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Al doped ZnO (AZO) films are fabricated by using sol-gel spin coating method and changes in electrical, optical and structural properties due to variation in film thickness is studied. AZO films provide c-axis orientation along the (002) plane and peak sharpness increased with film thickness is evident from XRD analysis. Conductivity (σ) of AZO films has increased from 2.34 (Siemens/cm) to 20156.27 (Siemens/cm) whereas sheet resistance (R_{sh}) decreases from 606300 (ohms/sq.) to 2.08 (ohm/sq.) with increase of film thickness from 296 nm to 1030 nm. Optical transmittance (T%) of AZO films is decreased from around 82% to 62% in the visible region. And grain size (D) of AZO thin films has been found to increase from 19.59 nm to 25.25 nm with increase of film thickness. Figure of Merit is also calculated for prepared sample of AZO. Among these four sample of AZO thin films, L-15 sample (having thickness in 895 nm) has provided highest figure of merit which is 5.49*10^-4 (Ω^{-1}). https://doi.org/10.1063/1.5023020

I. INTRODUCTION

Al doped ZnO (AZO) is considered as a promising candidate for transparent conductive oxide (TCO) due to its good opto-electronics properties. As transparent conductive oxide having low resistivity, high optical transmittance in visible wavelength range, it has wide application in optoelectronic devices.[1,2] In recent years ITO is commercially most popular TCO material but it is expensive and there is a possibility of scarcity of indium in future.[3,4] To find appropriate alternative of ITO, a group of materials have been investigated so far. This group containing zinc-oxide (ZnO), aluminum doped zinc-oxide (AZO), gallium doped zinc-oxide (GZO), fluorine doped tin oxide (FTO) etc. Among these ZnO films have good electrical and optical properties and chemically composite with low cost, non-toxic material. But when this ZnO films are doped with some impurities like Al, Ga then the resultant films provide much higher conductivity. Al doped zinc-oxide (AZO) is cheaper than Ga doped zinc-oxide. So all of these films AZO is the most superior alternative of ITO because it has good electrical and optical properties, containing nontoxic, abundant, inexpensive materials and low cost in fabrication.[5]

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Al doped ZnO films can be prepared by using several methods. Such as chemical vapor deposition, electron beam evaporation, sputtering, molecular beam epitaxy, pulsed laser deposition, spray pyrolysis, sol-gel etc. Among these methods sol-gel is more preferable than the others.[6] Sol-gel spin coating is easier, inexpensive process for depositing film on glass substrate.[7] Solution concentration, doping level, homogeneity can also be maintained easily during this process.

This study conducts with the electrical, optical and structural properties of AZO thin film deposited by spin coating with variation of film thickness to identify in which thickness AZO films provide better properties.

II. EXPERIMENTAL PROCEDURE

To prepare AZO solution zinc acetate dehydrate (Zn $(CH_3COO)_2 \cdot 2H_2O$) and aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$) were dissolved in a solution of 2-Methoxy ethanol. Then monoethanolamine (MEA) was added. There Zinc acetate dehydrate (Zn $(CH_3COO)_2 \cdot 2H_2O$), Aluminium nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$), 2-Methoxy ethanol and monoethanolamine was respectively used as chemical precursor, dopant precursor, solvent and stabilizer. The molar ratio of monoethanolamine (MEA) to zinc acetate is 1. The concentration of Al as a dopant is of 2 wt% with respect to Zn and the concentration of zinc acetate is 0.75 M. This solution was stirred on magnetic stirrer at 60-70^{0}C for 1 hour. A clear and homogeneous solution of AZO was left for aging for 24 hours. AZO films were deposited on the glass substrate using a spin coater. For deposition technique the SPS Spin 150 spin coater had been used with 3000 r.p.m. for 30 seconds. The sample with AZO films was put in the ED53 electric oven at 300 degree for 10 minutes and left for natural cooling for 10 minutes. Film thickness was varied by depositing several layers on the substrate. The process was repeated to obtain certain thickness with 5,10, 15, 20 layers and named as L5, L10, L15, and L20 respectively. Then these prepared thin film samples were annealed at 500 ^{0} C for 1 hour in the KLS 10/12 furnace.

In this study only the effect of changing thickness on the properties of the films was studied keeping doping concentration and annealing temperature constant.

III. RESULTS AND DISCUSSION

Bruker's Dektak XT Stylus Profiler was used to measure the thickness of prepared AZO thin film.

