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The Role of Air Annealing On the Structural and Electrical Properties of Zinc Oxide (Zno) Thin Film Deposited By Rf Sputtering Technique

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Abstract: Transparent conducting Zinc Oxide (ZnO) thin films with an average thickness of **130.5** nm were deposited on glass substrate at room temperature by RF sputtering technique. Three of the samples were then annealed in open air at **1500**C, **3000**C and **4500**C respectively. The fourth sample is reserved as the as-deposited or reference sample. The structural and electrical properties of the films were studied using X-ray diffraction and four-point probe technique. The XRD analysis of the annealed samples shows that they are poly crystalline with prepared orientation of [**002**], [**102**] and [**103**] planes. The spectra of the as-deposited sample appeared with a peak at [**002**] plane with low intensity. The as-deposited sample was found to have a resistivity of **11**Ω.cm while that of the annealed samples lies between **1.2** Ω.cm to **5.6** Ω.cm. Other parameters calculated include the sheet resistance, Zn-O bond length, the figure of merit, strain and the stress.
Keywords: ZnO, Air annealing, Sputtering technique, Film stress, Bond length.

INTRODUCTION

Presently, nano crystalline materials in the form of thin films have opened new chapter in the field of electronic applications, since material properties could be changed by changing the crystallite size and/or thickness of the film. Development of such materials, whose structural and electrical properties could be controlled, will be useful in many ways. For example, optoelectronic devices, particularly solar energy conversion devices could be modified accordingly. The synthesis of binary metal chalcogenide of groups II–VI semiconductors such as ZnO in a nano crystalline form has been a rapidly growing area of research due to their important non-linear optical properties, luminescent properties, quantum-size effect and other important physical and chemical properties.

The properties of materials prepared by different methods are critically dependent on the nature of preparation technique and subsequent heat treatments like annealing in air, vacuum or different gaseous environments like H_2, N_2, Ar, etc.

Zinc oxide (ZnO) is an inexpensive strategic material for various photonic applications. As one of the most important binary II-VI compounds, ZnO is a direct semiconductor of wurtzite structures that is suitable for short wavelength optoelectronic applications [1, 2]. ZnO exhibits a direct bandgap of 3.3 to 3.37 eV at room temperature and efficient radiative recombination. Its large exciton binding energy of 60 meV which is 2.4 times higher than that of gallium nitride (GaN), makes it transparent in visible light and operates in the UV to blue wavelengths, paves the way for an intense near band edge excitonic emission at room and even higher temperatures [3, 4]. ZnO thin films presents many remarkable characteristics due to their large bond strength, good optical quality, extreme stability of excitons and excellent piezoelectric properties. For this reason, ZnO thin films have many potential applications in various technological domains such as transparent conducting films/electrodes in display devices and solar energy cells, surface and bulk acoustic wave devices (SAW) and acoustic-optical devices, light emitting diodes (LEDs) and laser diodes (LDs).

ZnO thin films have been prepared by a variety of deposition techniques such as rf sputtering [5-8], Spin coating [9], Spray pyrolysis [10], Electrochemical deposition [11, 12], Sol-gel [13, 14], Thermal evaporation [15], SILAR [16, 17] and Aqueous Chemical Growth method [18].

In this contribution, thin films of ZnO were

deposited on glass substrate by rf sputtering technique. Three of the four samples were annealed in open air to analyze their structural electrical properties. Sputtering offers a wide range of advantages, such as easy adaptation to large-scale and reproducible manufacturing. After all annealing is known to improve crystalline qualities conductivity of thin films [4].

MATERIALS AND METHODS

Substrate cleaning

Commercially available corning glass 7059 micro slides of dimensions 25.4mm ×76.2mm × 1.2 mm were boiled in chromic acid for 2 hours at 100^{o}C in an ultrasonic bath, boiled in dilute hydrogen peroxide solution for 15 minutes, rinsed in acetone, cleaned with double distilled water and finally dried with flowing Nitrogen gas and placed in the sputtering chamber.

ZnO thin film formation

After evacuating the chamber to a base vacuum of 1×10^{-5} torr, argon/oxygen of (4N purity) gas mixture was fed to the system. The ZnO target (99.99% pure) of 4 cm in diameter was sputtered in pure argon/oxygen atmosphere for about 5 minutes to remove the surface layer of the target before the deposition of the film. ZnO films were deposited on the glass substrates at room temperature to a film thickness of 130.5 nm. The RF power used was 60W, target to substrate distance was constantly kept at 7cm.This deposition was carried out under argon/oxygen gas flow of 10 sccm.

