

Structural and Optical Properties of Phosphorous and Antimony doped ZnO thin films Deposited by Spray Pyrolysis: A Comparative Study

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Abstract: A study of structural and properties of pure (undoped) Zinc oxide (ZnO) and phosphorous (P) and Antimony (Sb) doped Zinc Oxide films has been carried out. The films were deposited by an automated spray pyrolysis equipment on both microscope glass at various elevated temperatures (270 °C - 420 °C) and on fluorine doped tin Oxide (FTO) substrates at 420 °C. Structural characterization using Raman spectroscopy showed the presence of the main peak for ZnO at 437 cm⁻¹ for all the films. Antimony doped films showed other peaks associated with the doping but phosphorous doping did not show extra peaks. Optical characterization using a UV-VIS-NIR Shimadzu (Model DUV 3700) double beam spectrophotometer provided both reflectance and transmittance data and Scout software was used to compute the band gap. At a wavelength of 600 nm, the average transmittance of the pure ZnO films was ~62 % while it was transmittance was ~85 % and ~80 % for Sb and P doped films respectively, an increase of ~23 % and ~18 % respectively. For the undoped ZnO films, high deposition temperatures led to band gap narrowing from 3.25eV to 3.10eV while doping resulted in band gap widening from 3.10 eV to 3.30 eV (for P-doped) and 3.10 eV to 3.33 eV (for Sb-doped), an observation confirmed by the increased transmittance on doping. The band gap narrowing for ZnO films makes the film become a better materials for visible light absorption which is good for photovoltaic applications. The wide gap broadening on doping makes the film more transparent to solar radiation making it suitable for transparent conducting oxide applications.

Keywords: Spray pyrolysis, Band gap, optical characterization, resistivity, doped ZnO, Transparent conducting oxides, photovoltaics,

I. INTRODUCTION

Zinc Oxide (ZnO) has aroused much interest in recent times due to its interesting properties which make it suitable in a number of applications. Due to its wide band gap ~ 3.37 eV and large exciton energy of 60 meV at room temperature, it has found potential applications in short wavelength piezoelectronic and optoelectronic device applications like nanosensors^[1-3], dye-sensitized solar cells^[4], field effect transistors (FETs)^[5], photodetector^[6], lasers^[7], light emitting diodes^[8], UV detection^[9] among other applications. ZnO is by default an n-type semiconductor material but has been converted to p-type by suitable doping with some elements^[10-13]. Different doping elements have been used on ZnO: Copper^[11], Aluminium^[14,15], Magnesium^[16], fluorine^[17], (gallium, nitrogen, indium)^[18-21]. A variety of findings have been reported. For instance, good stoichiometry, transparency and conductivity^[14, 22-24] and in other studies a decrease in band gap^[11]. However, some workers have suggested that doping with group V elements such as Antimony (Sb), Phosphorous, and Arsenic (As), produced materials with superior electrical properties^[24-27] and this has led to focus on such dopants^[12,13,23,28-30]. A number of techniques have been used to deposit both pure and doped ZnO films: chemical vapour^[31], wet chemical reaction^[22], spray pyrolysis^[11], radio frequency magnetron sputtering^[12], sol-gel^[15], molecular beam epitaxy (MBE)^[23], filtered vacuum arc deposition, aqueous based chemical technique^[30] and Metal Organic Chemical Vapour Deposition (MOCVD)^[6,14]. Among the deposition techniques used, spray pyrolysis (which is used in this study), is one of the best due to the flexibility, low cost and its industrial large scale applicability. Although some work has been done on doped ZnO films, most of the research has focused on only certain aspects of the material properties. Furthermore, we have not come across much work on phosphorous and Antimony doped ZnO films deposited by the spray pyrolysis technique and in particular a comparative study of the properties of phosphorous and Antimony doped ZnO films, which is the focus of this study.

