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Characterization of Aluminum Doped Zinc Oxide (Azo) Thin Films Prepared by Reactive Thermal Evaporation for Solar Cell Applications

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Abstract

Aluminium doped Zinc Oxide (AZO) thin films have been deposited using reactive thermal evaporation technique using an Edward Auto 306 Magnetron Sputtering System. Transmittance and reflectance data in the range 300 nm-2500 nm were obtained using UV-VIS NIR Spectrophotometer Solid State 3700 DUV for all the thin films samples that were prepared. Transmittance values of above 70% were observed. The optical measurements were simulated using SCOUT 98 software to determine optical constants and optical bad gap of the thin film. The optical properties in these films were varied by varying Aluminums doping percentages. It was observed that the transmission over the visible range decreased as the concentration of Aluminum increased. This is due to free carriers coupling to the electric field hence increasing the reflection. Optical band gap for various samples of Aluminum doped thin films show a direct allowed transition and a shift in the optical absorption edge as the Aluminums concentration increased. These results show values of band gap ranging between 3.2 eV and 3.5 eV. Between 0% - 3% the optical band gap reduces. This is followed with widening of the band gap for doping between 4%- 6%. Urbach energy gradually increased with increasing band gap. The band gap reduced due to formation of localized states near the conduction band corresponding to increase in Urbach energy.

Keywords: Aluminums doped Zinc Oxide (AZO); Thin films; Optical properties; Reactive thermal evaporation technique; Solar cell applications

Introduction

Zinc Oxide (ZnO) films have become technologically important due to their range of electrical and optical properties, together with their high chemical and mechanical stabilities, which make them suitable for a variety of applications such as flat panel display electrodes and gas sensors. Moreover, these films can be used as surface acoustic wave devices, because of their large piezoelectric constant, and also as solar cells, since their optical band gap (3.3 eV) is wide enough to transmit most of the useful solar radiation [1]. ZnO is an n-type semiconductor and its conductivity can be controlled by thermal treatment or by adequate doping [2]. The doping of ZnO films with the group III elements can increase the conductivity of the films. In comparison with other elements, Aluminum and Gallium are the best dopants because their ionic radii are similar to that of Zn^{2+} [3,4].

Many techniques have been used for fabricating ZnO films, such as chemical vapour deposition, pulsed laser deposition, dc reactive sputtering, spray pyrolysis and the sol–gel process [3]. The structural, optical, and electrical properties of ZnO and ZnO:Al films prepared by thermally evaporating zinc acetate and $AlCl_3$ in vacuum have been investigated in detail, together with the effects of heat treatment in air and vacuum. The properties of the deposited ZnO and ZnO:Al films depend on the deposition parameters such as substrate temperature, evaporation rate of zinc acetate and Aluminum concentration [5].

The Al-doped ZnO film exhibits remarkable electrical conductivity, together with high charge carrier density and mobility [6]. The ZnO doped with Al^{3+} is used extensively for photo-electronic devices [6], Theoretically, spatially organized ZnO doped with Al^{3+} could result in improving electrical properties. For this reason, only few studies of the conduction mechanism in heavily Al-doped ZnO films have been reported. Slightly doping was explained by a limited incorporation of Al into the ZnO lattice, and Aluminum acts as a donor [6].

Selmi et al., [1] studied deposition time and its effects on the properties of ZnO:Al films. It is shown that films grow with the hexagonal c-axis perpendicular to the substrate surface. The morphological characteristics show a granular and homogenous surface and the cristallinity of the films are enhanced with increased deposition time. The deposited films show good optical transmittance (80%–90%) in the visible and near infrared spectrum.

