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Effect of Deposition Parameters on Optical and Electrical Properties of SnO_2: Al Thin Films Prepared by Spray Pyrolysis Technique for Optoelectronic Devices

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Abstract: Transparent Aluminum doped tin oxide (SnO_2:Al) thin films with different Al percentage (1.96%, 3.85%, 5.66%, 7.41% and 9.09%) were fabricated using a low cost spray pyrolysis technique at optimized deposition parameters. Substrate temperature, carrier gas pressure and spray outlet to substrate distance were varied to obtain optimum conditions for deposition. Optical characterization of the deposited films was carried out to the average transmittance, optical constants (refractive index (n) and extinction coefficient (k)) and the band gap. The calculated refractive indexes of the films with various Al concentrations were in the range of 1.469 Al at. % to 1.914 Al at. % w with 5.37% at. % being the optimum, while the average transmittance was between 70% and 80% and band gap of 3.96 eV. The calculated resistivity was in the order of 10-4 Ωcm.

Keywords: Optical constants, Electrical properties band gap light emitting diodes.

1 Introduction

Tin oxide is one of the transparent conductive oxide (TCO) that is most studied. It has a wide band gap between 3.5 – 4.0 eV [1] hence employed in many applications like sensors, light emitting diodes and solar cells [2]. SnO_2 behaves as an n-type semiconductor [3], however, it can be converted in to a p-type semiconductor when doped with material such as aluminum, magnesium, gallium etc. [4]. Among the various dopants, aluminum is highly preferred because it produces high transparency in the visible range [5]. Many works have been achieved on tin oxide (SnO_2) thin films because of their high electrical conductivity, high transparency in the visible range, and high reflectivity in the infrared region [6]. Spray pyrolysis is one of the commonly used deposition techniques to prepare SnO_2 due to its capacity to deposit large uniform area, low fabrication cost, simplicity and relatively high deposition temperature of up to 600ºC on glass substrates [7-8].In this work, spray pyrolysis deposition method was employed to study the effect of deposition parameters such as substrate temperature, carrier gas pressure andnozzle substrate distance on the optical and electrical properties of Al doped SnO_2 films. The Optical Constants such as refractive index (n), extinction coefficient (k), thickness, band gap of Al doped SnO_2 films for different Al concentrations (1.96 Al at. %, 3.85 Al at. %, 5.66 Al at. %, 7.41 Al at. % and 9.09 Al at. %) were calculated at optimized conditions of the parameters and the results discussed. Resistivity of the deposited films at different substrate temperature (300ºC, 320ºC, 340ºC, 370ºC, 400ºC, 410ºC, 420ºC and 440ºC) and Al doping concentrations was also studied and results discussed. The outlook was to achieve a device from the films for optoelectronic devices.

2 Experimental Procedures

The spray pyrolysis set up used in this study is shown in Figure 1.We deposited all films on transparent silicon glass slides. First, we cleaned the slides using the procedure below:

a) We made a mixture of deionized water, liquid detergent and sodium hydroxide in a ratio of 3:2:1 shaken well in a wash bottle to form foam.

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b) We applied foam to a cotton swab and both sides of the slide were scrubbed.
c) Lens cleaning tissue was folded severally and held at angle 45 degrees to drag and wipe the slide to remove the foam.
d) We soaked a new set of lens cleaning tissue at one edge in Isopropyl alcohol and used it to drag and wipe the slide. We repeated the same but this time we used acetone to drag and wipe the glass slide.
e) We dried the glass slide with spray of pressurized oxygen gas.

We used tin (IV) choride ($SnCl_4.2H_2O$) of 99.99% purity and aluminum chloride ($AlCl_3$) of 99% purity as a doping source. We used a concentration of 0.1 M and the doping ratio Al/Sn of 1.96% in the solution, dissolved both precursor and doping compound in ethanol and stirred for 2 minutes to ensure all dissolved. We varied substrate temperature, carrier gas pressure and set up outlet to substrate distance from 300ºC - 440ºC, 0.5 bars – 2.5 bars and 2cm – 6cm respectively. We used solid spectrophotometer DUV 3700 to measure the spectrally resolved transmittance and configured Keithley meter as a four-point probe to get sheet resistivity of the films.

We used SCOUT software version 2, [9] to simulate transmittance data to get the optical constants like absorption coefficient among others. Drude, OJL, TauchLourntz, Extended Drude and Harmonic Oscillator models were used to simulate the data. These models are inbuilt in the software. The models simulate refractive index, dielectric function, absorption coefficient real and imaginary parts and energy loss parameters for plotting graphs, we used micro Cal Origin version 7 software [10].

