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Preparation and Characterization of Al doped SnO_2 Nanocrystalline Thin Films by Spray Pyrolysis Technique

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Abstract: Al-doped Tin Oxide (SnO_2) nanostructured (ATO) thin films are prepared by Spray Pyrolysis technique on glass substrates Prepared at 400˚C and annealed at 500°C, 600°C. Using a solution consisting of $SnCl_4.5H_2O$ starting material and doping source was $AlCl_3$ with various Al doping ratio. $Sn_{1-x}Al_xO_2$ (x = 0.04, 0.06 and 0.08) were dissolved in ethanol and stirred four hours at 50˚C. The effect of changes in doping content and annealing effect of Al:SnO_2 nanostructured thin films was investigated. The result of X-ray diffraction has shown that peak located at around 2Ɵ = 37.9° is corresponding to (200) plane which confirmed the presence of SnO_2 in tetragonal crystal system. All the observed characteristic peaks are well matched with the standard data base values. The UV-Visible transmittance figures are clearly depicting that all the prepared thin films are having transparency of 80%, the optical band gap was estimated to be around 2.56ev to 3.6ev. The scanning electron microscopic (FESEM) analyses show the crack-free and dense nature of the thin film formation. The size of the particle was measured from FESEM images and it was found to be in the range of 40-54nm. In AFM the average crystallite size was estimated 45nm and the root mean square roughness value was found to be 20 nm. EDAX to confirm the presence of dopant elements in the nanostructured thin films.
Keywords: Spray Pyrolysis, XRD, morphological and optical properties.

I. INTRODUCTION

The transparent conducting tin oxide (SnO_2) thin films have been widely used in many field owing to their, unique properties such as high electrical conductivity and high transmittance in the UV-Visible region[1,2]. Its properties are strongly depend on the deviation of stoichiometry, oxygen deficiency and the nature of the presence of impurity [3,4]. This material has proved itself to be one of the most attractive materials for gas sensor applications due to its special properties such as chemical and thermal stability and non-stoichiometry. Many researchers have been working to tailor the physical properties of SnO_2 thin films by employing different cationic and anionic dopant like Fluorine, Antimony, Zinc, Nickel, Aluminium etc., Depending upon the dopant, the SnO_2 thin films exhibit n-type or p-type conductivity. Aluminium is one of the acceptor impurity which acts as a lower valence cation in SnO_2 and can cause the p – type conductivity. Al doped tin oxide (ATO) nanocrystalline thin films can be prepared by a number of method such as spray pyrolysis [5], sputtering [6], CVD [7], Plasma and sol-gel methods [8-11].Spray Pyrolysis is suitable for a variety of oxide materials and relatively inexpensive. ATO thin films have been prepared using a spray pyrolysis technique and different amount of Al doped SnO_2 thin films were prepared at T_S=400°C and annealed at 500°C, 600°C. The effect of Al doping on the structural, optical, morphological and electrical properties of SnO_2 thin films have been studied. The prepared Al doped SnO_2 thin film has been used to many applications for gas sensing device.

Tin Oxide (SnO_2) is one of the transparent conducting Oxide (TCO) material having wider band gap of 3.6 eV [12] and ionic radius is Sn^{4+} r = 0.71Å [13]. To our knowledge undoped SnO_2 is an n-type semiconductor due to the presence of intrinsic defects like oxygen vacancies. Recent investigations have been focused on increasing n type conductivity of this material [14, 15], while both high quality n-and p type SnO_2 are essential for fabrication of SnO_2 based semiconductor devices. SnO_2 behaves as an n–type semiconductor, However when there is a suitable dopant doped with it, the carrier conversion takes place and change to P type semiconductor [16]. A lower valency cation as acceptor impurity such as Al^{3+} (ionic radius r = 0.51Å) [13] in tin oxide decreases n type conductivity and increases the hole concentration and hence the p – conductivity. However, it is to be noted that in a successful acceptor doping process, besides doping level, effect of annealing and the atomic or cationic size of the acceptor dopant is very important. The current investigation was done on the fully transparent conductive sprayed Al: SnO_2 nanostructure thin films. The n type SnO_2 inverted to P type conductivity prepared by SPD was evidenced [13].