Figure 1 shows L-5, L-10, L-15 and L-20 AZO thin film sample had thickness of 296 nm, 585 nm, 895 nm and 1030 nm respectively.

GBC EMMA 147 X-Ray diffractometer (XRD) using CuKα radiation, λ=0.154 nm have been used to analyze structural properties of AZO thin film and from the obtained result grain size was

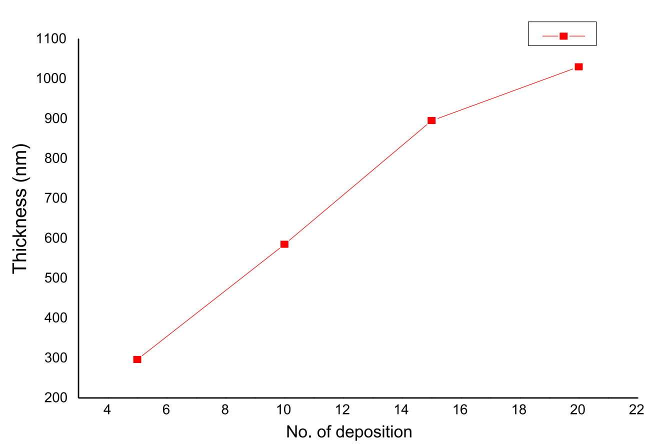

FIG. 1. Film thickness for the L-5, L-10, L-15 and L-20 AZO thin film sample.

studied in relation with film thickness. Four point probe method was used to measure the sheet resistance and conductivity of the prepared film. Optical transmittance of the film was measured by using Hitachi UH4150 spectrometer.

A. Structural characterization

Figure 2 provides the X-ray diffraction spectrum for L-5 (296 nm), L-10 (585 nm), L-15 (895nm) and L-20 (1030 nm) AZO thin film. In this XRD spectrum these L-5, L-10, L-15, L-20 samples provide the peak at diffraction angle of 34.8^0, 34.82^0, 34.85^0 and 34.99^0 which matches to card no ICDD-00-051-0037 for AZO. The 2θ peak angle refers to (002) plane having c-axis orientation. From previous research study it has been realized when the AZO film annealed below 500 ^{0} C there is no strong diffraction peak. That's why in this present context AZO film had annealed at 500 ^{0} C and strong diffraction peak has been found at (002) plane in c-axis orientation for all the samples.[8]

With increase of film thickness, the value of diffraction angle, 2θ increases slightly from 34.8^0 to 34.99^0 for L-5, L-10, L-15, L-20 samples. This happens due to the reduction of stress in the crystal grain which causes reduction of inter planar spacing.[9–11] According to grain boundary theory[12,13] during the initial stage of film growth the film consists of small crystallite. Stresses in small crystallites can be quiet high. When they coalesce a tensile stress is generated and the gap between them is decreased until cohesion begins to develop between the crystals with the film growth. At some point by increasing thickness of the film the interaction between them is strong enough to close the gap by elastic deformation of the crystallites of the film and thus stress is released.

Two additional peaks were also found approximately at 31.9^0 and 36.5^0 refereeing to (100) and (101) plane respectively for all four samples. For L-10 sample there is a peak shift at 36.99^0 referring to (101) plane. This can occur due to various reasons like strain contribution resulting from planar stress, temperature and zero drift from XRD. Strain can be observed for both compressive stress and tensile stress. Another reason for peak shift is zero error meaning that the sample is not calibrated at fixed position every time. If both the high and low angle peaks are shifted by the same amount it can be concluded that peak shift has occurred for zero error. For L-10 sample both the high and low angle peaks are shifted by the same amount. So it can be said that the shift occurred here for zero error.

For L-20 there is an additional peak at diffraction angle of 30.99^0 approximately. According to card no ICDD 00-002-1420, there is presence of Al_2O_3 in the L-20 sample. It can happen due to slight fluctuation of heating temperature in the oven or poor adhesion between substrate and solution.