3 Results and Discussion

3.1 Optical Properties

3.1.1 Substrate Temperature and Average Transmittance

Thin films of SnO_2: Al were deposited at varying temperature of 300ºC, 320ºC, 340ºC, 370ºC, 400ºC, 410ºC, 420ºC and 440ºC at a wavelength range of 300 nm – 1200 nm using the precursor solution as shown in table 1. The substrate temperature was determined by a thermocouple when the tip of the thermocouple touched the substrate during deposition.

Figure 2 shows transmission spectrum obtained. From the figure the transmittance increases steadily below 400 nm and between 400nm and 700 nm (visible range), we obtained an average transmittance of above 76%.

To obtain optimum temperature for deposition of SnO2: Al, we plotted average transmittance in the visible wavelength range against temperature and the inset graph of figure 2 shows the effect of temperature on the wavelength that, as temperature increases, the average transmittance also increases. This is due to increase in crystallinity of the sample because of increase in grain size of the SnO_2 films with the increase in temperature [11]. This occurs up to an optimum temperature after which the transmittance drops drastically. At lower temperatures, milky films are formed due to incomplete decomposition of the sprayed droplets.

Using Gaussian equation 1 [12] and inset of figure 2, optimum temperature obtained was 407.36 $\pm$ 3.70 º C.

$$y = y_0 + \frac{A}{w \times \sqrt{\frac{p_1}{2}}} e^{-2\times(\frac{x-x_C}{w})^2} \qquad (1)$$

where, *A*is the height of the curve's peak, $x_c$is the position of the centre of the peak, p_1 standard deviation of the data and *w*controls the width of the curve.

3.1.2 Spray Outlet to Substrate Distance and Average Transmittance

We deposited films of SnO_2: Al at different spray outlet to substrate distance at a temperature 400ºC and used the data obtained to plot transmission spectrum obtained as shown in figure 3. Inset of figure 3 is graph of average transmittance versus distance.

From figure 3, it is observed that as spray outlet to substrate distance increases, average transmittance also increases to an optimum after which it drops. Lower transmittance at lower spray outlet to substrate distance is because of sprayed solution droplets reaching the substrate early, so the mechanism of spray pyrolysis is not completed perfect resulting to rough and whitish-blue films. At optimum spray outlet to substrate distance, the thermal energy gained by the droplet is such that it vaporizes just above the substrate and gives a good, highly transparent film. In the case of a high spray outlet to substrate distance, the droplets vaporize entirely above the nucleation centre of the film onto the preheated substrates hence the homogeneous reaction takes place in the vapour phase, which diminishes the deposition efficiency and the molecules condense as microcrystallites. They form a powdery precipitate on the substrate, resulting in a decrease in transparency. The decrease in optical transmittance at higher spray outlet to substrate distance is due to re-crystallization of the crystallites in the film[13]. Using equation 1, we obtained an optimum distance of 4.57 cm.