In this paper, we report the effect of Al doping percentage and annealing effect of films, variation on structural, electrical and optical properties of SnO_2:Al thin films prepared by homemade Spray pyrolysis technique.

II. EXPERIMENTAL

Aluminum doped SnO_2 films were deposited onto the glass by Spray pyrolysis technique. The starting material for Sn was ($SnCl_4.5H_2O$) and doping source was aluminum chloride ($AlCl_3$). Both precursor and doping compound were dissolved in ethanol. The starting doping ratio (Al/Sn) was 4% in the solution. The resulting solution were stirred four hour at temperature 50ºC, spray rate and substrate to nozzle distance were maintained respectively at 10ml/min and 25cm. The glass substrate was mounted on hot plate then heated to 400ºC which was controlled by dimmastrate and digital thermometer connected to the hot plate. Then prepared samples were annealed at 500ºC and 600ºC by muffle furnace. After synthesizing the films, their structural, optical and electrical characterizations were performed. The structural properties of our samples were carried out by a Rigaku X–ray Diffractometer model DMAX 2200 with a copper anticathode (CUKα, λ = 1.5Å) with an angle range (2θ) of 20-70º. The optical parameters of the as – synthesized and annealed Al - SnO_2 films were measured using a shima DZU UV – 3101PC double beam spectrometer. The samples surface morphology was analyzed by the Field emission scanning electron microscope (FESEM:JEOL JSM 6701F), Atomic Force Microscopy (AFM). The elemental composition of the samples was determined by oxford instrument– INCAPENTAFET-X3 Elemental dispersive X-ray analyzer (EDAX).

III. RESULT AND DISCUSSION

A. *Structural Properties*

The effect of Al doping on SnO_2 has been investigated by various researchers in the past [17, 18]. With increasing Al dopant and annealing temperature in the tin oxide film, the crystalline of SnO_2 decreased. Hence the doping element Al is a grain growth inhibitor. The X-ray diffractogram of Al doped SnO_2 thin films prepared at the substrate temperature T_S= 400˚C and annealed at 500˚C, 600˚C are shown in Figures (1a),(1b) and (1c). A peak located at around 2Θ=37.9° is corresponding to (200) plane which confirmed the presence of SnO_2 in tetragonal crystal system. All the observed characteristic peaks are well matched with the standard data base values (JCPDS File No.88-0287). It can be clearly seen that the intensity of observed peaks are decreasing upon the increase of doping concentration. At the same time by comparing the XRD pattern of pure SnO_2 thin film a very small peak shift is observed in the case of Al doped SnO_2 thin films. This peak shift and the decrease in the intensity are due to the hinder of grain growth. The crystallite size was calculated using Scherrer's formula [19] and the average crystallite size found to be 32, 37,40 nm for 400˚C, 500˚C and 600˚C respectively.

Furthermore increasing the temperature leads to higher degree of crystallization and as a result new characteristic peak corresponding to (211) is observed. There is no any peak corresponding to Aluminium oxide, which implies the substitution of Al inside the SnO_2 lattice. It was observed that the peaks base was broadened. It should confirm the nanostructures occurrence of the Al - SnO_2 sample. This was in well agreement with the FESEM and EDAX. Fig (1b) shows that Al doping content and annealing effect to reduce the grain size. and annealing effect to reduce the grain size.

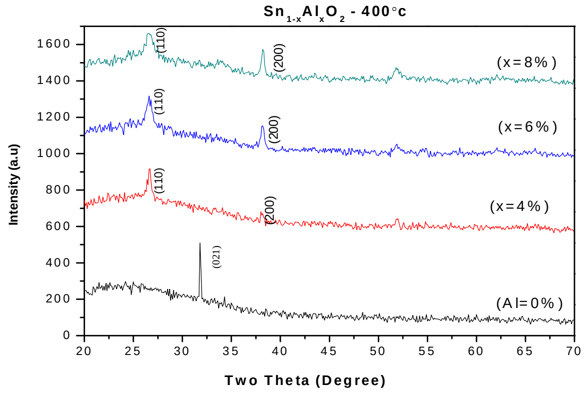

Fig. 1a XRD pattern of Al doped SnO_2 films deposited on glass substrates at 400ºC