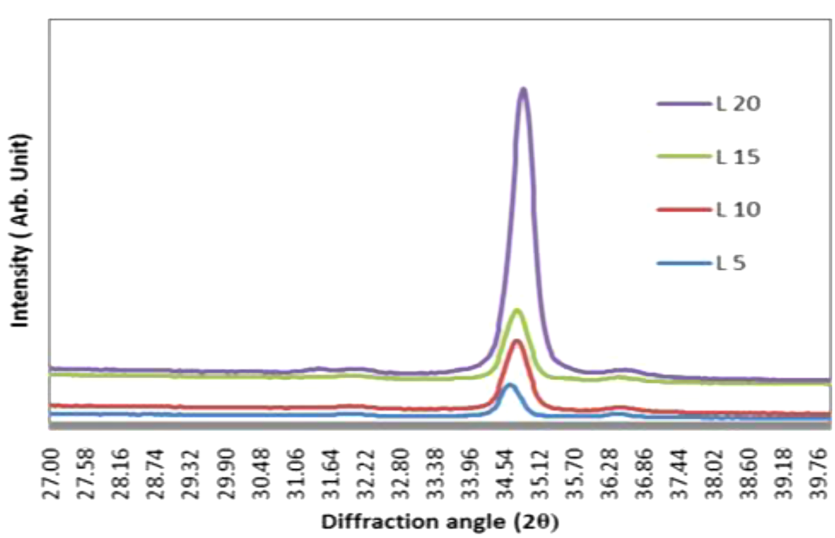

FIG. 2. XRD pattern respectively for AZO thin film with film thickness variation.

L-5, L-10, L-20 sample had FWHM (full width at half maximum) of respectively 0.42^0, 0.4^0, 0.39^0 and 0.33^0. Film strain is related to FWHM

$$\varepsilon = \frac{\beta cos\theta}{4} \tag{1}$$

Here β is the FWHM in radian. From Eq. (1) it is clear that stress in directly proportional to FWHM. So with the increase of film thickness as FWHM decreases the stress on the film also decreases. As the annealing temperature was kept unchanged for L-5, L-10, L-15 and L-20 sample its effect on crystalline properties were not studied.

Grain size is inversely proportional to this FWHM. By using Scherrer formula grain size can be calculated and this formula is:[14]

$$D = \frac{K\lambda}{\beta Cos\theta} \tag{2}$$

Here D is grain size, k is a constant and its value is 0.9. λ, β and θ are respectively X-ray wavelength, full width at half maximum (FWHM) of the (002) plane in radian and Bragg angle in degree respectively.

Samples having larger grain size and smaller value of FWHM at (002) plane provides uniform c-axis orientation and superior crystalline quality. From the XRD spectrum of L-5, L-10, L-15 and L-20 AZO thin film the calculated grain size is 19.59 nm, 20.82 nm, 21.38 nm and 25.25 nm respectively. Among these three AZO thin film samples the value of FWHM is gradually decreased but grain size increases with increase of film thickness. This indicates improvement of crystalline quality.[11,14] It can be considered that with increase of film thickness the structural property of film is improved. The effect of annealing temperature has not been studied and it was kept constant. The effect of defects are not being considered for calculating grain size. The SEM image was not obtained due to technical difficulties but following Eq. (1) it can be said that stress reduced as FWHM reduced. These AZO films also provide good step coverage.

Figure 3 shows L-5, L-10, L-15 and L-20 AZO thin film had grain size of 19.59 nm, 20.82 nm, 21.38 nm and 25.25 nm respectively.

B. Electrical characterization

The sheet resistance and conductivity of L-5 sample is respectively 606300 (ohms/sq.) and 2.34 (Siemens/cm). In Figure 4 L-10 (585 nm), L-15 (895 nm) and L-20 (1030 nm) AZO thin film had conductivity respectively 315.05 (Siemens/cm), 961.50 (Siemens/cm) and 20156.27 (Siemens/cm) where sheet resistance is gradually decreased in 148.43 (ohm/sq.), 18.58 (ohm/sq.) and 2.08 (ohm/sq.) with increase of film thickness. This indicates that among these samples of Al doped ZnO which sample having higher thickness is more conductive than the others. For four-point probe measurements resistivity can be calculated by using following equation:[6]

$$\rho = R_{sh}t \tag{3}$$

$$\text{Again } \rho = \frac{\pi tVF}{\ln(2)I} \tag{4}$$

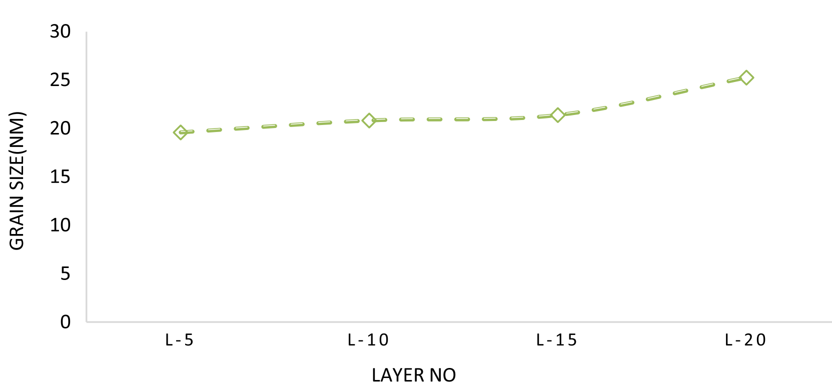

FIG. 3. Variation in grain size of Al-ZnO film with film thickness.