Table 1. Table for precursor solution for deposition of *p*-SnO_2: Al

Chemical	Mass	volum e	Molarit y
$SnCl_2.2H_2O$	0.564 0	25ml	0.1M

$AlCl_3$	0.006 7	0.5 ml	0.1M

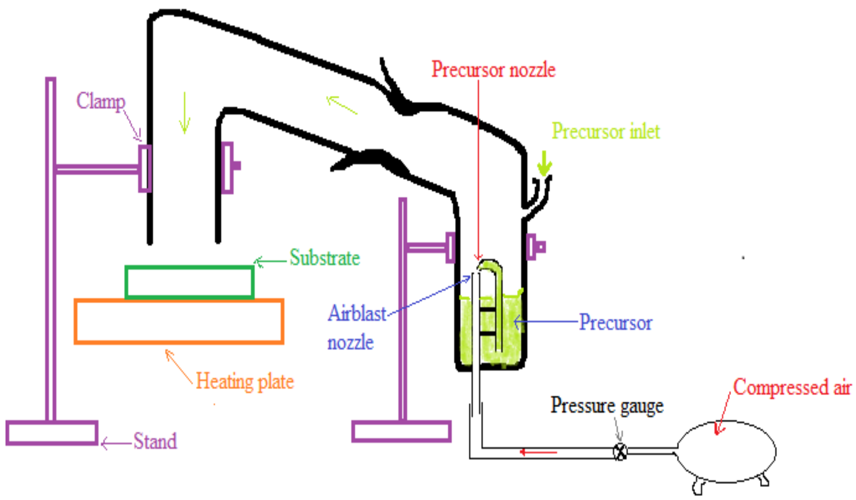

Figure 1. Spray pyrolysis set-up

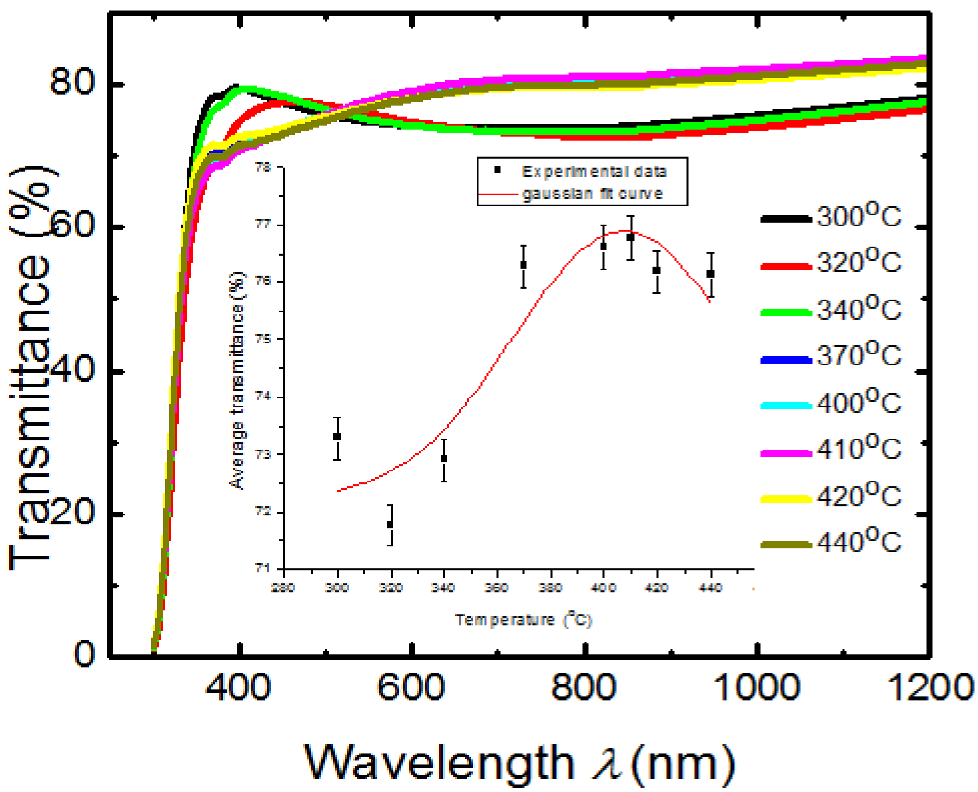

Figure 2.Graph of transmittance vs. Wavelength

The effect of spray outlet to substrate distance is insignificant and therefore the process of film formation is best described that gaseous phase is constituted by the vapors of the precursor which volatilizes near the substrate and subsequently adsorbs on its surface where undergoes decomposition to yield a dense and adherent film. It should be pointed out, however, that a heterogeneous reaction could also denote a liquid–solid reaction with the solid phase being the substrate and the liquid being the melted precursor[14].

3.1.3 Carrier Gas Pressure and Average Transmittance

We deposited SnO_2: Al at spray outlet to substrate distance of 4.57 cm, substrate temperature = 400°C with varying carrier gas pressure. Transmission spectrum is as shown in figure 5 and the inset is graph of average transmittance against pressure.
From figure 5, it is observed that, as carrier gas pressure increases, average transmittance also increases. This occurs up to an optimum carrier gas pressure after which it drops. This is because at lower pressures, the size of the solution droplets becomes large, which results in the presence of recognized spots on the films and then reduction of transparency. This situation increases the scattering of light from the surface and then reduces the transmittance of the films. Using equation 1, we obtained an optimum pressure of 2.01 $\pm$ 0.03 bars

3.1.4 Doping and Average Transmittance

After optimizing substrate temperature, carrier gas pressure and spray outlet to substrate distance parameters, we investigated the effect of doping on transmittance. We used different aluminum doping concentrations of 1.96 Al at. %, 3.85 Al at. %, 5.66 Al at. %, 7.41 Al at. % and 9.09 Al at. % in SnO_2 to deposit different thin films of SnO_2: Al. Concentration in terms of atom percent of element 1 in an alloy containing 1 and 2 atoms. C_1' is defined by equation 2 and 3[5].

$$C'_1 = \frac{n_{m1}}{n_{m1} + n_{m2}} \times 100\% \quad (2)$$

$$n_{m1} = \frac{m'_1}{A_1} \quad (3)$$

Where m_1' and A_1 denote the mass (in grams) and atomic weight, respectively, for element 1.
We used precursor solution of $AlCl_3$ for element 1 (Aluminum) and $SnCl_2.2H_2O$ precursor solution for element 2 (tin oxide).