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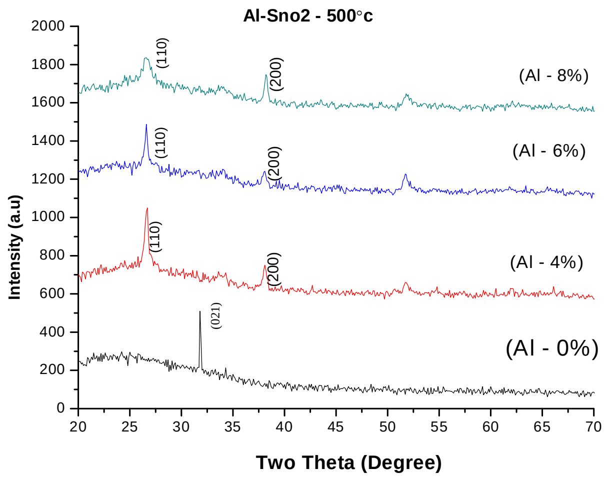

Fig. 1b XRD pattern of Al doped SnO_2 films deposited on glass substrates annealing at 500ºC

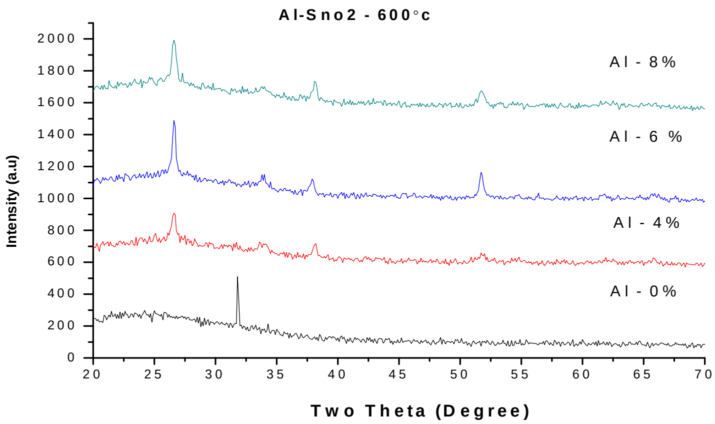

Fig. 1c XRD pattern of Al doped SnO_2 films deposited on glass substrates annealing at 600ºC

B. Optical Properties

Figures (2a-c) shows the UV-Visible spectra of Al doped SnO_2 thin films prepared at the temperature of T_S = 400°C and annealed temperature at 500°C and 600°C respectively. These figures are clearly depicting that all the prepared thin films are having transparency of 80%. Thin films annealed at 500°C shows the highest transparency (Figure 2a) of 90%. Further increasing the annealing temperature leads to the decrease of transparency. This is may be due to the increase of the density of the films upon the increasing of temperature. . From the fig it is observed that the transmission of the film decreases with increase in Al concentration and annealing effect. The average percentage of transmission of all the thin film samples is lies between (25% - 85%) in visible region. The optical band gap of the deposited Al - SnO_2 thin films are calculated by using the following formula [19]

$$(\alpha h\nu) = (h\nu - Eg)^{1/2} \qquad (1)$$

Where α (m^{-1}) is the absorption coefficient h (J.S) is Planck's constant ν (HZ) is the photon frequency Eg (eV) is the band gap energy. Figure (3a), (3b) and (3c) show the Tauc's plot drawn between $(\alpha h\upsilon)^2$ and hυ (eV). As seen from these figures, the band gap energy was found to be 4% to 8% aluminum content at deposition temperature 400ºC (prepared), annealing at 500ºC and annealing at 600ºC. The calculated direct band gap values of Al - SnO_2 films lay in the range 3.62 eV to 2.63ev for Al doped and un doped SnO_2 respectively. Which are also comparable with the values already reported 3.604 to 4.105 eV [20], 3.87 to 4.21eV [18]. The band gap narrows down due to the decrease in the number of charge carriers with increasing in Al doping and annealing temperature.

