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Study of electrical and optical properties of Zr-doped ZnO thin films prepared by dc reactive magnetron sputtering

Satyesh Kumar Yadav[a], Satya Vyas[b]
Ramesh Chandra[c],G. P. Chaudhary[d] and S.K. Nath[e]
[a,b] UG students, [d,e]Department of Metallurgical and Materials Engineering
[c] Institute Instrumentation Centre
Indian Institute of Technology Roorkee
Roorkee 247667, INDIA
Email:[a]satyeshyadaviitr@gmail.com, [b]vyas.satya@gmail.com
[c] ramesfic@iitr.ernet.in, [d]chaufmt@iitr.ernet.in
[e] indiafmt@iitr.ernet.in,

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Abstract

This paper establishes DC reactive magnetron sputtering as synthesis process for Zr doped ZnO thin film. Zr can be doped in ZnO using various techniques. Some research groups have doped ZnO with Zr by radio frequency magnetron sputtering using target made of ZnO and ZrO_2 powder. Radio frequency has low rate of deposition because deposition takes place only in one of two half cycles. Uniform mixing of small amount of ZrO_2 powder in ZnO is expensive process as well as time consuming. To overcome the constraints, Zn and Zr metal target was used and film was made by DC reactive magnetron sputtering. Various parameters of the process was established by varying variables, such as sputtering power of the Zn and Zr, oxygen partial pressure in the chamber. Optimum flow rate of Argon is 16 sccm and Oxygen is 4 sccm. Sputtering power of 150 watt for Zn and 10 watt for the Zr gives good result. Films obtained are polycrystalline with a hexagonal structure and have preferred orientation along the c axis. Resistivity of the film is as low as 0.07 Ω-cm. Average transparency of film is above 85% in visible range.

Introduction

Thin films of ZnO got attention of researches as Transparent Conducting Oxide (TCO) because of its good conductivity and high transmittivity [1]. Transparent and conductive layers of tin oxide or indium oxide have found numerous applications because of their high stability, hardness and adherence to many substrates in comparison with metallic thin films which, for thicknesses less than 10 nm, are transparent but very fragile [2]. TCO finds application in optoelectronic devices, such as liquid crystal displays, organic light emitting diodes, and solar cells. As Transparent Conducting Oxide based on In and Sn got expensive, importance of the ZnO increased [3].

A lot of work is in progress to increase conductivity of the ZnO film. Work includes doping of various elements in ZnO by different methods. Doping of Zr in ZnO has been done using radio frequency magnetron sputtering. Target used was pellet made by mixing ZnO and ZrO_2 powder in different ratio [4].

This paper is aimed to establish DC reactive magnetron sputtering as manufacturing process for Zr doped ZnO. Constraints as uniform mixing of the small amount of ZrO_2 and low rate of deposition due to deposition taking in only one half cycle is addressed by making film by DC reactive magnetron sputtering using Zn and Zr metal targets.

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Experimental details

Zr doped ZnO thin film was prepared by DC reactive magnetron sputtering on glass substrate. Target used was metal Zn and Zr (2 inch diameter). Sputtering chamber was evacuated to base pressure of 10^{-6} torr using rotary and turbo pump one after the other. Glass substrate was heated to 200°C. Ratio of Oxygen to Argon flow rate is maintained at different level (as shown in table) 18:2, 16:4 and 14:6. Sputtering pressure is maintained at 15 mtorr. Sputtering powers ratio for Zr and Zn is varied (as shown in table). Sputtering was carried out for 30 minute for all samples [5-7]. Fig. 1, shows schematic arrangement of target and substrate in sputtering chamber. Sputtering yield of Zr at 500 eV bias is .65 and that of Zn is 5.103 [5].