II. MATERIALS AND METHODS

Film deposition was done on two different substrates: microscope plain glass substrates (for structural and optical characterization) and fluorine doped tin oxide (FTO- Hertford Glass Company, United States of America (for electrical characterization). The substrates were soaked in a detergent and sodium hydroxide for 30 minutes and then scrubbed using cotton buds. They were then rinsed with distilled water and then placed in an ultrasonic bath for 10 minutes at room temperature after which rinsing with distilled water was done before ultra-sonication in acetone for about 15

minutes. Finally, the substrates were rinsed with distilled water and dried at room temperature. The deposition solution for undoped ZnO was made by making a 0.5M of solution by dissolving 10.97g of zinc acetate ($Zn(CH_3COO)_2$) (99.99% of pure) in 50 ml methanol (CH_3OH) (Macron Fine Chemicals Limited) and thoroughly mix with a magnetic stirrer at a temperature of 150 °C. The solution with antimony dopant was prepared as follows: Antimony chloride ($SbCl_3$) AR/ACS (99% pure) was prepared at different concentrations by weight (0 -10 wt%) in a solvent of 10ml acetone in which 20ml of zinc acetate dehydrate was added under magnetic stirring. As for phosphorous doping, phosphorous pentachloride (PCl_5), CDH (99% pure) (Kobian Company Limited) was prepared at different concentrations also by weight but the solvent was 10 ml of deionized water. Film deposition was done using an automated Holmarc Spray Pyrolysis Equipment Model No: HO-TH-04 (Opto-Mechatronics PVT LTD) onto a substrate at a varying temperature (270 °C - 420 °C). A spray rate of 2 ml/min was used, and the spray head was about 13 cm from the substrate and was automated to move over the substrate uniformly for about 1 minute while spraying. The spray pressure was varied from 5×10^{-5} Pa to 8×10^{-5} Pa. Structural studies were done using a Raman Spectroscopy Equipment Model (SEKI TECHNOTRON CORP.). Optical measurements were carried out using a double beam UV-VIS-NIR Shimadzu (Model DUV 3700) spectrophotometer (Shimadzu, Japan). The optical parameters were obtained using Pointwise Unconstrained Minimization Approach (PUMA) and SCOUT softwares. The thickness of the films was determined using an Alpha-Step Stylus Profiler Model (KLA Tencor Limited).

III. RESULTS AND DISCUSSION

The Raman spectra of the undoped ZnO films, Sb-doped ZnO and P-doped are shown in figure 1(a)-(c) below.

