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Research Article

Comparative Studies on Thin Film of Zinc Oxide (ZnO) Deposited by Spray Pyrolysis and RF Sputtering Technique

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Abstract: Thin films of ZnO were deposited on corning glass (by rf sputtering and spray pyrolysis) and annealed at 573 and 673 K respectively. It has been noted that the samples deposited by Spray pyrolysis have an average transmittance, refractive index and extinction coefficient as 80% to 90%, 1.33 to 1.44 and 13.11 to 27.52 respectively. While those deposited by sputtering method have 34% to 80%, 1.51to 1.58 and 0.11 to 0.37. The XRD patterns of the samples shows that they are polycrystalline. Other optical parameters analyzed include the refractive index (n), absorption coefficient (α) and the extinction coefficient (k).
Keywords: Zinc Oxide, Spray pyrolysis, RF Sputtering, Optical properties, Structural properties.

INTRODUCTION

Transparent conducting oxides (TCOs) are electrical conductive materials with a comparably low absorption of light. They are usually prepared with thin film technologies and used in opto-electrical devices such as solar cells, displays, opto-electrical interfaces and circuitries. Glass fibers are nearly lossless conductors of light, but electrical insulators; silicon and compound semiconductors are wavelength dependent optical resistors (generating mobile electrons), but dopant dependent electrical conductors. Transparent conducting oxides are highly flexible intermediate states with both these characteristics. Their conductivity can be tuned from insulating via semiconducting to conducting as well as their transparency adjusted. As they can be produced as n-type and p-type conductivities, they open a wide range of power saving opto-electrical circuitries and technological applications [1].

Nowadays Zinc Oxide (ZnO) thin films are investigated as transparent conductive electrodes for use in optoelectronic devices including flat displays, thin films transistors, and solar cells because of their unique optical and electrical properties [2].

Zinc oxide is a unique material that exhibits semiconducting and piezoelectric dual properties. In addition, ZnO is a wide band-gap (3.37 eV) compound semiconductor that is suitable for short wavelength optoelectronic applications. The high exciton binding energy (60meV) in ZnO crystal can ensure efficient excitonic emission at room temperature. It is transparent to visible light and can be made highly conductive by doping. It is a versatile functional material that has a diverse group of growth morphologies, such as nanocombs, Nano rings, Nano helixes/Nano springs, Nano belts, nanowires and Nano cages [3-4].

ZnO thin films have been grown by various deposition techniques such as thermal oxidation of Zinc [5-6], thermal evaporation [7], [4] PLD [8], Sol-gel [9-10] Hydrothermal method [11] chemical bath deposition [12Ouerfelli] Pulsed spray pyrolysis [13-14], electron beam evaporation [15], atomic layer deposition [16-18], DC sputtering [19] and RF sputtering [20-23].

In this paper, we compare the structural and optical properties of ZnO thin films deposited by rf sputtering and spray pyrolysis.

MATERIALS AND METHODS

A. Substrate preparation by rf sputtering

Before the deposition, the substrates were kept in a dilute chemical detergent solution at 100°C in ultrasonic bath for 10 minutes to remove oils and protein molecules and rinsed with double distilled water to remove possible left detergent contaminants. To

remove organic contaminants, the substrates were boiled in dilute hydrogen peroxide- (H2O2) solution for 15 minutes and were later dried with nitrogen gas before being introduced into the sputtering chamber.

B. Thin film deposition:

Zinc Oxide thin films of approximately 75 nm in thickness were deposited onto corning glass (7059) substrate using an RF power of 60W. A Zinc Oxide target with 4N purity and 4cm in diameter was located on the cathode, which was about 7cm from the substrate mounting plate. The deposition was carried out at room temperature. Prior to deposition, the chamber was evacuated to 4.6×10^{-3} mbar. For plasma formation, research grade argon with 4N purity was used at a pressure range of 10^{-2} -10^{-1} mbar, oxygen was also added to facilitate the formation of ZnO on the substrate. Other deposition parameters that were kept constant include the deposition temperature, oxygen/argon flow rate and the sputtering RF power. The details of the deposition parameters are shown on table1.

C. Preparing precursor solution for spray pyrolysis

To obtain precursor solution for deposition 1.1g of zinc acetate were poured into a cleaned beaker. 15ml of distilled water were added into the beaker.30ml of ethanol was also added into solution. 5ml of acetate acid and 50ml acetone were poured into the solution. Allow the solution to cool for about 10minutes. The solution obtained is called precursor solution and are ready to be used for deposition.