Transparent Conductive Oxides (TCO) films are degenerate wide band gap semiconductors with low resistance and high transparency in the visible range. For these reasons these materials, are widely used in optoelectronic applications such as flat panel displays, solar cells and electro chromatic devices. Usually, the TCO films are n-type semiconductors such as Indium Tin Oxide (ITO), Tin Oxide (SnO_2) and Zinc Oxide (ZnO), whereas ITO film is the one most used in these devices up to now. Recently, Al doped ZnO (ZnO:Al) film is one of the materials which could replace the ITO films. The direct optical band gap of ITO films is generally greater than 3.75 eV although a range of values from 3.5 to 4.06 eV have also been reported in the literature [7].

This research study uses ZnO:Al. It is widely used because the films have electrical and optical properties similar to those of ITO, and because it is stable in a hydrogen atmosphere. Thin ZnO films should be doped by aluminum, since it has been remarked that extrinsic donors due to the dopant atom are more stable than intrinsic donors due to the native defects. The electrical conductivity in ZnO:Al film is higher due to the Al^{3+} ions in substitutional sites of the Zn^{2+} ions and the Aluminum interstitial atoms, in addition to Oxygen vacancies and Zinc interstitials [4]. The Bond enthalpy of Zn-O is 159 ± 4 kJ/mol while that of Al-O is 511 ± 3 kJ/mol [4].

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Experimental Techniques

Deposition of Aluminum doped zinc oxide (ZnO:Al)

Zinc (99.9% purity) and Aluminum (99.99% purity) were mixed at varying doping percentages of Aluminum (0-6%) and then heated in closed glass tube until they melted to form a compound. Glass substrates were cleaned to remove stains on them by boiling in dilute chromic acid to remove surface contaminants and rinsing thoroughly with distilled water and ethanol and allowed to dry completely. The substrate was then mounted on a rotating substrate holder and the compound was then placed in a Molybdenum boat. The chamber was covered tightly and pumped down to 5.0×10^{-6} mbars. A current of 4.0 A was supplied to the heater to evaporate the materials at a temperature of about 800 K. The shutter was removed to permit deposition on glass substrate in the presence of oxygen which was let into the chamber. Since Zinc is more reactive than Aluminum, ZnO:Al thin films were formed. The Bond enthalpy of Zn-O is 159 ± 4 kJ/mol while that of Al-O is 511 ± 3 kJ/mol [4].

Thin film thickness measurements

Thin film thickness was estimated using Tencor alpha step surface profilometry (resolution of 5 Å) equipment with a diamond stylus of radius 12.5 µm. During measurement, the stylus was moved across the film surface while keeping the sample and the sample stage stationary. The step created during the deposition process enabled the film's thickness to be read directly as the step height. SCOUT 98 software was also used to simulate the film thickness. This was used to validate the measurements obtained by Tencor alpha step surface profilometry equipment with comparisons to thickness with Quartz crystal monitor.

Optical measurements

Optical measurements (reflectance and transmittance) in the spectral range from 300 nm - 2500 nm were carried out using UV/VIS/NIR 3700 double beam Shimanzu spectrophotometer. Photons of selected wavelengths and beam intensity I_o (photons/cm^2-s) were directed at the film of thickness (t) and their relative transmissions observed. Wavelengths of photon are selected by the spectrophotometer. Photons with energies greater than band gap (E_g) are absorbed while those with energies less than E_g are transmitted. The spectrophotometer had two radiation sources; a deuterium lamp for UV range and a halogen lamp for visible (VIS) and near infrared (NIR) range. The radiation source changed automatically to access the wavelength range during measurements. During transmission measurements, samples were placed in front of the integration sphere and behind it during reflection measurements. SCOUT 98 software was used to simulate transmittance data to get the optical constants like absorption coefficient among others. Drude, OJL, Tauch Lourntz, Extended Drude and Harmonic Oscillator models were used to simulate the data. These models are inbuilt in the SCOUT 98 software [8]. The models simulate refractive index, dielectric function, absorption coefficient real and imaginary parts and energy loss parameters.