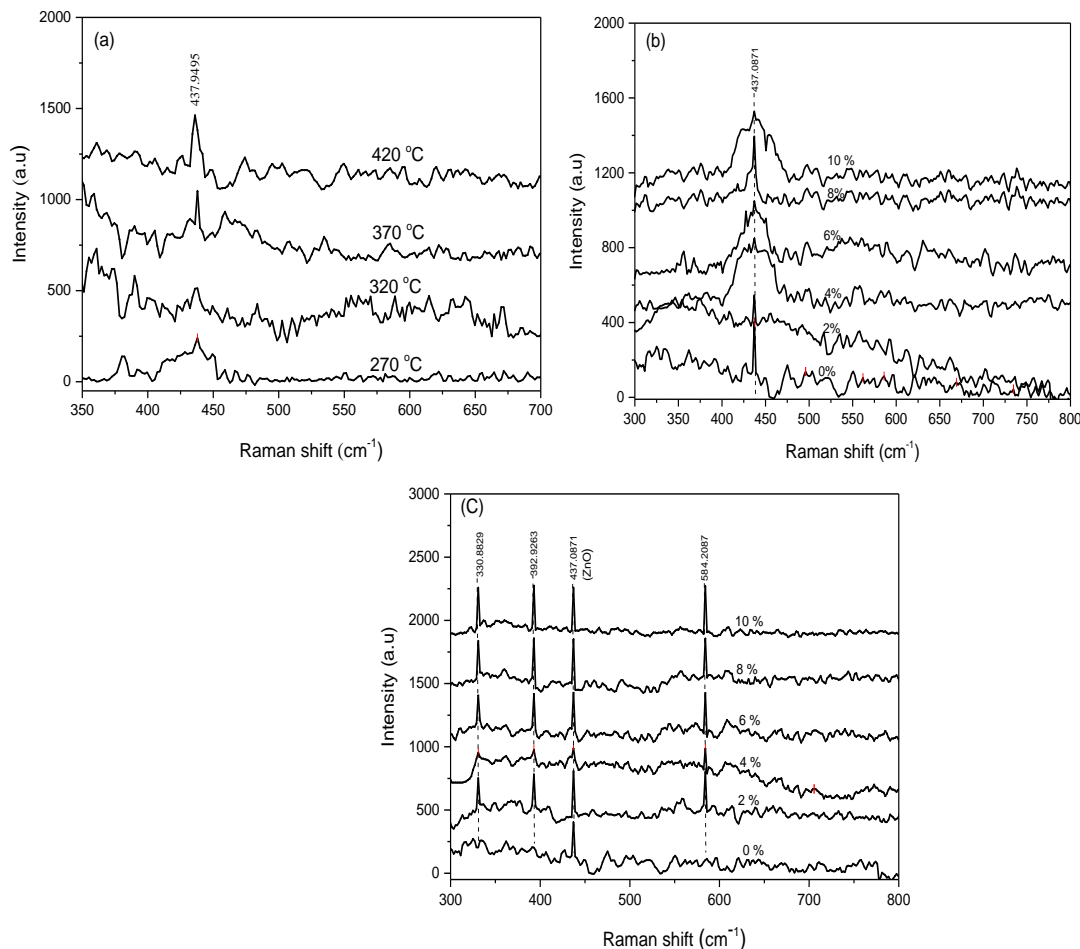


Fig 1: Raman spectra of undoped ZnO deposited at various deposition temperatures (a)antimony (Sb) doped ZnO at varying Sb concentrations at 420 °C (b) and Phosphorous (P) doped ZnO at various dopant concentrations (c) at 420 °C.

From figure 1(a), it is observed that there is one distinctive peak at 437 cm^{-1} which corresponds to the ZnO peak in line with results by Cerqueira *et al*^[32]. The peak reduces in breadth and becomes sharper with increased deposition temperature. This is due to increased crystallinity of the film as the deposition temperature is increased, result which concur with that of Schumm *et al*^[33]. When the ZnO was doped with antimony, other peaks emerged which were associated with multi phonon process mode, impurities and oxygen defects. We did not notice effect of doping on the peak sizes. Similar observation have been made by Rao and Santhoshkumar^[34].

Unlike in Fig. 1b, it is noted in fig. 1(c) shows that phosphorous doping does not result in extra peaks as compared to undoped ZnO as depicted in fig. 1(a). This could be due to the small ionic radius of the phosphorous compared to zinc, making it hard for the signal to detect the ions. This is contrary to the case of Sb whose ionic radius is similar to that of Zinc. It is also observed that phosphorous doping leads to broadening of the main ZnO peak figure 1 (c), (except for 2 and 8 % doping for which there need to do further investigation as to why). The broadening is as a result of the crystallinity decreases as the dopant concentration increases.

Optical Studies

Figure 2 (a)-(c) shows the transmittance of the undoped, antimony-doped and phosphorous-doped ZnO films.