From figure 5, it is observed that increasing Al do pant in the tin oxide film, average transmittance improved up to an optimum level due to increase in crystallinity of SnO_2 but with continued increase in Al dopant the average transmittance decreases. This is due to decrease in crystallinity of SnO_2. Using equation 1, we obtained optimum aluminium dopant of 5.37% Al at. % .

3.1.5 Optical Constants

The knowledge of optical constants of thin films is significant since they can determine the exact application of the films. The refractive index of the semiconductor is a measure of its transparency to incident spectral radiation. We determined the refractive index (*n*) and extinction coefficient (*k*) of the thin films using SCOUT software version 2, using models as explained by [11].
It is clear from figure 6 a) that refractive index of the film does not depend upon the concentration of Al. For all the deposited films, the refractive index value lies between 1.58 and 1.91. We also determined extinction coefficient (*k*) and variation of *k* with *hv* plotted as shown in figure 6 b). Irrespective of Al concentration all the films exhibit same trend. The value of *k* for all the films behave a linear trend up to 3.9 eV after which there is a sudden increase in the extinction coefficient value. The blue shift in the extinction coefficient value denotes that the films are stronger absorbing medium in this range.

3.1.6 Optical Band Gap and Thickness of SnO_2: Al

We deposited thin films of SnO_2: Al using the optimized parameters and determined their optical band gap (*Eg*) by extrapolating the linear part of the curve $(\alpha h\nu)^2$ which intercepts the energy axis. From figure 7 it can be seen that the band gap of all the deposited SnO_2: Al films on glass substrate lies between around 3.98 eV which is close to the band gap of 3.7 eV for sprayed aluminium doped SnO_2 films deposited onto ITO substrate obtained [15]. The optical band gap (Eg) of the films can be determined by the Tauc law equation 4 [16].

$$(\alpha h\nu)^2 = B\,(h\nu - Eg) \quad (4)$$

where, *h* the Planck's constant, ν the photon frequency and *Eg* the band gap energy.
B is an energy-independent constant and α is the absorption coefficient calculated from transmittance data [17].

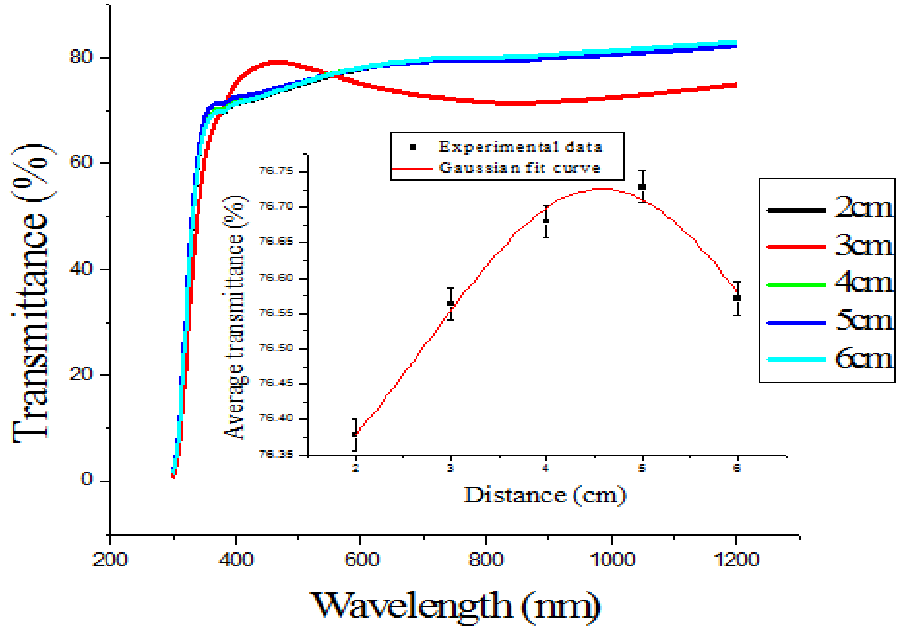

Figure 3. Graph of Transmittance versus wavelength at different spray outlet to substrate distance.