Sheet resistivity measurements

The four point probe technique (Figure 1) was used to measure the sheet resistivity of the Aluminum doped ZnO semiconductor thin film samples. With a symmmetrical square geometry adopted, the four leads from the probe head were connected to Keithley Source Meter via relay switching circuit as per the Van der Pauw set-up for Voltage and Current measurements [9-11].

Discussion of Experimental Results

Optical characterization of AZO thin films

In this research study, optical constants from near normal reflectance and transmittance data for ZnO:Al are studied. SCOUT 98 software [8] was used to simulate the transmittance data to generate the corresponding optical constants. Drude and OJL models are essential in simulations of transmittance data.

Optical characterization of ZnO:Al thin films: The optical transmittance spectra of ZnO:Al films as a function of wavelength in the range (300 - 2500 nm) were plotted in Figure 2. The high transmission (≥ 70%) is understood because ZnO is a semiconductor with wide direct band gap of 3.3 eV [1,3]. Due to the high transmission, these films have good optical properties for solar cells window applications. It was observed that the transmission over the visible range decreases as the concentration of Aluminum increases. This is due to free carriers coupling to the electric field hence increasing the reflection. This agrees very well with Elmin et al. [12] who reported significantly reduced transmission when ZnO was doped with higher percentages of Aluminum.

From the transmittance graph on Figure 2 the absorption edge

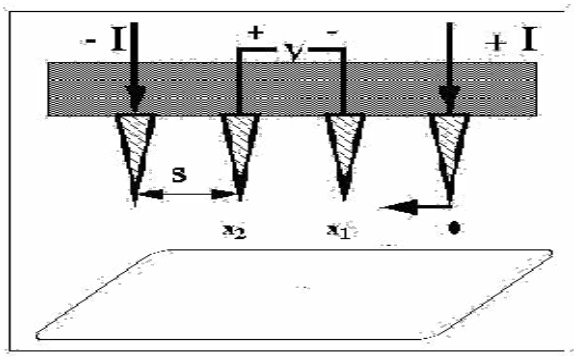

Figure 1: Schematic diagram of a four point probe used to measure surface sheet Resistivity [15].

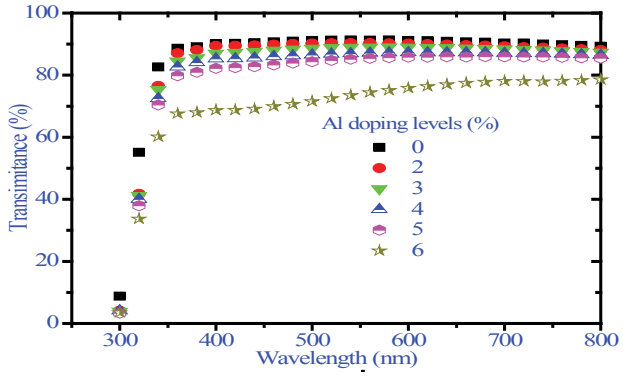

Figure 2: Spectral graph of transmittance (%) against wavelength (nm) various doping levels of AZO.

shifted toward higher wavelength as the doping levels increased. All films exhibited sharp fundamental absorption edge. Reflectance data (Figure 3) show that the average reflectance is below 45% within the visible range. All films exhibit low absorption in the visible spectrum range. The film had thickness range between 95 nm to 130 nm.

Simulated and Experimental graphs for AZO transmittance data: The experimental and simulated spectral for transmittance data were plotted against wavelength for the different samples. Using the SCOUT 98 software, the simulated curves fitted perfectly in to the experimental curves as shown in Figure 4 (b) - (e) below. From the graphs, the optical band gap energies and thickness of the films were simulated.