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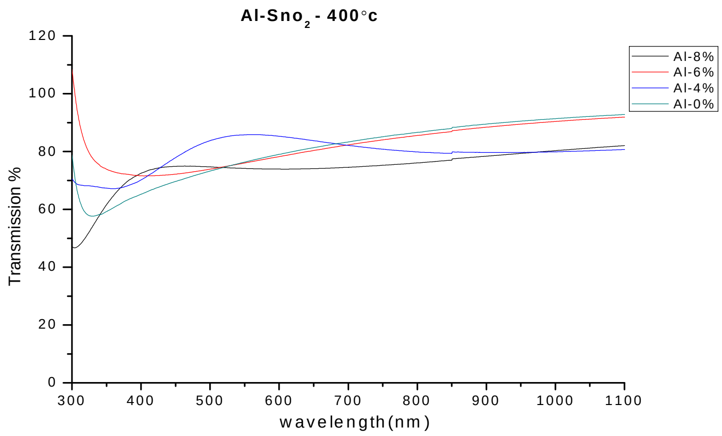

Fig. 2a Transmission spectrums of Al doped SnO_2 films deposited on glass substrates at 400ºC

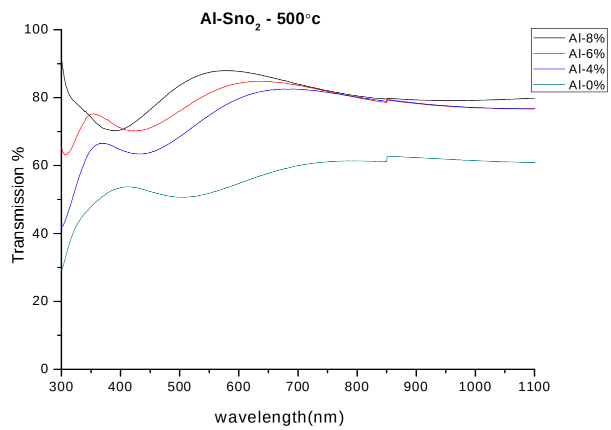

Fig. 2b Transmission spectrums of Al doped SnO_2 films deposited on glass substrates annealing at 500ºC

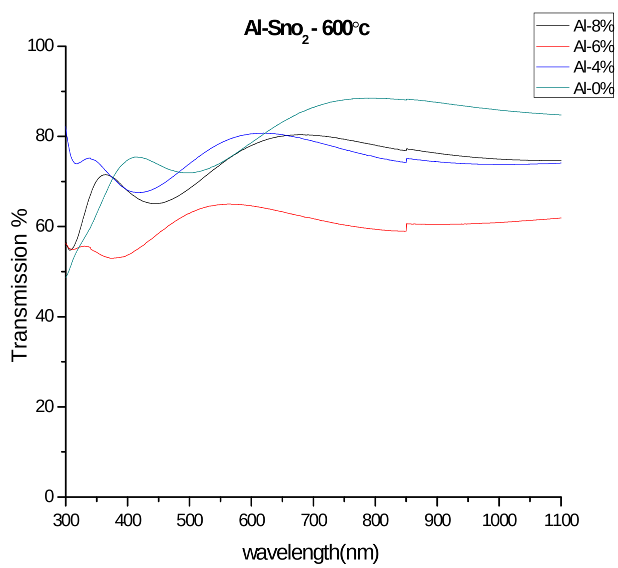

Fig. 2c Transmission spectrums of Al doped SnO_2 films deposited on glass substrates annealing at 600ºC

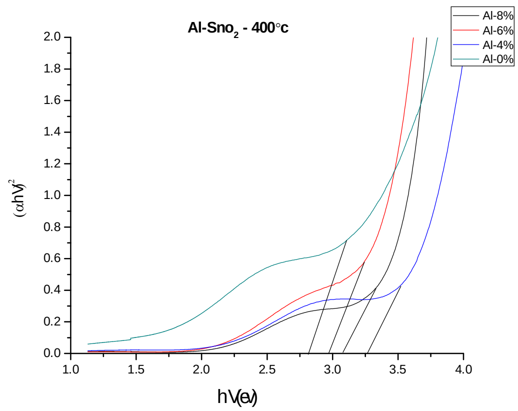

Fig. 3a Optical band gap of Al doped SnO_2 films deposited on glass substrates at 400ºC