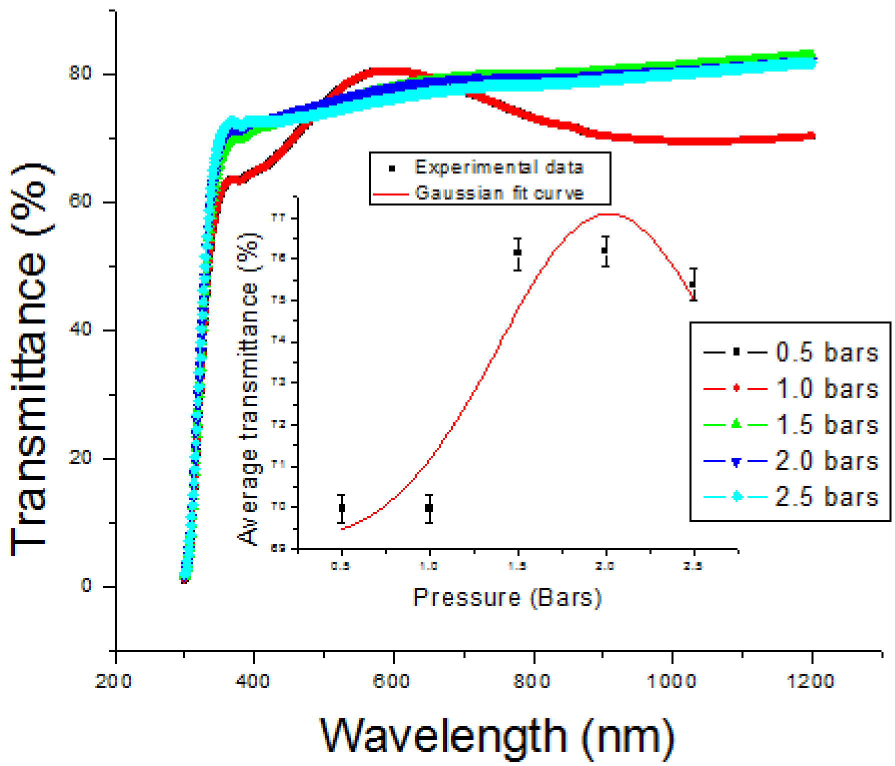

Figure 4. Graph of transmittance versus wavelength at different carrier gas pressure.