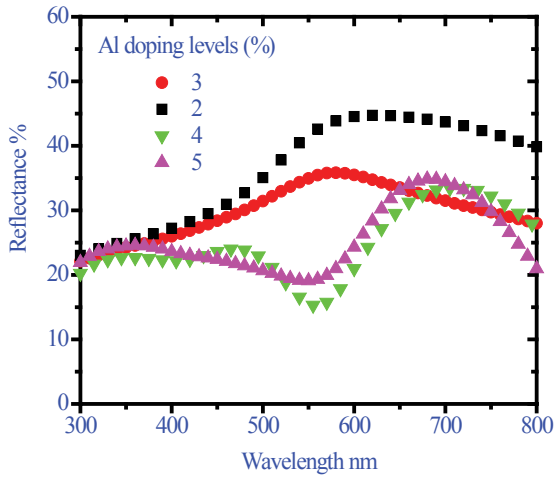

Figure 3: Spectral graph of reflectance % in the visible, IR, and UV regions against wavelength (nm) for different doping levels of AZO.

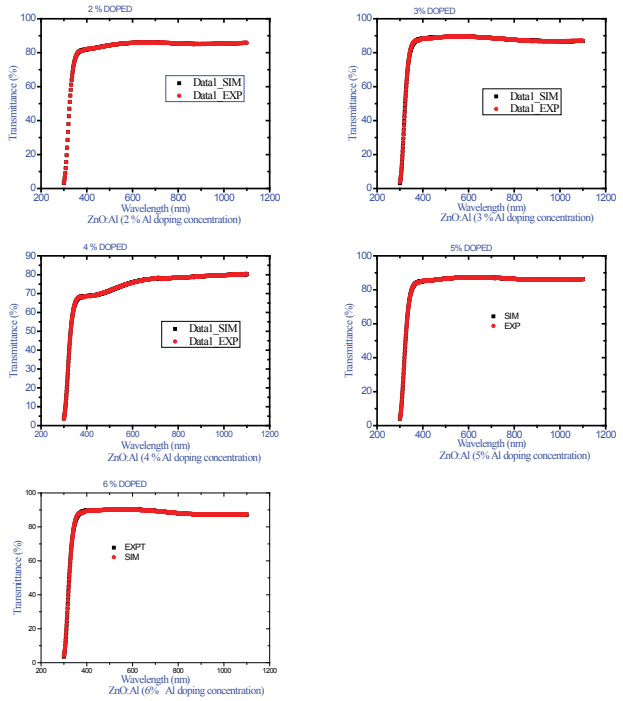

Figure 4: Doping Concentration of Al: ZNO and transmittance spectra for ZnO doped with Al at various Al doping levels.

Optical band gap and urbach energy for AZO thin films: Optical band gap for various samples of Aluminum doped thin films as simulated from SCOUT 98 software are shown in Table 1. The reduction in transmittance also led to variation in band gap. This may be due to the Oxygen vacancies and the behaviour of free carrier's concentration with increasing the ZnO doping. This compares very well with studies conducted by Wang Wang [13] and Shadia [14] who both got values of band gap ranging between 3.2 eV and 3.5 eV. Between 0 - to 3% the optical band gap reduces. This is followed with widening of the band gap for doping between 4% - 6%.

From Table 1, Urbach energy gradually increased with increasing band gap. This is consistent with the variation of the conductivity of the film with doping concentration. When band gap was reducing due to formation of localized states near the conduction band, it corresponded to increase in Urbach energy. Increased impurity formed more localized states within the band gap despite that beyond the 3% doping there was increased scattering. Increased doping at 4% to 6% did not enhance conductivity despite Urbach energy in from Figure 5, there was a general drop in the band gap up to a doping level of 3%. Decrease in optical band gap energy can be attributed to creation of new donor levels in the forbidden zone; and a shift in the fermi level causing a change in the band structure of the films. At room temperature aluminum atoms occupy the zinc sites in the ZnO lattice. They are singly ionized donors giving one extra electron. There after the band gap starts to widen, this

Doping % of ZnO With Al	Optical bandgap ±0.2 eV	Thickness (nm) ± 5nm	Urbach energy ± 0.01 ($x10^{-4}$) eV
0	3.34	113	2.02
2	3.28	115	2.04
3	3.18	112	2.07
4	3.21	108	2.09
5	3.32	101	2.12
6	3.42	98	2.18

Table 1: Values of the optical band gap at different doping levels for AZO.