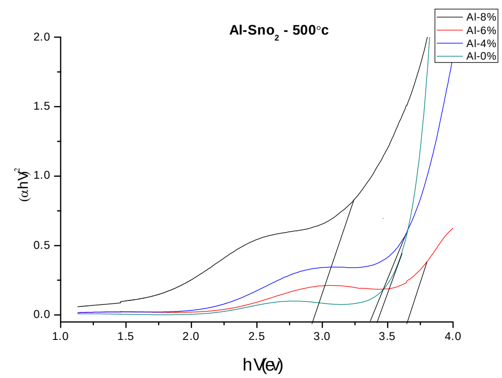

Fig. 3b Optical band gap of Al doped SnO_2 films deposited on glass substrates annealing at 500ºC

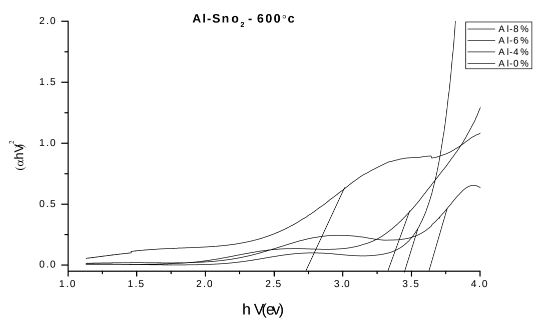

Fig. 3c Optical band gap of Al doped SnO_2 films deposited on glass substrates annealing at 600ºC

C. Morphological and Elemental Studies

In order to ascertain the film nature and the morphology, the prepared thin films have been examined by FESEM analysis. Figure (4a) showing the FESEM image of Undoped SnO_2 thin films prepared at the substrate temperature of T_S=400°C, Figures (4b), (4c) and (4d) are showing the FESEM images of 4%, 6%, and 8% of Al doped SnO_2 thin films prepared at the substrate temperature of T_S=400°C and annealed temperature at 500°C and 600°C respectively. Those figures show the crack-free and dense nature of the thin film formation. But there are agglomerated particles present on the film surface. Increasing the doping concentration leads to decrease of agglomeration. In all the cases FESEM images depicted the clear and dense nature of the film surface with homogeneous distributions of spherical shaped nanoparticles. The size of the particle was measured from FESEM images and it was found to be in the range of 40-54nm. Also the increase of particle size with increased of annealing temperature caused by the grain growth.

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The presence of aluminum in the SnO_2 thin films (prepared at T_S=400°C and annealed temperature at 500°C and 600°C) was confirmed by EDAX spectra Figures (5a), (5b) and (5c). All the EDAX spectra showed the Al peaks and some other peaks are also found which is due to the substrate. The peaks show the element that has been detected from the sample confirming the presence of Al, Sn and Oxygen in Al - SnO_2 thin films.

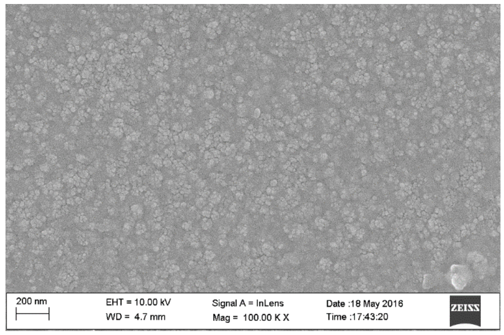

Fig. 4a FESEM of undoped SnO_2 films deposited on glass substrates at 400ºC

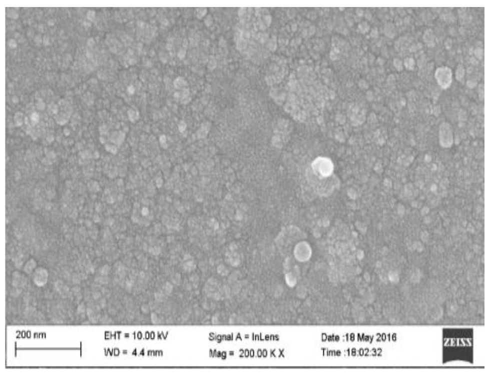

Fig. 4b FESEM of Al doped SnO_2 films deposited on glass substrates at 400ºC

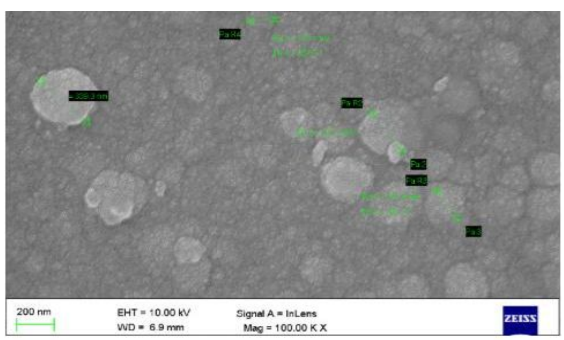

Fig. 4c FESEM of Al doped SnO_2 films deposited on glass substrates annealing at 500ºC