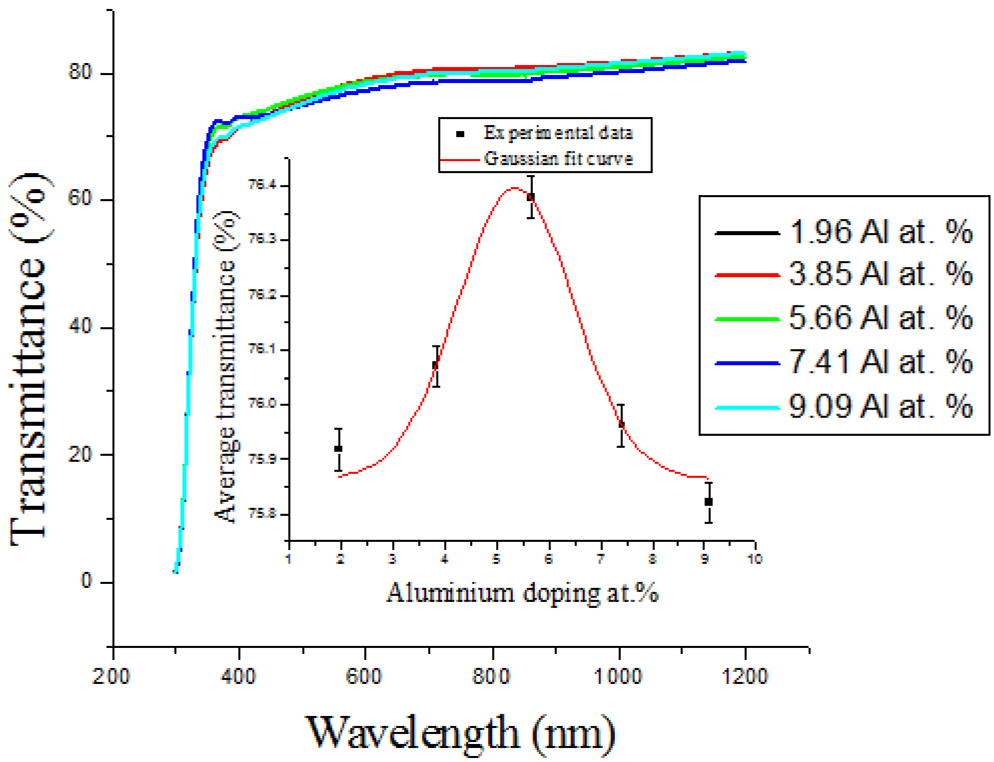

Figure 5. Graph of transmittance verses wavelength at different Aluminium doping atomic %.

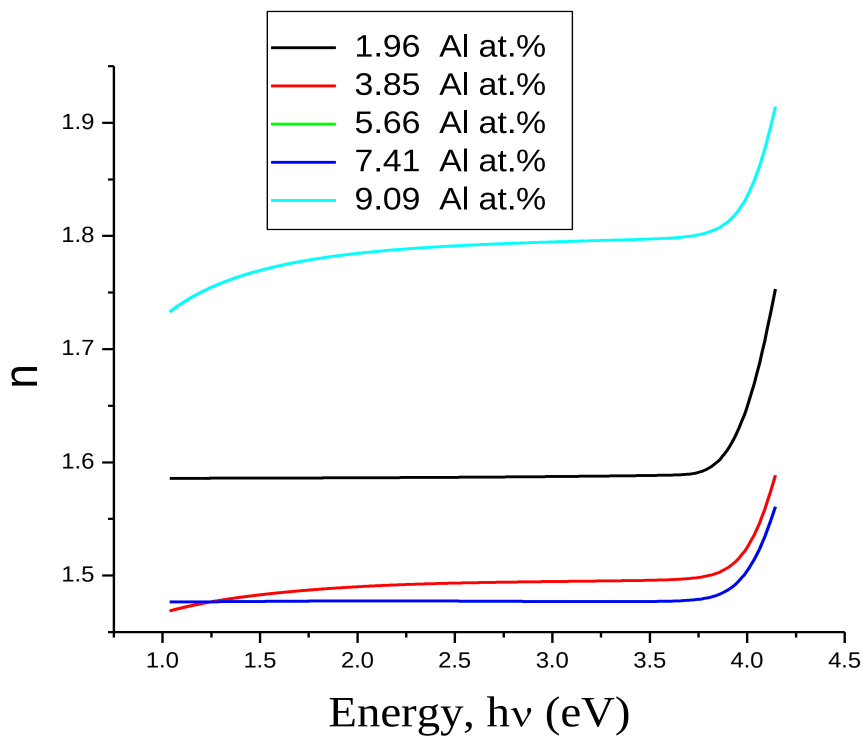

Figure 6 a). Variation of refractive index photon energy of Al doped SnO_2 thin films.