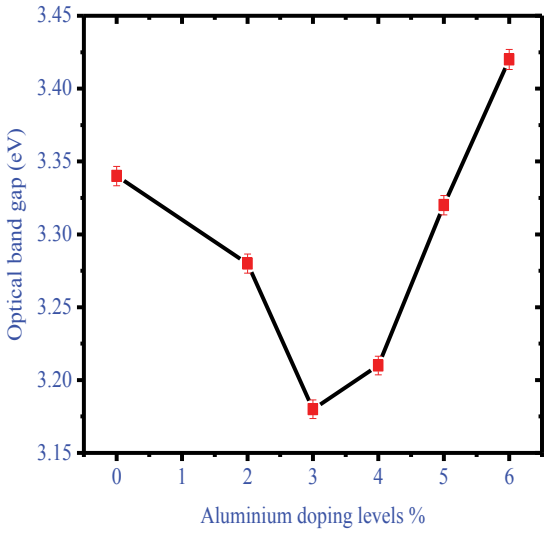

Figure 5: Variation of optical band gap for ZnO:Al with various doping levels of Aluminum (%).

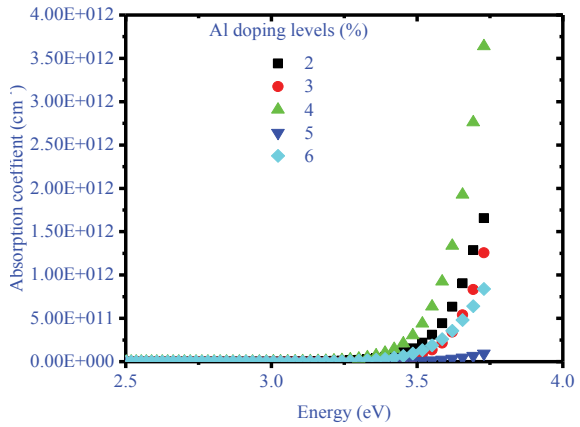

Figure 6: Graph of variation of absorption coefficient for various Al doping levels against photon energy.

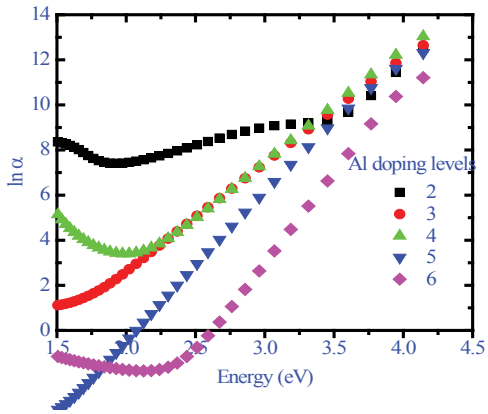

Figure 7: Graph of lnα against energy for various Al doping levels.

can be explained by Burstein Moss effect [15]. Increased concentration of donor atoms causes more electrons to occupy states at the bottom of the conduction band causing it to be filled up with donor electrons which results in widening of band gap. It is clear that the variation of α (cm^{-1}) versus photon energy (eV), Figure 6 which is near straight line, indicate the presence of direct optical transitions. Excess doping also destroys the structure stoichometry hence reducing the conductivity of the ZnO films [16].

The Urbach energy which is interpreted as the width of tails of localized states in the gap region were calculated from the following relationship, $Eu = (d\ln\alpha/d\hbar\nu)^{-1}$. It is obvious when $(In\alpha)$ is plotted against (ħω), the inverse of slope will be the value of tail localized state [17]. The values of Urbach energy E*u* for all composition are tabulated in Table 1. This is extracted from spectral graph in Figure 7.