D. Deposition of precursor solution by spray pyrolysis

Zinc oxide is deposited on glass substrates by electric low-cost spray pyrolysis machine equipped with deposition controller.

The following steps were taken to achieve the deposition of zinc oxide;

i. 1.01ml of precursor solution was obtained by syringe chamber.
ii. The spray chamber was then opened and 3 substrates were mounted vertically on the substrate holder and additional substrate was mounted horizontally to support the three and screwed the plunger at 11.0cm as the source to substrate distance.
iii. The chamber was then closed and heated.
iv. An automatic voltage of 17kva was set and kept constant throughout the experiment.
v. The electrostatic and heater were on until the temperature reached 300k.
vi. The precursor solution was sprayed for about 10 minutes when zinc oxide started spraying and depositing on the substrate, flow rate was maintained at 0.8ml/min.
vii. The electrostatic was off and the remaining solution was exhausted from the syringe, and the make one complete run.
viii. The above procedure was repeated three times.

E. Heat treatment/annealing

Samples deposited by sputtering are referred to as Spt_1-Spt_3. Samples deposited by spray pyrolysis are named as Spp_1-Spp_3. Samples Spt_2 and Spt_3 together with Spp_2 and Spp_3 were carefully inserted (one after the other) into a glass pipe of 2 inches in diameter and 36 inches in length. The glass pipe was later inserted into the tube of the furnace. Nitrogen gas was passed at 0.5sccm flow rate after setting the annealing set point and the ramp rate. The furnace was then switched on. In all there were four samples. Table 1 gives the details of the annealing temperature ranges used with respect to each sample.

Table 1: Details of the annealing temperatures

S/no	Sample	Substrate temp.	Annealing temp.
1	Spp_1	Room Temp	No annealing
2	Spp_2	Room Temp	573K
3	Spp_3	Room Temp	673K
4	Spt_1	Room Temp	No annealing
5	Spt_2	Room Temp	573K
6	Spt_3	Room Temp	673K

F. Characterization of the samples

Optical properties of all the samples wereanalyzed by AVASPEC spectrophotometer in the range 172-1100nm at room temperature. The crystal structure of the films on the other hand were inspected using PANALYTICAL XPERT PRO Diffractometer performed in $2\theta/\omega$ at a voltage of 45KV and a current of 40mA.The sweeping angle was 20 to 80 degrees the scan speed was 0.8 degrees/minute at a scan step of 0.02 and employing a CuKα radiation (λ = 1.5406Å).

RESULTS AND DISCUSSION

A. Optical transmittance

Figure 1 shows the optical transmittance of as-deposited sample and samples annealed at 573K and annealed at 673K of ZnO thin films deposited by spray pyrolysis. It can be seen from the Figure that for the as-deposited sample, an average transmittance of 80% was exhibited. However, for the films annealed at 573K and 673K, a transmittance of 85% and 90% was observed which shows that transmittance increases with increase in annealing temperature. These may be due to complete evaporation of the parent residual organic compound and water molecules at increased temperature, uniform oxidation and improvement in lattice orientation [3], increase in grain size, structural homogeneity and crystallinity [24-25]. It should be observed that for all samples, transmittance increases with increase in wavelength up to 500nm. Beyond 500nm the transmittance is almost constant for all the samples.

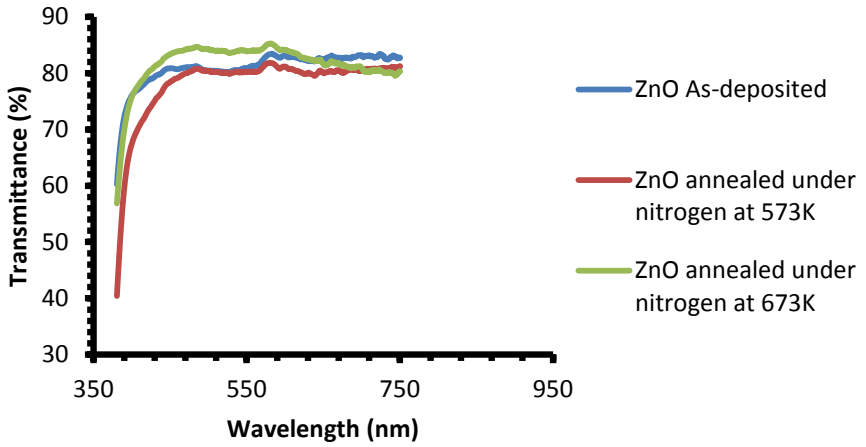


Fig-1: Transmittance vs wavelength for as-deposited sample and samples annealed under Nitrogen atmosphere.