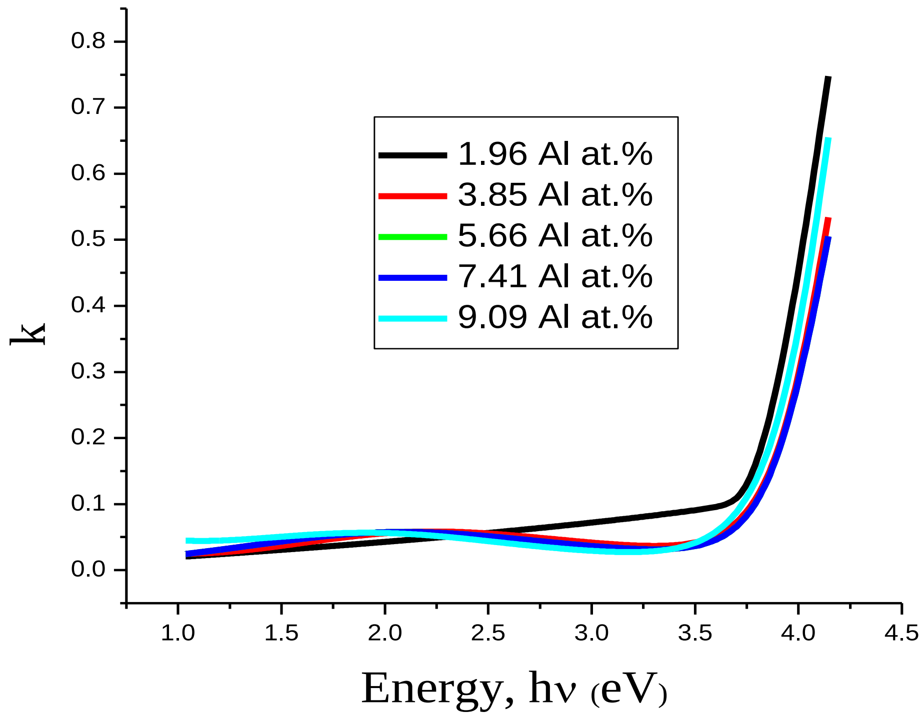

Figure 6 b). Extinction coefficient with photon energy of Al doped SnO_2 thin films.

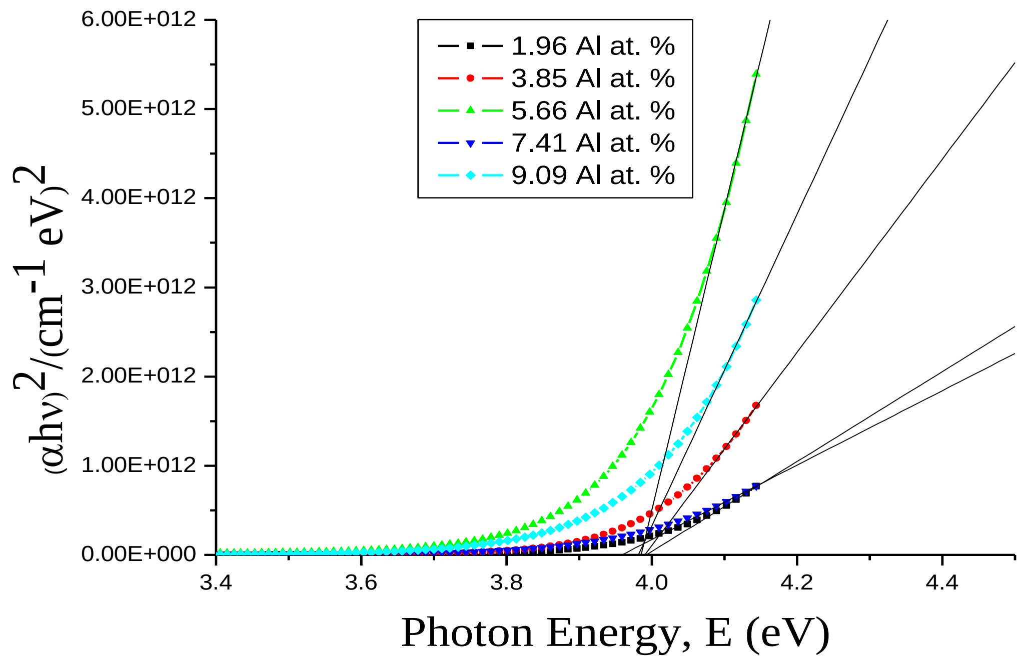

Figure 7. Dependence of $(\alpha h\nu)^2$ on photon energy of different thin films of SnO_2:Al grown on glass silicon substrate.

3.2 Electrical properties

3.2.1 Temperature and Resistivity

Different films of Al doped SnO_2 were deposited at optimized spray outlet to substrate distance of 4.5 cm and carrier gas pressure of 2 bars with varying substrate temperature. Four-point probe set up was used to measure sheet resistivity then resistivity calculated using equation 5[18].

$$\rho = R_S t \qquad (5)$$

where ρ is the resistivity, $R_S$the sheet resistivity and t, the thickness of the films.