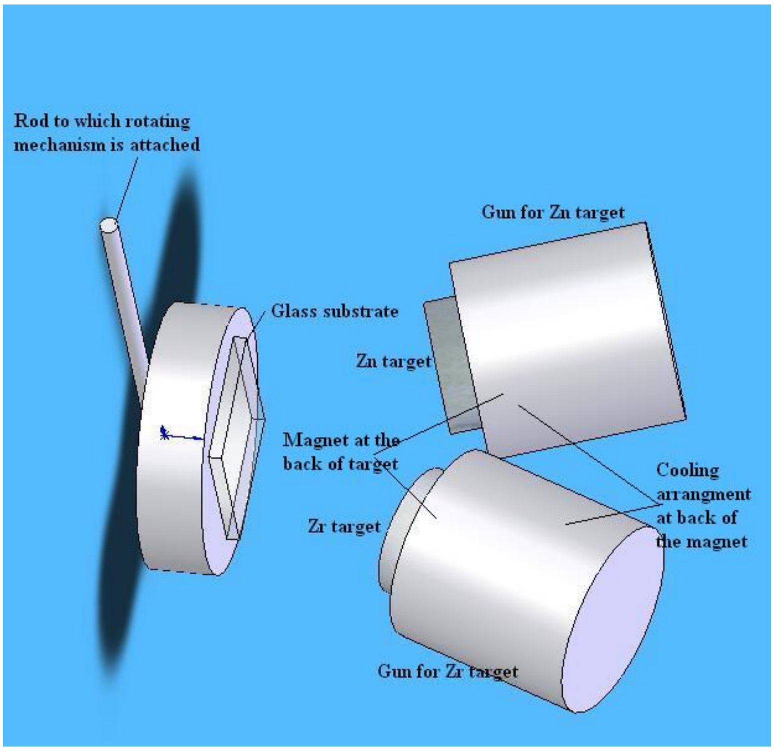


Fig. 1 Setup of the DC reactive magnetron sputtering

Table 1. Sputtering parameters

Sample	Power Zr Watt	Power Zn Watt	Power Ratio Zn/Zr	Flow rate Ar sccm	Flow rate O_2 sccm
S-1	31.5	99.88	10/3	18	2
S-2	47.7	100.5	10/5	18	2
S-3	39.2	101.3	10/4	18	2
S-4	37.16	98	10/4	18	2
S-6	20.02	147.9	15/2	16	4
S-7	14.95	158.4	16/1.5	16	4
S-8	9.9	149.6	15/1	16	4
S-9	25.8	153.6	15/2.5	16	4
S-10	30.39	153	15/3	16	4
S-11	20.22	127.1	12.5/2	14	6
S-12	10.03	154.8	15.5/1	14	6

Transparency of the film was measured using transmittance curve of UV-Visible Spectroscopy. Transmittance curve is also used to find film thickness. AFM (Atomic force microscopy) is used to find roughness of the film. Resistivity of the film is found using four probe technique. XRD spectra confirm presence of ZnO and its growth along c axis. EDAX gives elemental composition of the film deposited [9].

Results and discussion

Fig. 2 shows XRD pattern of various sample peaks correspond to plane (002). This confirms that ZnO crystal has grown along c axis which is the 002 plane. Shift in the peak by 0.2 to 0.4 degrees confirms the assimilation of Zr in ZnO crystal structure. Most samples have only one peak corresponding to (002) plane. This indicates that all the Zr is assimilated inside the ZnO and has not precipitated on the grains. Samples S-2, S-3 and S-6 other peak of Zr shows some deviation due to excessive Zr, which has precipitated out [10].

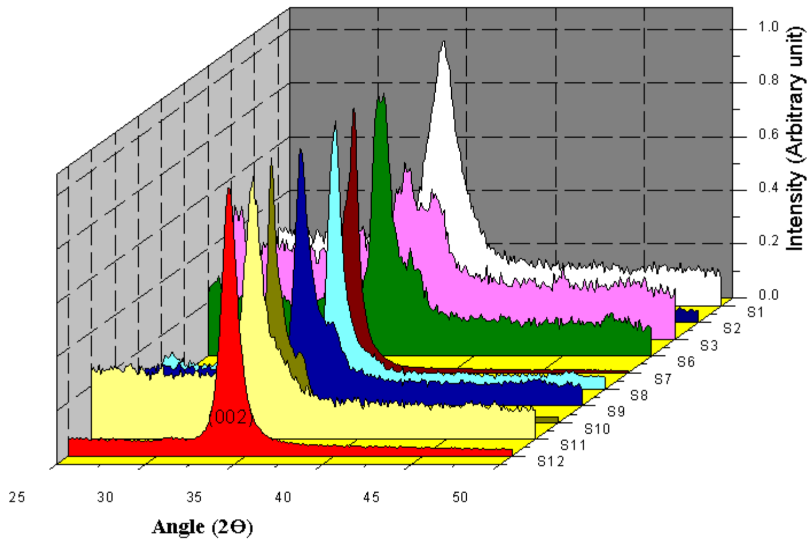
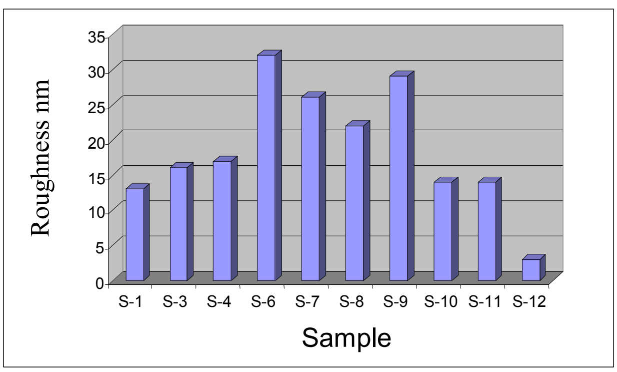


Fig. 2 XRD spectra of various sample peaks correspond to plane (002)

AFM (Atomic force microscopy) is used to find film roughness shown in Fig. 3. Calculated root mean square surface roughness of film is about 15 nm for most of the surfaces. This shows that the film has a compact and relatively smooth surface implying a good crystallinity [11].