There were four samples from which 3 were annealed in open air for 60 minutes at 150^{0}C, 300^{0}C and 450^{0}C. The fourth sample was reserved as the reference or as-deposited sample.

Characterization of ZnO thin films

The thickness of the deposited films was measured using Veeco Dektak 150 profilemeter. The crystal structure of the films was inspected using an X-ray diffraction performed in $2\theta/\omega$ at a voltage of 45kv and a current of 40 mA. The sweeping angle is 20 to 80 degrees, the scan speed is 0.8 degrees/minute at a scan step of 0.02, employing a $Cu\,k\alpha\,tube$ ($\lambda = 0.1540598\,nm$) radiation. The electrical analysis of the samples was carried out using four-point probe.

RESULTS AND DISCUSSION

XRD studies

Figure 1 shows XRD pattern for the as-deposited as well as the annealed samples. This XRD spectra reveal that all the annealed thin films were polycrystalline with hexagonal structure (JCPDS 36-1451) [19]. There are no visible peaks for the as-deposited sample except that of peak [002] which appeared with low intensity. An improvement in the XRD structure can be noticed in the structure of the annealed samples. This indicates that annealing can enhance the structure of thin film as sizes of grains on the surface increases [20]. The diffraction peaks of the annealed samples are indexed as (002) plane at 2θ = 34.02^{0}, 34.38^{0} and 34.43^{0} respectively. The peak position and the intensity are in accordance with the JCPDS card number #01-074- 9942. The XRD patterns of all the annealed samples indicated enhanced preferred orientation along the c-axis.

The grain size was calculated using Debye-Scherrer's formula [21, 22] given by Eq. (1).

$$d = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

where "d" is the grain size or crystallite size, 'λ' the wavelength of the X-rays (1.5405Å), 'θ' the diffraction angle, and β is the full width at half maximum of (002) peak of the XRD data.

The lattice constants a and c, for a hexagonal structure are calculated by [16] using Eq. (2);

$$d_{hkl}^2 = \left(\frac{4(h^2+k^2+hk)^2}{3a^2} + \frac{l^2}{c^2}\right)^{-1} \quad (2)$$

where d is the interplanar space and h, k, l are Miller indices.

The strain (ε) and stress (σ) in the film, along the c-axis were found to be within an acceptable range by using Eq. (3) and Eq. (4) [22].

$$\varepsilon = \frac{c_{film}-c_{bulk}}{c_{bulk}} \quad (3)$$

$$\sigma = 2.33\times10^{11}\left(\frac{c_{film}-c_{bulk}}{c_{bulk}}\right) \quad (4)$$

where c_{film} and c_{bulk} (5.2 Å) are the lattice parameters of the film and unstrained ZnO respectively.

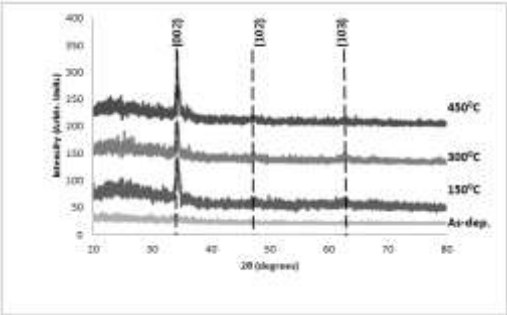

Fig-1: XRD pattern for as-deposited and the annealed samples

The calculated lattice constants are given in table 1. These lattice constants are seen to be in an acceptable range compared with those measured by [12-14] and also in agreement with lattice constants of ZnO Zincite phase existing in the literature of ASTM card: a =3.2648Å and c =5.2194 Å. The calculated d-spacing is also within the range of JCPDS data (36-1451) for (002) planes given as 2.6049.

The slight variations seen in d-spacing could be due to the interstitial zinc and it suggests that the unit cell might be elongated along the c-axis, and there is stress in the plane. The FWHM of the as-deposited sample stood at 0.5760. The FWHM increases with increase in the annealing temperature for the annealed samples. The grain size (D) for the as-deposited sample is 2.5199. Grain size increases with increase in the annealing temperature for the annealed samples. An increase in the FWHM indicates a degradation in the crystal quality [23]. The Zn-O bond length was also calculated [22] using Eq. (5) and Eq. (6).