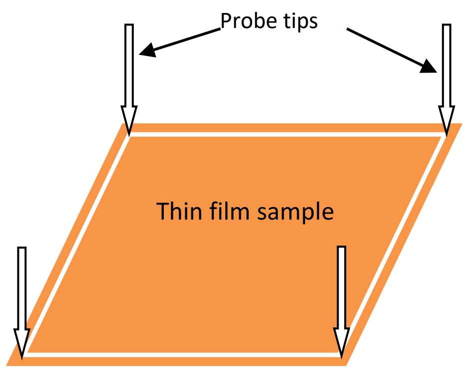

Figure 8. Four-point probe square setup

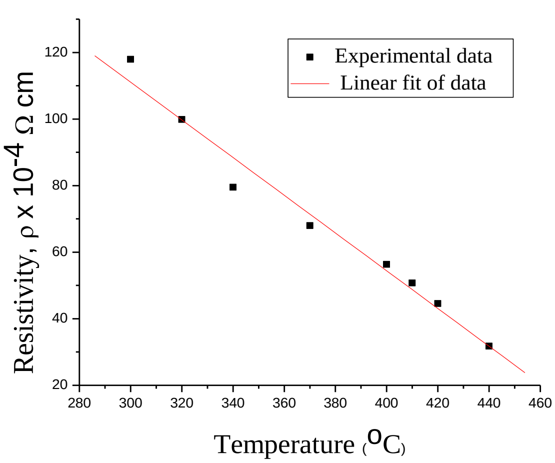

Figure 9 a). Graph of Resistivity of thin film against substrate temperature.

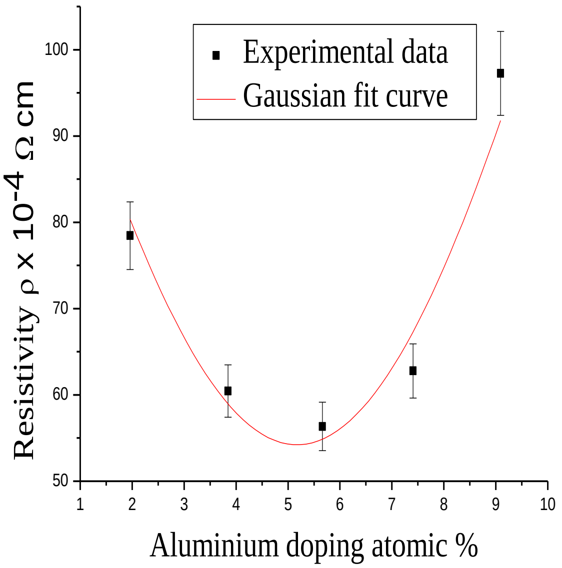

Figure 9 b) Graph of Resistivity of thin film against aluminum doping atomic %.

From figure 9 a), it is observed that; as substrate temperature increases, resistivity decreases significantly. The decrease in resistivity may be because of improvement in crystallinity with increased thickness, and increase in grains size which contribute to the increase of carrier mobility [20].

3.2.2 Doping and Resistivity

Effect of aluminum doping at. % on resistivity of thin films was also investigated. Equation 1 was used to calculate resistivity which was recorded as in table 7 and hence used to plot graph shown in figure 9 b).

From figure 9 b), it is observed that, as Aluminium dopant increases, resistivity decreases up to an optimum doping of 5.17 Al at. %. above this doping, resistivity of the thin film increases. This is due to substitution of Al^{3+}at the Sn^{2+} site which creates one extra free carrier. However, after a certain level of doping, the extra Al atoms occupy the interstitial positions and form Al_2O_3 leading to distortion of the crystal structure which gives rise to the greater electron scattering, i.e higher resistance.

4 Conclusions

We successfully deposited SnO_2:Al films using spray pyrolysis technique at different deposition parameters such as substrate temperature, carrier gas pressure and spray outlet to substrate distance and analyzed the data to determine their effect on optical and electrical properties of the films. Average transmittance of the film samples increased due to increase in crystallinity of the sample because of increase in their grain size with the increase in temperature. This occurs up to an optimum temperature after which it dropped drops drastically. At lower temperatures, milky films are formed due to incomplete decomposition of the sprayed droplets.

The effect of spray outlet to substrate distance is insignificant and therefore the process of film formation is best described that gaseous phase is constituted by the vapors of the precursor which volatilizes near the substrate and subsequently adsorbs on its surface where undergoes decomposition to yield a dense and adherent film. It should be pointed out, however, that a heterogeneous reaction could also denote a liquid–solid reaction with the solid phase being the substrate and the liquid being the melted precursor.As carrier gas pressure increases, average transmittance also increases. This occurs up to an optimum carrier gas pressure after which it drops. This is because at lower pressures, the size of the solution droplets becomes large, which results in the presence of recognized spots on the films and then reduction of transparency. This situation increases the scattering of light from the surface and then reduces the transmittance of the films.

We noted that increasing Al dopant in the tin oxide film, average transmittance improved up to an optimum level due to increase in crystallinity of SnO_2 but with continued increase in Al dopant the average transmittance decreases. This is due to decrease in crystallinity of SnO_2 that had an effect on average transmittance of the films.
We therefore determined that spray pyrolysis deposition parameters has an effect in deposition of SnO:Al and hence optimization of the parameters is necessary to obtain best films for analysis.

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