee., A., K.L. Chopra,. Thin Solid Film. 108 (1983).33.
6. J. Hu., R. G Gordan .,Solar Cell, 30 , (1991) 437.
7. D. Laser, Thin Solid Films, 90 (1982) 317.
8. L. A. Ryabova., Ya. S. Savitskaya, Thin Solid Films, 2 (1968) 141.
9. H. Dislich., E. Hussmann, Thin Solid Films, **77** (1981) 129.
10 R.Kaur, A.V Singh, R.M .Mehra Journal of Non-Crystalline Solids, 352 (2006) 2565

11. F. Aktaruzzaman, G. L. Sharma., L. K. Malhotra. This Solid Films, 198 (1991) 67.
12. .S. Takata, T. Mianmi and H. Nanto, Thin Solid Films, 135 (1986) 183.
13. T. Minami, K. Ohashi and S. Takata, Thin Solid Films, 193/194 (1990) 721.
14. Akio. Suzuki, T. Matsushita, N. Wada, Y. Sakamoto and M. Okuda, Transactions Mat. Res. Soc. Jpn., 20 (1996) 526.
15. D. Chrisey and G. K. Hubler, Pulsed Laser Deposition of Thin Films~Wiley, New York, 1994.
16. Hiramatsu, K. Imaeda, N. Horio, and M. Nawata, J. Vac. Sci. Technol. A 16, 669 (1998)
17. C. Coutal, A. Azema and J-C. Roustan, Thin Solid Films, 248 (1996) 248.
18. J. P. Zheng and H. S. Kwok, Thin Solid Films, 232 (1993) 99.
19. Y. Ning, S. H. Cheng, S. B. Ge, Y. Chao. Z. Q. Gang. Y. X. Zhang and Z.G. Liu, Thin Solid Films, 307 (1997) 50.
20 Y. R. Ryu , S. Zhu, J. D. Budai, H. R. chandraseakhar, P. F. Miceli and H. W. White, J. Appl. Phys., 88 (2000) 201