Figure 2 shows the plot of transmittance against wavelength for the as-deposited sample and samples annealed at 573K and 623K respectively (i.e. Spt_1, Spt_2 and Spt_3). It can be seen that with the exception of Spt_3 (film annealed at 623K), the average transmittance stood at 81.49% and 84.26%. This clearly shows that annealing improves transmittance significantly from 34% for the as-deposited sample to about 90%. The changes seen in the transmittance may be as a result of the displacement of the absorption edge [26]. Displacement of the absorption edge is due to Fermi level moving into the conduction band with the increase in carrier concentration according to the theory of Burstein-Moss effect [21]. Peaks and valleys seen on the figures of transmittance for all the samples are associated with interference effect [8].

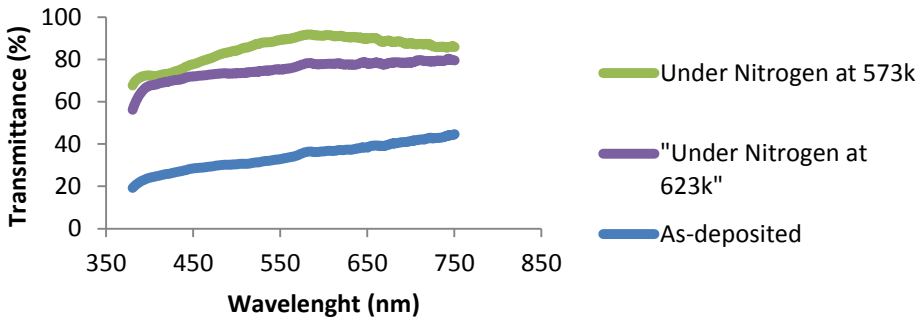


Fig-2: Transmittance vs wavelength for as-deposited sample and samples annealed under Nitrogen atmosphere.

B. Optical band-gap energy

Figures 3a, 3b, and 3c exhibits the optical band-gaps of Spp_1-Spp_3 obtained by plotting $(\alpha hv)^2$ versus photon energy hv and by extrapolating the linear portion of the absorption edge to find the intercept with energy axis of $(\alpha hv)^2 = 0$. Higher photon energies indicate that the films are essentially direct transition n-type semiconductors [27]. It can be seen that the optical band-gap energy of the Zinc oxide thin film decreases with increase in annealing temperature. Samples

annealed at 573Kand 673K gives the optical band-gap energy of 5.19eV and 5.10eV. The As-deposited sample has a band-gap energy of 5.20eV, which is close to the standard value of Zinc oxide thin film (ZnO) grown by spray pyrolysis technique. The decrease in the optical band-gap energy for the annealed samples may be attributed to the falling of the Fermi-level into the conduction band of a degenerate semiconductor which leads to energy optical energy band-gap narrowing, in accordance to Brustein–Moss effect [28]. It may also be attributed to the formation of deep acceptor center [10]. According to quantum confinement theory, the energy band-gap of a semiconductor depends on the crystal size optical band-gap energy will decrease with an increase in crystal size [4], or the element of the annealing atmosphere which is the best acceptor with low ionization energy in the fifth group of the periodic table. It occupies oxygen sites with the bond length of *dN–Zn* = 1.88 Å; [29]. The band gap was determined from the Tauc's formula (1) as given by [4, 30];

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad (1)$$

The absorption coefficient (α) was calculated from (2) given by [7]

$$\alpha = \frac{A}{h\nu}(h\nu - E_g)^{\frac{1}{2}} \qquad (2)$$

where A is a parameter that depends on probability of transition and the refractive index of the material, h is the Plank's constant, v is the photon frequency.