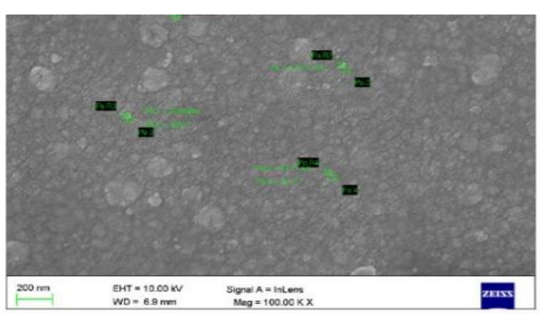

Fig. 4d FESEM of Al doped SnO_2 films deposited on glass substrates annealing at 600ºC

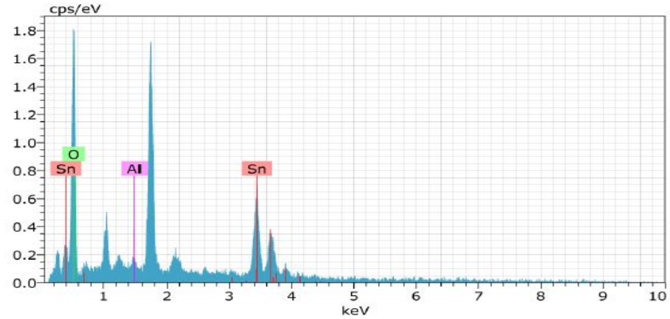

Fig. 5a EDAX of Al doped SnO_2 films deposited on glass substrates at 400ºC

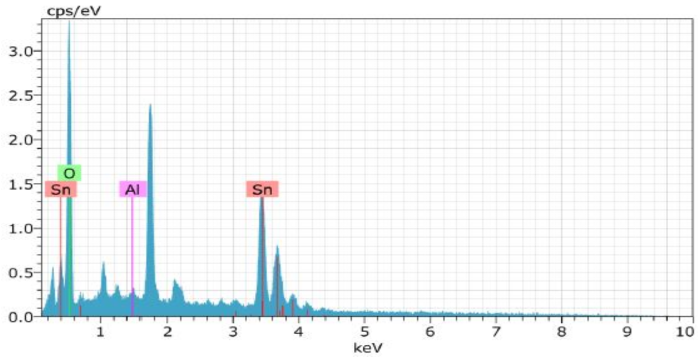

Fig. 5b EDAX of Al doped SnO_2 films deposited on glass substrates annealing at 500ºC

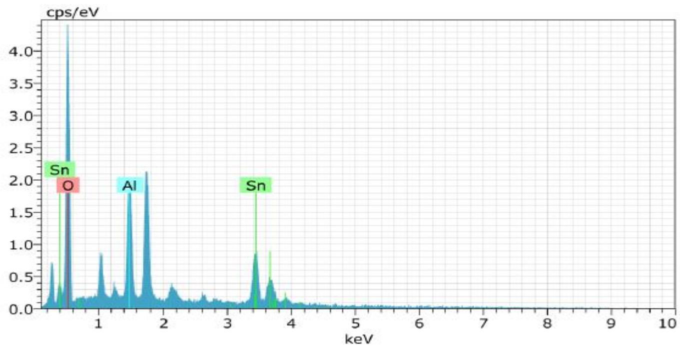

Fig. 5c EDAX of Al doped SnO_2 films deposited on glass substrates annealing at 600ºC

D. AFM Analysis

The prepared thin films have been subjected to analyze the topography and nanostructure of the prepared Al doped SnO_2 thin films and the corresponding 3D AFM, Figure (6) showing the AFM image of Undoped SnO_2 thin film. The Figure 6a shows the homogeneously distributed crystallites. As seen from the figure 6b and 6c, the crystallites have grown from the inner towards the surface. This indicates that the growth of crystallites at 500°C has been faceted towards the top of the surface and looking like nano tips. There is no any presence of voids in the films. The average root mean square roughness (R_{ms}) values of the film (20nm) determined using the relation [13]. The estimated crystallite size is in consistent with the crystallite size measured from XRD data. A similar kind of topography was found in the literature [14]. Furthermore, increasing the annealing temperature caused the agglomeration.