It is observed that, the Urbach energy increased gradually with increasing the Aluminum doping levels (Table 2). This may be due to the fact that, ZnO doping causes a shift in the optical absorption edge therefore change in the band structure of the films. Variation in the optical absorption edge of the films with increasing the ZnO ratio indicate that, the dopant ratio is responsible for the width of localized states in the optical band of the films and causes an increase in the energy width of localized states thereby affecting the optical energy gap.

The band tailing (Urbach energy) is the effect of impurity or disorder and any other defects. In the exponential-edge region (Figure 6), the absorption coefficient is expressed by the Urbach relationship. The Urbach's absorption edge is formed in the region of photon energies below the forbidden band gap. The interaction between lattice vibrations and localized states in the tail of the band gap of the compound has a significant effect on the optical properties of the thin film. The increase in aluminum doping creates crystal strain in ZnO crystal since Al-O has a higher bond enthalpy of 511 kJ/mol compared to 159 kJ/mol of Zn-O. This increases structural defects and thereby increasing Urbach energy.

Electrical characterization of ZnO:Al thin films

Using a four point probe [11] the following results for sheet resistivity of AZO thin films were realized as in Table 3.

Surface sheet resistivity at room temperature was as in Table 3. The

Doping % of ZnO With Al	Urbach energy ± 0.01 (x10^{-4}) eV
0	2.02
2	2.04
3	2.07
4	2.09
5	2.12
6	2.18

Table 2: Values of Urbarch energy at different doping levels of ZnO with Al.

Aluminium doped Zinc Oxide	
Doping %	Sheet resistivity ±2 Ω-cm
0	48.23
2	44.26
3	36.24
4	44.71
5	51.72
6	55.21

Table 3: A summary of electrical surface sheet resistivity for AZO thin films.

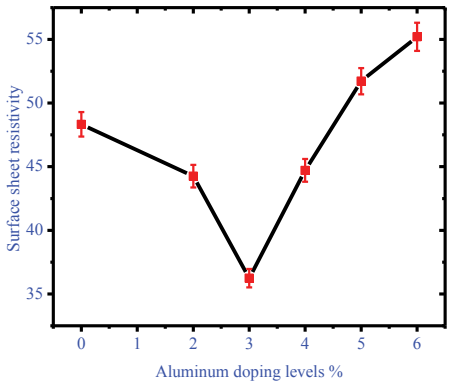

Figure 8: Graph of Aluminum doping levels with sheet resistivity.

electrical properties greatly depend on deposition parameters and film thickness. During the deposition, the substrate temperature was kept at 780 K. Figure 8 shows the variation of doping concentration with sheet resistivity. The mobility of the ZnO:Al reduce with the doping concentration, Such behaviour was expected as a result of substitution doping of Al^{3+} at the Zn^{2+} site creating one extra free carrier in the process. As the doping level is increased, more dopent atoms occupy lattice sites of Zinc atoms resulting in more charge carriers. This leads to a higher polarization of the electron by the addition of Al and thus increasing the electron phonon coupling. Strong scattering implies short carrier lifetimes and thus lower mobility.

Lower electron mobility causes reduction in conductivity hence high sheet resistivity. Thus, the resistivity increases with the doping concentration. However, after a certain level of doping, the do-pant atoms in the crystal grain and grain boundaries tend to saturation. In this case, high doping concentration will lead to a large quantity of ionized impurity. This ionized impurity provides strong scattering centre's for charge carriers. According to the Conwell-Weisskoft theory [5], when degenerate charge carriers are scattered by impurity ions, the energy dependence of ionized impurity scattering mobility due to a high doping concentration will lead to a larger quantity of ionized impurity, resulting in a decrease in the mobilities of the ZnO:Al films [5]. This result compares well with other studies [18,19] who reported sheet resistivity of 40– 60 Ω – cm.