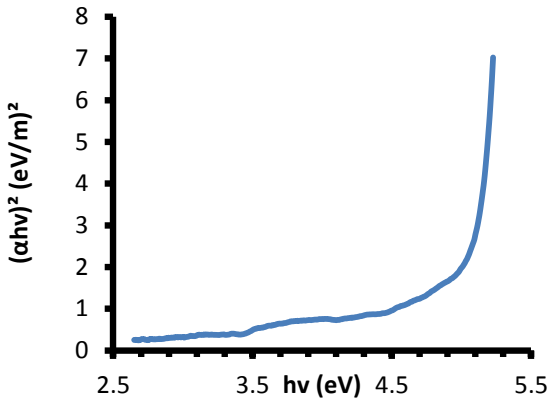


Figure 3a Plot of (αhv)² as a function of photon energy (hv) for as-deposited Zinc Oxide thin film.

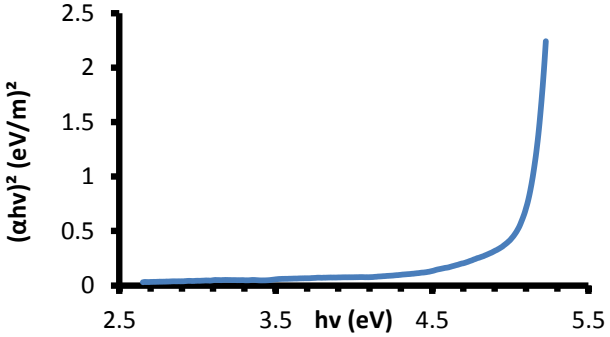


Figure 3b Plot of (αhv)² as a function of photon energy (hv) for Zinc Oxide thin film annealed at 573 K.

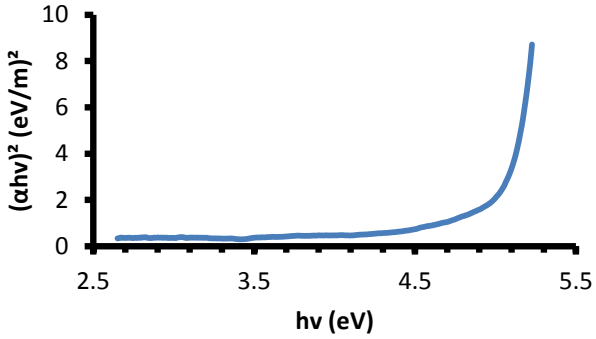


Figure 3c Plot of (αhv)² as a function of photon energy (hv) for Zinc Oxide thin film annealed at 673 K.

The band gap of ZnO thin films deposited by sputtering technique (Spt_1-Spt_3) are shown on Figure 4. The figure showed fluctuations with respect to the annealing conditions. It can be seen that the average value of band gap is 3.24eV which agrees with [20]. There is decrease from the band gap of bulk ZnO (3.34 eV). This decrease may be as a result of the oxygen deficiency in the preparation of the films. It may also be attributed to the creation of allowed energy states in the band gap at the time of the film preparation [31]. The value of the optical band gap increases for the films that were annealed if compared with the as-deposited. It has also been observed that the optical band gap of all the films falls within a range of 3.15 to 3.28eV, which is a typical range for solar cell window layer. With this value of energy bandgap, the films will transmit all solar radiation of wavelength greater than the absorption edge wavelength (380nm) and this include substantial part of the visible radiation [33].

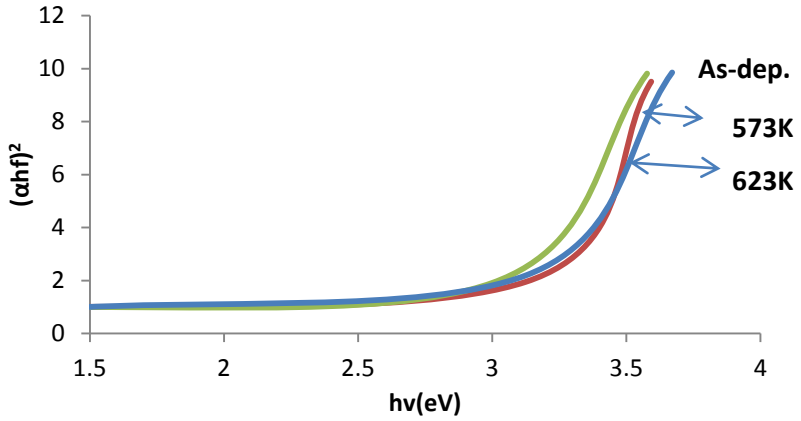


Fig-4: Plots of $(\alpha hv)^2$ as a function of photon energy (hf) for thin films of ZnOannealed under Nitrogen.