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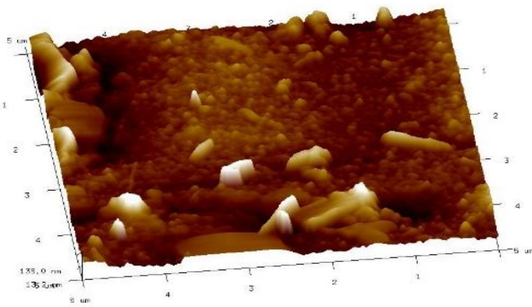

Fig. 6a AFM image of undoped SnO_2 films deposited on glass substrates at 400ºC

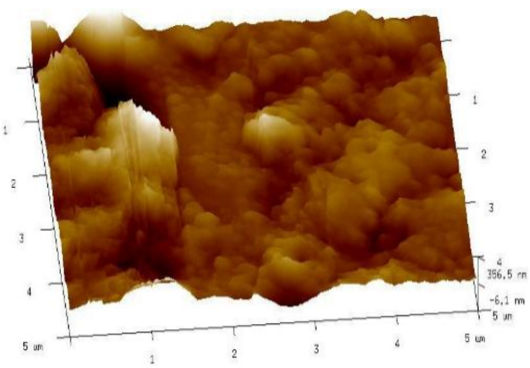

Fig. 6b AFM image of Al doped SnO_2 films deposited on glass substrates at 400ºC

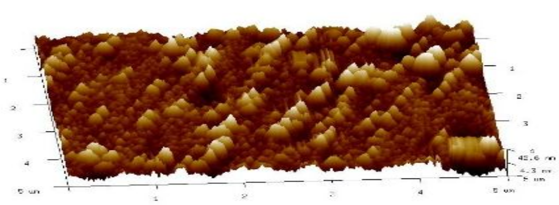

Fig. 6c AFM image of Al doped SnO_2 films deposited on glass substrates annealing at 500ºC

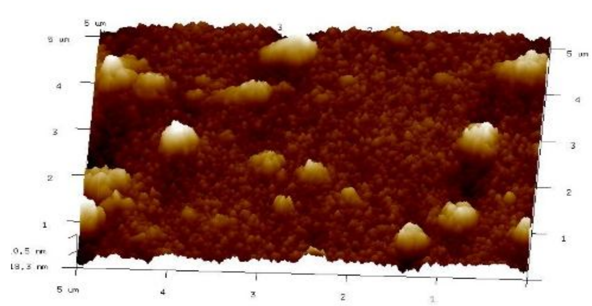

Fig. 6d AFM image of Al doped SnO_2 films deposited on glass substrates annealing at 600ºC

IV. CONCLUSION

Aluminium doped SnO_2 nanocrystalline thin films have been successfully deposited onto glass substrate using simplified low coast homemade Spray pyrolysis technique with various of aluminum concentration (4%, 6%, 8%) and annealing at 500ºC and 600ºC. The effect of Al concentration and annealing to influence the changes of physical properties in Al: SnO_2 thin films, the presence of SnO_2 with tetragonal crystal structure were confirmed by XRD analysis and the average crystallite was estimated to be 45nm. The X-ray diffraction patterns confirmed the proper phase formation of material and EDAX studies of the films showed that the exact amount of Al in the films are less that taken in the solution. FESEM images demonstrated the presence of nano sized particles and substantiated the presence of Al, Sn and O elements. The prepared thin films are having good transparency (65%-85%) in the visible range, in the visible region and the transparency decreases with the increase of Al doping and annealing effect in the films. The direct allowed band gap of the films has been found to lie with the range of 2.6 to 3.6eV. More interesting the particle size, band gap decreasing with increasing Al concentration and annealing temperature. AFM image showed the dense and nanotips like topography for the thin films annealed at 500°C. High electrical conductivity and high carrier concentration that we obtained are quite promising for gas sensing devices and solar cell application.