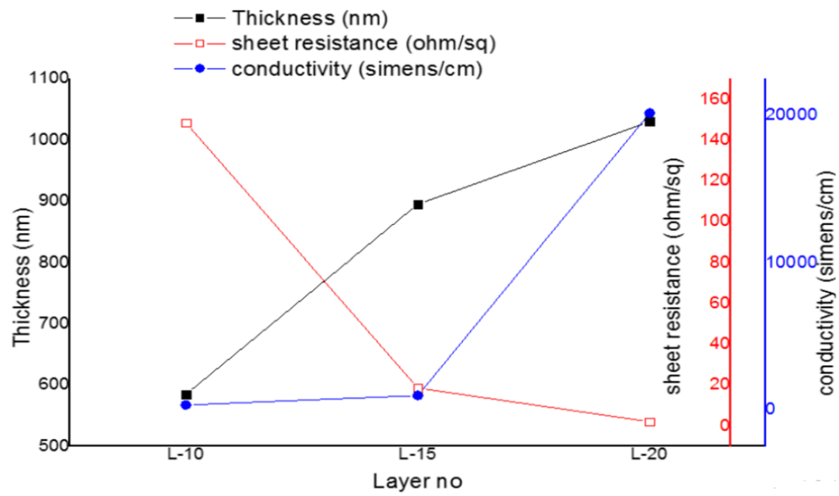

FIG. 4. Variation in sheet resistance and conductivity of Al-ZnO with film thickness.

Where ρ is resistivity (Ω-cm), R_{sh} is the sheet resistance (Ω/sq.), t is the film thickness, V is the voltage, I is the current, F is the correction factor.

From Eq. (3) it can be realized that sheet resistance has inverse relation with the film thickness assuming other parameter keeping constant. If the film thickness is higher, then sheet resistance is lower. This type of variation is shown at Figure 4 where L-20 (1030 nm) AZO film had lowest sheet resistance of 2.08 (ohm/sq.) and highest conductivity of 20156.27 (Siemens/cm) than the others.

Resistivity is constant for a particular sample as the given thickness and sheet resistance is constant. In this study as the thickness is varied the resistivity changes along with sheet resistivity. Specific conductance is defined as

$$k = 1/\rho \tag{5}$$

From Eqs. (3) and (5) it can be said that

$$k = 1/R_{sh}t \tag{6}$$

In this present context the sheet resistance of AZO thin film decreases much compared to increase of its thickness. So overall the conductivity increases.

C. Optical characterization

From Figure 5 it can be said that L-5 had maximum transmittance of approximately 82% between 900 nm and 770 nm wavelength. Below 770 nm wavelength the transmittance decreases gradually to 70% at 533 nm. Transmittance is very low from 500 to 380 nm wavelength. L-5 had high average transmittance of 78% between 900 nm to 533 nm which covers a considerably large part of the visible spectrum.

In case of L-10 sample maximum transmittance of 80% was observed between 900 nm to 861 nm wavelength which is slightly less than L-5 samples. Also transmittance of L-10 decreases faster with decrease of wavelength compared to L-5 sample. Below 596 nm the transmittance is less than 70% where as L-5 had transmittance lower than 70% for wavelength below 533 nm. The average transmittance is 76% between 900nm to 590 nm and if taken over 900 nm to 533nm it is 75.41%. Below 590 nm the transmittance reduces and becomes as low as 32% at 380 nm.