$$L = \sqrt{(\frac{a^2}{3} + (\frac{1}{2} - u)^2)c^2} \quad (5)$$

$$u = \frac{a^2}{3c^2} + \frac{1}{4} \quad (6)$$

Table-1: Grain size and FWHM for as-deposited sample and samples annealed in air

Sample	FWHM(2θ)	Crystallite size (nm)	2θ (002) Peak only	d-spacing	Lattice parameters a and c (Å)	Bond Length (L)(Å)	Strain(ε) $\times 10^{-2}$	Stress(σ) Gpa
As-deposited	0.5760	129.82	34.40°	2.60	a=3.18 c=5.18	2.11	-0.38	8.9
Annealed at 150^0C	1.1520	61.94	34.02°	2.63	a=3.23 c=5.10	2.15	-0.19	4.5
Annealed at 300^0C	0.6720	109.77	34.38°	2.61	a=3.19 c=5.15	2.13	-0.96	2.2
Annealed at 450^0C	0.4800	158.92	34.43°	2.60	a=3.18 c=5.20	2.14	0	0

Electrical resistivity and sheet resistance

Table 2 shows the resistivity and the sheet resistance of the ZnO thin films deposited by RF sputtering technique. According to the table, the as-deposited sample exhibits the highest resistivity of 11 Ω.cm. The resistivity of the annealed samples varies with the annealing temperature. Decrease in resistivity for the annealed samples as compared with the as-deposited samples indicates the semiconducting nature of the samples. Resistivity of the TCO film depends strongly on the chamber oxygen pressure as well as the stoichiometry of the film. The electrical resistivity of thin films may also be affected by isotropic background scattering (arising from phonons and point defects), external surface scattering and grain boundary scattering [22].

The sheet resistance of the samples is also displayed in table 2. The as-deposited sample shows the highest sheet resistance of 4.99 Ω. Sheet resistance varies for the annealed samples. The high sheet resistance observed for the as-deposited sample and the sample annealed at 150^0C could be attributed to surface scattering and the decrease in carrier concentration [24]. For these films, more defects act as scattering centers which results in the formation of trapping states capable of trapping carriers and thereby immobilizing them. This reduces the number of free carriers available for electrical conduction.

It has also been suggested that a decrease in sheet resistance with respect to increase in annealing temperature may be due to the better crystal orientation of the sample [25]. It is known that undoped ZnO thin films generally exhibit n- type conductivity, the value of which depends on the deposition parameters [26].

The suitability of transparent conducting

oxides (TCOs) for optoelectronic applications can be quantified by a factor known as the figure of merit (ϕ) which is a combination of high electrical conductivity and low absorption (reported elsewhere) of visible light, calculated using Eq. (7) [23]. The as-deposited sample exhibited the lowest figure of merit while the sample annealed at 300^{0}C exhibited the highest.

$$\phi \frac{1}{\alpha\rho} \quad (7)$$

where α is the absorption coefficient at 550 nm and ρ the electrical resistivity.

Table−2: Sheet resistance (R_S) and resistivity of as-deposited sample and samples annealed in air

Annealing Temperature(^{0}C)	Resistivity (Ω.cm)	Sheet resistance (R_s)Ω	Figure of merit (ϕ)(Ω^{-1})
As-deposited	11.0	4.99	0.99×10^{-6}
150	5.6	2.27	2.05×10^{-6}
300	1.2	0.544	3.29×10^{-6}
450	1.8	0.816	1.5×10^{-6}

CONCLUSIONS

From the above studies, it is concluded that the ZnO thin films deposited by RF sputtering technique at room temperature and annealed at various temperatures have wurtzite crystalline structure with preferential orientation along the c-axis. The magnitude of the figure of merit shows that these films can be used for optoelectronic applications.