C. XRD analysis

The XRD patterns of the thin films of ZnO deposited by spray pyrolysis labeled as Spp_1, Spp_2 and Spp_3 are shown in Figures 5a, 5b and 5c respectively. All the diffraction peaks were well indexed to the hexagonal Zinc Oxide wurtzite structure. The result indicates that the films have a polycrystalline hexagonal wurtzite structure with (1 0 0) and (1 0 1) orientation. In particular, (1 0 0) (ZnO-2) oriental growth is the most prominent peak of zinc oxide structure that belongs to hexagonal wurtzite system. The crystallite size was calculated from (3) by [34];

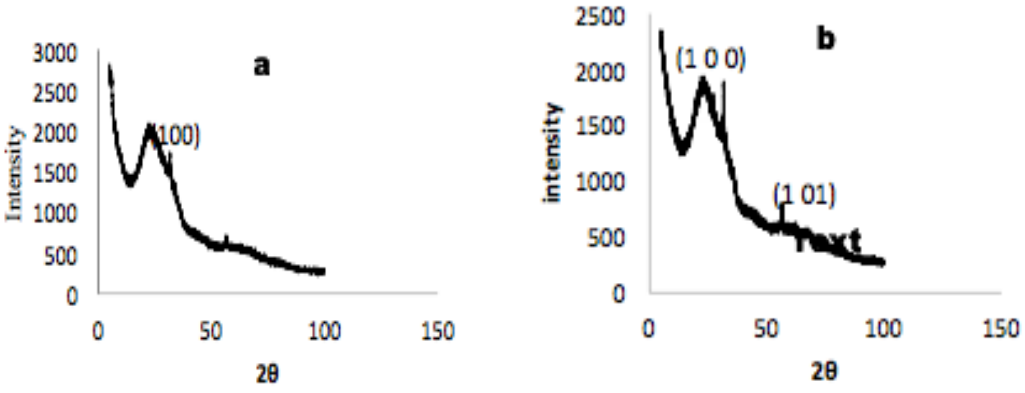
$$p = \frac{0.9\lambda}{\beta \cos\theta} \qquad (3)$$

where λ, is the wavelength of the X-ray and β is the full width at half maximum intensity in radians.

Analysis of the calculated d-spacing on the basis of hexagonal structure can be done from (4) given by [30];

$$d_{hkl} = \frac{1}{\sqrt{\frac{4}{3}\frac{h+hk+k}{a^2} + \frac{l^2}{c^2}}} \qquad (4)$$

where h, k and l are the Miller indices, a and c are lattice parameters.



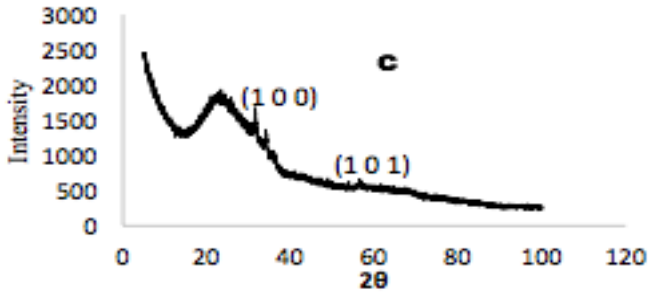


Fig. 5a, b and c X-RAY pattern of ZnO thin films deposited by spray pyrolysis.

Figure 6 represents the XRD pattern for Spt_1, Spt_2 and Spt_3. The diffraction peak around 32.65°,32.69° and 32.61° corresponds with index (100), together with the diffraction peak around 34.31°, 34.34° and 34.39° corresponding with the indexes of (002) are clearly observed. The predomination of (002) peak in the pattern proved that the ZnO films have Wurtzite crystalline structure with a preferential orientation along the c-axis. Increment of annealing temperature led to superior and narrower diffraction peaks that correspond with increase in crystallite size and qualities. The increase in annealing temperature increased the (002) peak intensity, while decreased those of the (100) orientation. The shift in position of the (002) peak can be attributed to better crystallinity with more relaxation caused by annealing. The values of FWHM ranges from 0.4 to 0.9 suggesting that nitrogen annealing caused noticeable changes in the crystallinity of the films. The shift of the (002) peak towards higher angles also implies relaxation of the residual strain introduced in the films during the deposition process. The indication that the grains are strongly oriented along the c-axis is because of the singular peak (002 at 2θ ~ 34.31° to 34.39°). This is in line with the findings [35]