For L-15 sample the maximum transmittance is 77% occurring between 900nm to 818 nm. Below 818 nm wavelength the transmittance reduces more rapidly than the other 2 sample. The average transmittance between 900 nm to 659 nm is 74.6%. L-20 sample had considerably poor transmittance compared to previous samples. Its maximum transmittance is 62% at 900 nm which is not desirable. So from the optical results it can be said that the transmittance reduces with reducing

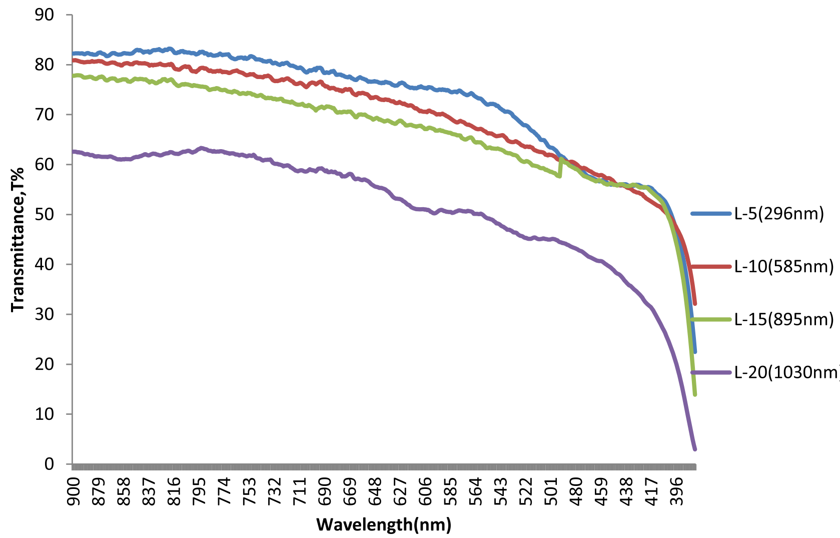

FIG. 5. Optical transmittance spectra of Al doped ZnO thin film with different film thickness.

wavelength irrespective of the thickness of the samples. However for samples with lower thickness the spectrum having desirable transmittance is wider. Transmittance also reduces with increasing thickness.

In several previous research studies on AZO thin films it has been noticed that this AZO film has optical transmittance near or above 80%.[9,15] This is closer to the transmittance spectra of the AZO films in this present context.

Optical transmittance can be expressed as:[15,16]

$$T = \frac{I}{I_0} = e^{-\alpha t} \tag{7}$$

where I_o is incident light on one side of the sample, I is the light leaving from the opposite side of the sample, the ratio of these two light is optical transmittance, T and α is absorption coefficient, t is the film thickness. This equation explains optical transmittance has inverse relation with the film thickness. Increase of film thickness causes absorption of more light as well as optical transmittance is decreased. This variation is observed in the above transmittance curve. Among these four samples the thinner film, L-5 AZO thin film had the highest average transmittance of 82%.

IV. PERFORMANCE EVALUATION OF Al DOPED ZINC OXIDE (AZO) THIN FILM AS TCO MATERIAL FROM EXPERIMENTAL DATA

Al doped zinc oxide (AZO) as TCO material require such an optimum thickness which providing both good electrical and optical property. To evaluate performance of TCO material an important parameter called figure of merit is used:[16,17]

$$\varphi_{tc} = \frac{T^{10}}{R_{sh}} \tag{8}$$

Where φ_{tc} is the figure of merit and it defines which sample provides better optical and electrical properties for a specific film thickness. T is the optical transmittance at 550 nm and R_{sh} is the sheet resistance.

Table I shows L-15 AZO film had highest value of figure of merit, φ_{tc}. Sample having higher value of figure of merit, φ_{tc} can be considered as good TCO material. Thus L-15 AZO thin film provides better optical and electrical properties than the other three.

TABLE I. Figure of merit for AZO thin film.

Sample no.	Film thickness (nm)	Sheet resistance (ohm/sq.) R_{sh}	Transmittance T%	Figure of merit φ_{tc} (Ω^{-1})
L-5	296	606300	72.12	6.27*10^-8
L-10	585	148.43	66.23	1.09*10^-4
L-15	895	18.58	63.23	5.49*10^-4
L-20	1030	2.08	48.99	3.82*10^-4

V. CONCLUSION

Fabricated Al doped ZnO thin film provides good electrical conductivity and high optical transmittance in visible wavelength. With increase of film thickness in this AZO film its electrical conductivity is increased but optical transmittance is decreased. Structural properties of these AZO films are also improved with increase of film thickness. L-20 AZO sample had highest conductivity of 20156.27 (Siemens/cm) but its optical transmittance is around 65% which is not satisfactory. An optimum film thickness is required for having both good electrical and optical properties as TCO material. Among the four prepared sample of AZO thin film L-15 which is 895 nm thick provides both better conductivity and optical transmittance. Which suggest film thickness need not to be much high than this 895 nm for AZO thin film as a good TCO material. It is difficult to keep constant the electric oven temperature always during fabrication at the time of heating the deposited film on glass substrate in the oven.

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