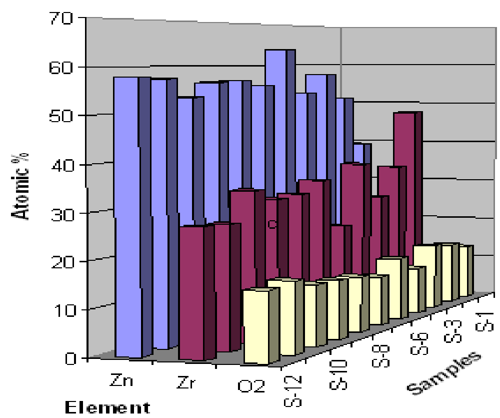


Fig. 3 Surface roughness

Fig. 4 Atomic percentages of various samples

Energy Dispersive Spectroscopy (EDS) is done to find percentage of various elements present in the film shown in Fig. 4. Ratio of atomic percentage of Zn to Zr increases as ratio of power applied in Zn and Zr increases. Atomic percentage of Oxygen increases as O_2 to Ar ratio in gas increases. If we consider the formula ZnO and ZrO_2, every sample is Oxygen deficient this is one of the reason for increased concentration of charge carriers [12].

Fig. 5 shows transmittance of the samples measured by Ultraviolet Visible Spectroscopy. Average absorption of most of the films is above 80% that shows films grown by this technique are transparent.

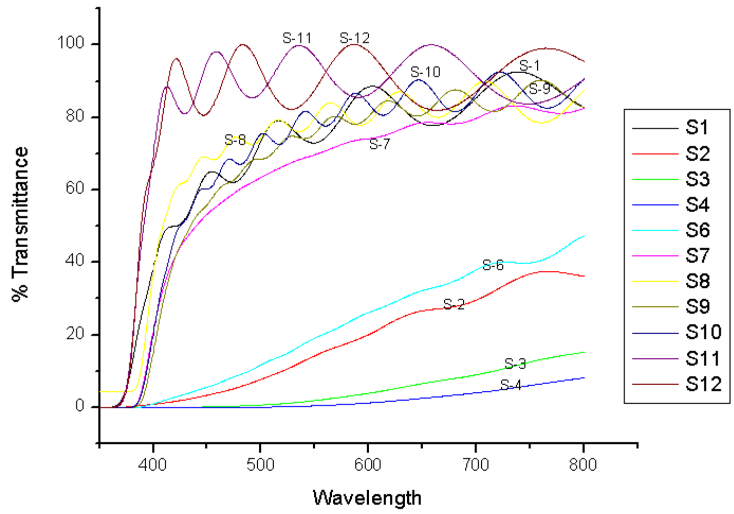


Fig. 5 Variation of transmittance with wavelength

Film thickness was found using formula given below, this formula is only applicable for films that are more than 80% transparent [8]

$$n=[N+(N^2-n_o^2 n_1^2)^{1/2}]^{1/2}$$

where $N=\dfrac{n_o^2+n_1^2}{2}+2n_0 n_1\dfrac{T_{max}-T_{min}}{T_{max}T_{min}}$

$$t=\frac{M\lambda_1\lambda_2}{2(n(\lambda_1)\lambda_2-n(\lambda_2)\lambda_1)}$$

Samples	thickness nm
S-1	891.486
S-10	988.934
S-11	781.546
S-12	653.78

n(λ_1)- refractive index at wavelength λ_1
n(λ_2)- refractive index at wavelength λ_2
λ_1 – one of two wavelength chosen in nm
λ_2- second wavelength in nm
n_o- refractive index of air
n_1- refractive index of the substrate
T_{max}- Max transparency (fraction) i.e. transparency at upper envelope
T_{min}- Minimum transparency (fraction) i.e. transparency at lower enve
t- film thickness
M- 1, for consecutive peaks (maxima or minima)

Resistivity was calculated using four probe technique [13]. Among the lowest resistivity measured of sample that have transmittivity above 85% resistivity of sample S-1 is 0.07692 Ω-cm and S-10 is 0.0849 Ω-cm. Decreased resistivity is due to increases carriers concentration carrier originate from intrinsic donors by lattice defects or extrinsic dopants or both [14-15]. In our case, the intrinsic donors are oxygen vacancies and metal atoms (Zn or Zr or both) on interstitial lattice sites, and the extrinsic doping is the substitution of Zr for Zn in ZnO structure. Two free electrons will be produced for every Zn replaced, which contributes to the electric conduction of the films as free carriers.

Conclusion

The films are polycrystalline with a hexagonal structure and a preferred orientation along the c axis. Conductivity of thin film improved by doping ZnO with Zr. Optimal ratio of flow rate of Ar to O_2 is 16:4. DC magnetron sputtering is more efficient in terms of rate of deposition than radio frequency magnetron sputtering. DC magnetron sputtering using metal target avoids time consuming and expensive process of mixing ZnO and ZrO_2 powder.

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