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REFERENCES

1. Shakti N, Gupta PS. Structural and optical properties of sol-gel prepared ZnO thin film. Applied Physics Research. 2010 Apr 20;2(1):19.
2. Alias MF, HKh A, Aljarrah RM. The role of thickness on the structural and electrical properties of DC magnetron sputtered nano ZnO thin films. Journal of Electron Devices. 2012 Jun;14:1178-85.
3. Şenay V, Pat S, Korkmaz Ş, Aydoğmuş T, Elmas S, Özen S, Ekem N, Balbağ MZ. ZnO thin film synthesis by reactive radio frequency magnetron sputtering. Applied Surface Science. 2014 Nov 1;318:2-5.
4. Zulkifli Z, Sharma S, Shinde S, Kalita G, Tanemura M. Effect of annealing in hydrogen atmosphere on ZnO films for field emission display. InIOP Conference Series: Materials Science and Engineering 2015 (Vol. 99, No. 1, p. 012030). IOP Publishing.
5. Viswanathan K, Shyju TS, Ramachandran D, Pradhaban G. Electric properties of ZnO thin films by RF Magnetron sputtering technique. Materials Today: Proceedings. 2016 Dec 31;3(6):1548-52.
6. Kumar GA, Reddy MR, Reddy KN. Structural and Optical properties of ZnO thin films grown on various substrates by RF magnetron sputtering. InIOP Conference Series: Materials Science and Engineering 2015 (Vol. 73, No. 1, p. 012133). IOP Publishing.
7. Shun-Fa H, Li W. PZT Thin Films Deposited by RF Magnetron Sputtering. Applied Mechanics and Materials. 2013; 302: 8-13.
8. Gonçalves R. S, Petrucio B and Cunha F. Optical and structural properties of ZnO thin films grown by magnetron sputtering: effect of the radio frequency power. Thin Solid Films. 2016; 616: 265-269.
9. Chaitra U, Kekuda D, Rao KM. Effect of annealing temperature on the evolution of structural, microstructural, and optical properties of spin coated ZnO thin films. Ceramics International. 2017 Jun 15;43(9):7115-22.
10. Gencyilmaz O, Atay F, Akyuz I. Influence of Thermal Process on Physical Properties of ZnO Films Prepared by Spray Pyrolysis. Acta Physica Polonica, A.. 2014 Dec 1;126(6).
11. Tazangi FE, Rahmati A. Characteristics of Electrodeposited ZnO Nanostructures: Size and Shape Dependence. Armenian Journal of Physics. 2016 Mar 19;9(1):20-8.
12. Hassiba R, Rafiaa K, Abed A, Mokhtar, G and Faycal, D. Electrodeposition and characterization of ZnO thin films using sodium thiosulfate as an additive for photovoltaic solar cells. Journal of Semiconductors. 2017; 38 (5): 1-7.
13. Mehmet Y. Characteristic properties of spin coated ZnO thin films: the effect of Ni doping. Phys. Scr. 2014; 89: 1-7.
14. Plugaru R and Plugaru N. Assessment of structural, optical and conduction properties of ZnO thin films in the presence of acceptor impurities. J. Phys Condens. Matter. 2016; 28: 1-11.
15. Farzana C. Influence of thickness variation on the optical properties of ZnO thin films prepared by thermal evaporation method. Journal of Electron Devices. 2011; 10: 448-455.
16. Raidou A, Aggour M, Qachaou A, Laanab L, Fahoume M. Preparation and Characterization of ZnO Thin Films Deposited by SILAR method. M. J. Condensed Matter volume. 2010; 12 (2): 125-130.
17. Mitra P and Mondal S. Structural and Morphological Characterization of ZnO thin Films Synthesized by SILAR. Progress in Theoretical and Applied Physics. 2013; 1: 17-31.

18. Mammah S I, Opara F E, Sigalo F B, Ezugwu S C, Ezema F I. Effect of Concentration on the Optical and Solid-State Properties of ZnO Thin Films Deposited by Aqueous Chemical Growth (ACG). Method Journal of Modern Physics. 2012; 3: 947-954.
19. Sahal MB, Hartiti BA, Ridah AM, Mollar B, Mari B. Structural, electrical and optical properties of ZnO thin films deposited by sol–gel method. Microelectronics Journal. 2008; 39: 1425– 1428.
20. Akbar Z, Marzieh S, Samira D and Mahdieh S. Effect of temperature and period of post-annealing on the optical properties of ZnO Thin films. Armenian Journal of Physics. 2010; 3 (4): 305-311.
21. Abdullahi S, Momoh M, Isah KU. Growth mechanism and optical properties of zinc oxide thin film. International Journal of Renewable Energy Technology. 2014 Jan 1;5(2):94-106.
22. Muchuweni E, Sathiaraj TS, Nyakotyo H. Synthesis and characterization of zinc oxide thin films for optoelectronic applications. Heliyon. 2017 Jan 4;3(4):e00285.
23. Camacho J, Castro-Rodríguez M R, Iribarren A, Chan y E, Díaz A. Duarte M and Sánchez SP. Structural, optical and electrical properties of ZnO thin films grown by radio frequency (rf) sputtering in oxygen atmosphere. International Journal of the Physical Sciences. 2011; 6(29): 6660-6663.
24. Jain A, Sagar P and Mehra. Changes of structural, optical and electrical properties of sol-gel derived ZnO films with their thickness. Materials science, Poland. 2007; 25 (1): 1-5.
25. Rakhesh V and Vaidyan VK. Effect of substrate temperature and post deposited annealing on the electrical and photoluminescence characteristics of Zinc Oxide films deposited by spray pyrolysis. Journal of Optoelectronics and Biomedical Materials. 2009; Vol. 1 (3): 281 – 290.
26. Suchea M, Christoulakis S, Katharakis M, Vidakis N, Koudoumas E. Influence of thickness and growth temperature on the optical and electrical properties of ZnO thin films. Thin Solid Films. 2009; 517: 4303–4306.