Composition and structural characterization of ZnO:Al thin films

X-ray diffraction of ZnO:Al thin film (as-deposited): XRD measurements show structural make-up and size of crystalline structures for AZO. The X-ray diffraction (XRD) spectra of all the AZO films show the presence of a sharp peak indicating that the films are highly oriented as shown in Figure 9. The XRD spectra of the films reveal that they have crystalline structure with the main diffraction peak located at angle $2\theta = 36^0$. Neither metallic Zinc or Aluminum peaks nor Zinc Oxide peaks were observed from the XRD patterns. This implies that Aluminum atoms replace zinc in the hexagonal crystal lattice. Peak intensity of the XRD diffraction reflections is determined by the crystalline grain, size and structure and axis orientation. These results are in agreement with those of Mujdat, [20]. XRD analysis reveals that the film exhibit only the (002) peak, indicating that they have preferred orientation, implying a c-axis growth perpendicular to the substrate surface. The dominant (002) peak becomes sharper, indicating the well-established c-axis orientation of ZnO:Al thin films. This shows the crystallinity of the AZO thin film [21].

Elemental composition of ZnO:Al thin film (as-deposited): Table 4 shows the elemental percentage concentration of the thin films as obtained by the X-ray florescence (XRF) MiniPal 2 machine. The analysis was carried out to ascertain the elemental composition of the thin films. The peak-based analysis technique is used where elemental intensities of thin films are calculated and respective spectral background obtained. Figure 10 shows the peak based analysis of the elemental composition of thin film samples.

Conclusion

Deposition of thin films of ZnO:Al was done by reactive thermal evaporation techniques. The reflectance and transmittance data of the films were measured. Aluminum-doped ZnO films have high transmittance above 70% and the corresponding reflectance of below 45% within the visible range. AZO observed optical band gap ranging between 3.18 eV and 3.42 eV. Conductivity increased with doping levels for AZO from 3.34 eV for undoped ZnO to minimum of 3.18 eV at 4% Aluminum doping. The XRD spectra indicate that the films were crystalline in nature for AZO.

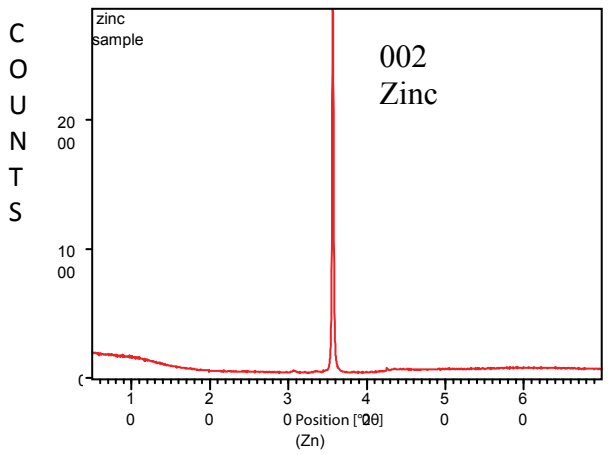

Figure 9: XRD spectra of optimized AZO thin film.

Compound/Elemental	Percentage Levels ± 0.05 %
Al	1.23
Si	59.0
Zn	39.77
SiO_2	53
ZnO	46.8
Al_2O_2	0.2

Table 4: XRF elemental percentage composition of optimized Al doped ZnO thin films.

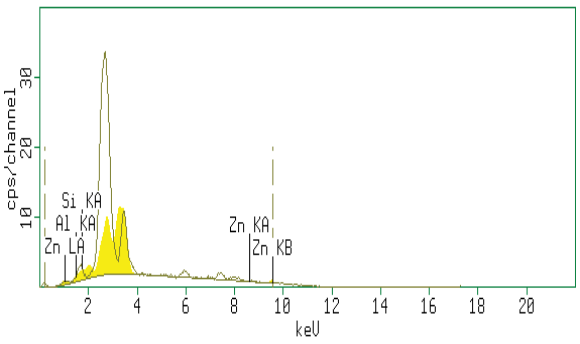

Figure 10: XRF spectra of as-deposited optimized AZO thin film.

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