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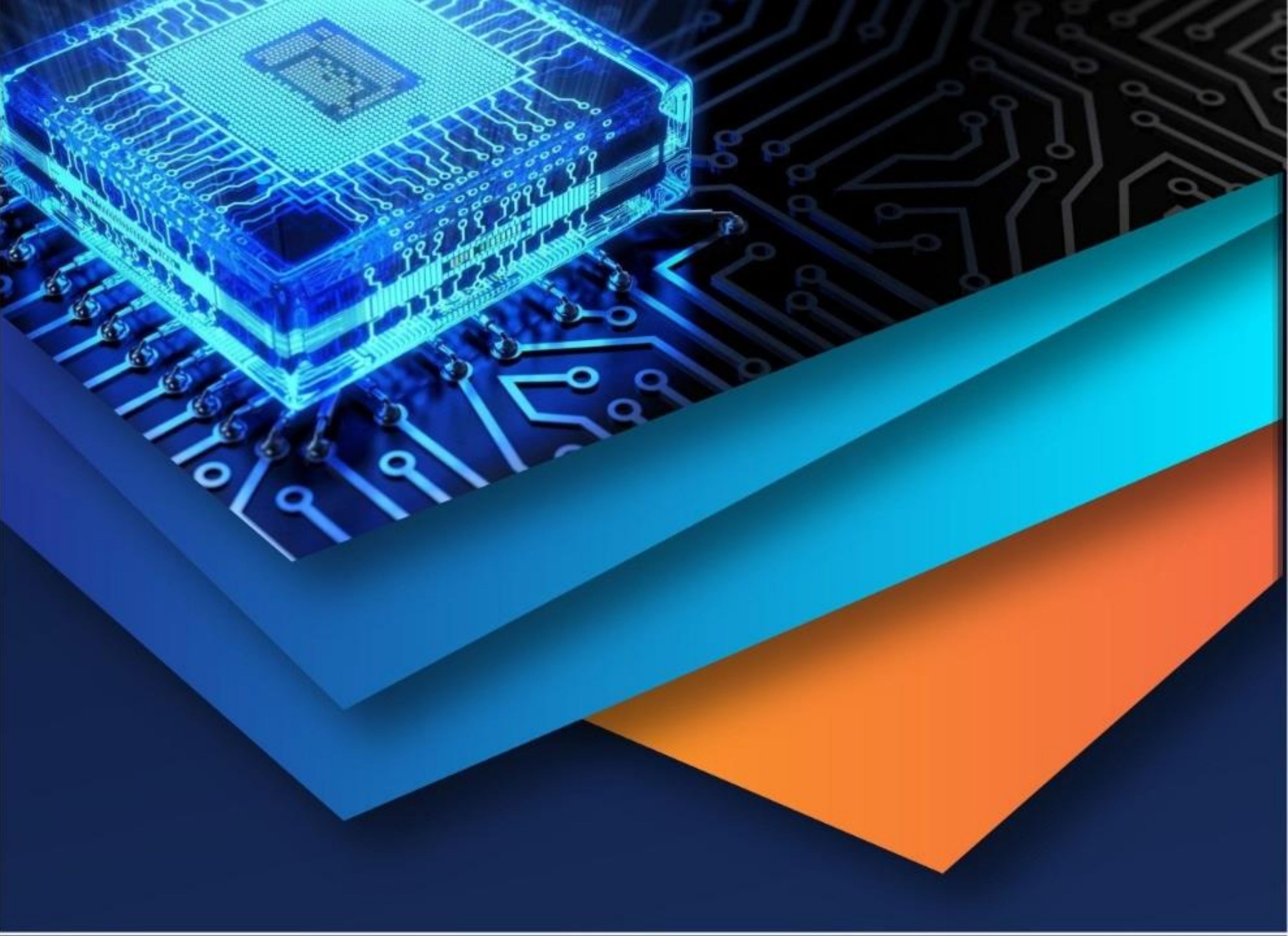

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