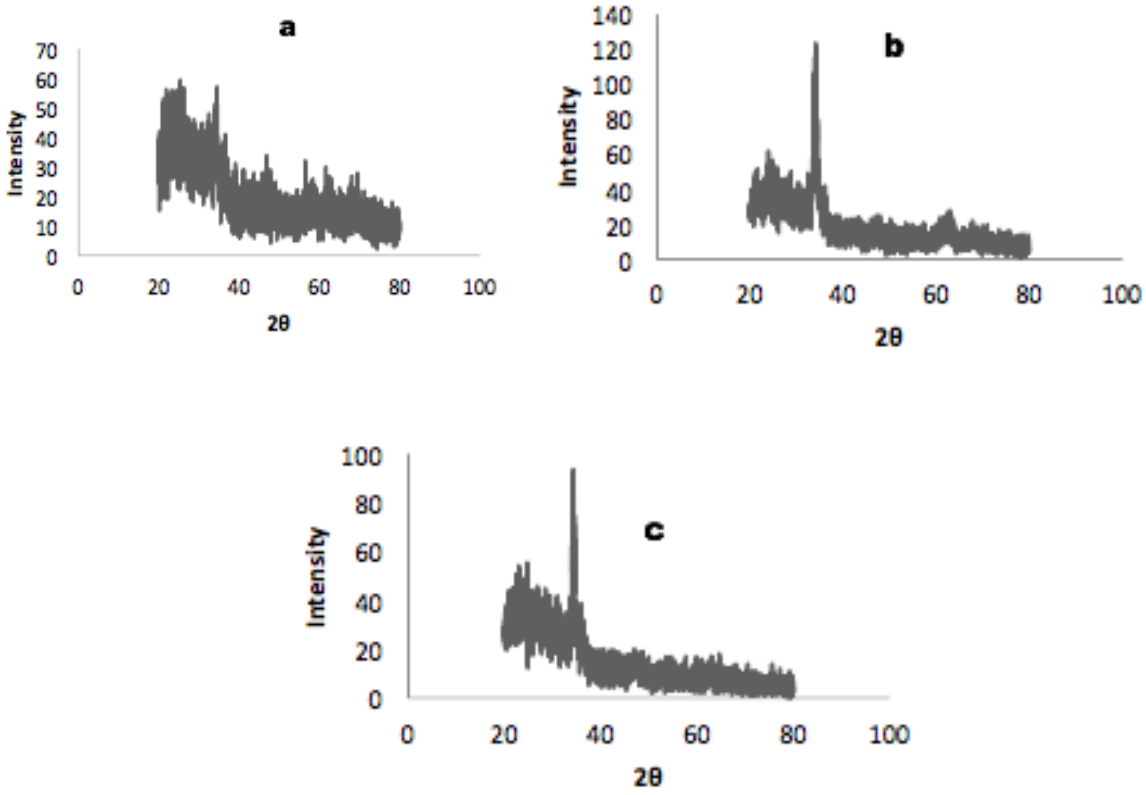


Fig. 6 a, b and c X-RAY pattern of ZnO thin films deposited by rf sputtering.

Table 2 presents other optical constants determined from the samples.

Table 2: Some optical constants of the samples

S/No	Sample	Ann. Temp	n	$(\alpha) \times 10^{-5} m^{-1}$	k
1	Spp_1	-	1.44	0.0022	27.52
2	Spp_2	573K	1.38	0.0015	15.21
3	Spp_3	673K	1.33	0.0017	13.11
4	Spt_1	-	1.58	25.49	0.3700
5	Spt_2	573K	1.51	3.89	0.1100
6	Spt_3	673K	1.52	6.7341	0.2000

CONCLUSION

Zinc Oxide thin films were prepared by spray pyrolysis and rf sputtering techniques. The optical and structural properties of the Zinc Oxide thin film were studied, it can be seen that the annealing temperature plays an important role in the optical as well as the structural properties of the Zinc Oxide thin films, the average values of transmittance shows that this material is a good candidate for optoelectronic applications if deposited by either of the two deposition methods mentioned above. The process parameters were optimized to have good quality crystalline films. XRD characterization of both as-deposited and annealed films revealed poly-crystalline structure. The rf sputtered samples exhibited band gap that is very close to that of bulk ZnO.

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