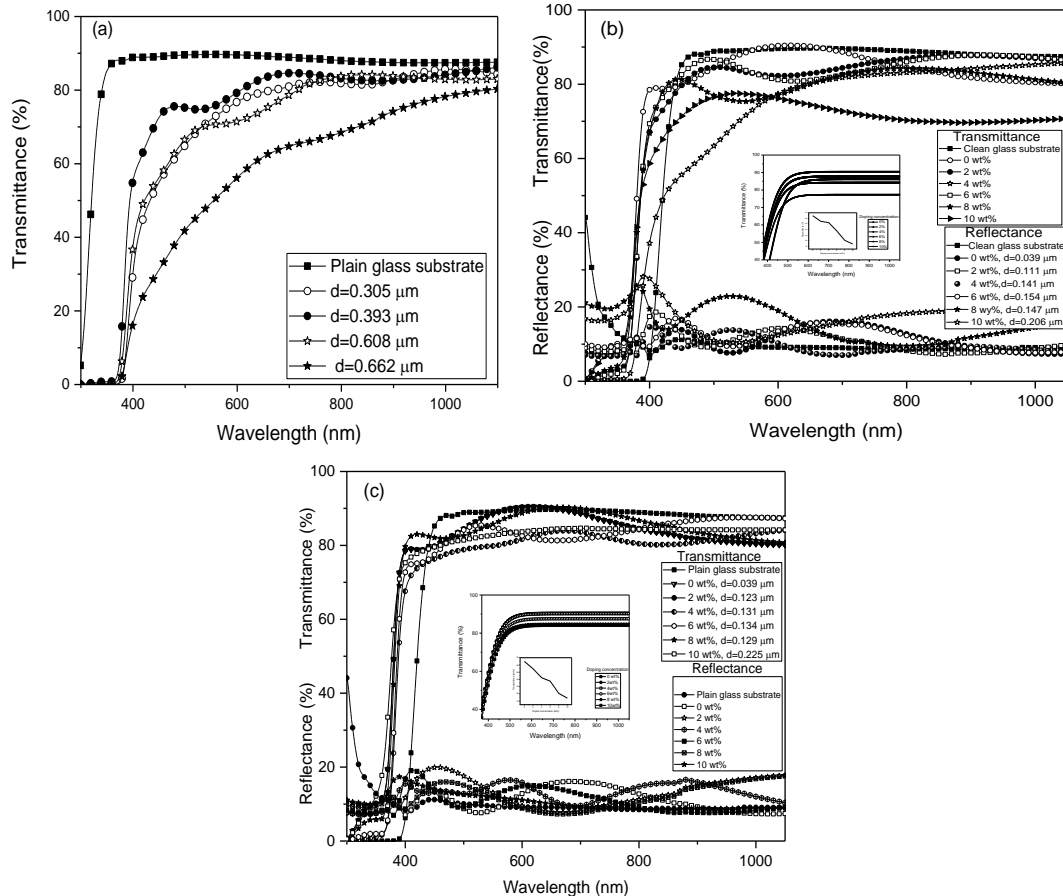


Fig2: Transmission characteristics for undoped ZnO films at various thicknesses (a) Sb-doped (b) and P-Doped (c) films. The inset is the transmittance at 700 nm for all doping concentration of ZnO:Sb and ZnO:P films. All films were deposited at a temperature of 420 °C,

Figure 2(a) for the undoped ZnO films shows the variation of transmittance with film thickness. Generally, the film transmittance decreases with increase in film thickness, an observation attributed to absorption as well as scattering within the films. It is observed that there is a tendency for the spectra for the films to lean away from short wavelength. This could have resulted from the change in the crystallinity from amorphous to wurtzite structures. The transmittance is between 20 % and slightly above 60 % for the thickest film and 40 % and 80 % for the other films. The wavelength range used was 300nm-700nm. A similar observation was done by Çetinörgü et al and for air-annealed chemical bath deposited CdS films[35] was explained as contribution of change of state from amorphous to wurtzite structure at higher deposition temperatures. Gumus *et. al.*,^[36] reported an average transmittance of 70% in the visible region while the transmittance obtained by our study was above 70%. As for fig. 2b showing transmittance of Antimony doped ZnO films, the transmittance is about 80-90% regardless of the doping level. Kumar *et. al.*,^[37] reported similar results for Boron doped ZnO while the same trend was observed by Yousofi^[38] when studying fluorine doped ZnO films. For the phosphorous-doped ZnO films fig 2c, transmittance tends to be more spread and ranges between 70 % and 90 %. ZnO:P had higher transmittance than both the undoped ZnO and antimony-doped ZnO films. From fig. 2c, there was a significant decrease in the transmittance with the increase of the dopant (phosphorous) concentrations. The prepared films had an average transmittance of about 78 % in the visible region. It is observed from the inset in figures b and c, there was a decrease in transmittance as the dopant concentration increased from 0 wt% - 10 wt%. This decrease in

transmittance is attributed to scattering losses at the surface of ZnO. It could also be due to increase in the fundamental absorption due to increased carrier concentration as more photons from the light source strike the film surfaces. The results obtained from the experiment are similar those reported by Nunes *et al.*,^[39] on the properties of ZnO thin films using spray pyrolysis technique, who obtained an average transmittance of 86%. According to Nunes *et al.*, this is one of the characteristic properties that is required for the opto electronic applications. ZnO:Sb had a better transmittance of 80 % as compared to the ZnO:P which had an average transmittance of 78 % which makes it a good material for opto-electronic applications.

Optical band gap

Fig 3 shows the absorption coefficient against photon energy (eV), for undoped ZnO as well as Sb and P-doped films. It can be observed that for the undoped ZnO, (Fig 2a), as the substrate temperature was raised from 270 °C to 420 °C, the band gap decreased from 3.25 eV at 270 °C to 3.1 eV at 420 °C. That is the band gap narrowed or reduced, an observation also noted by Cho^[40]

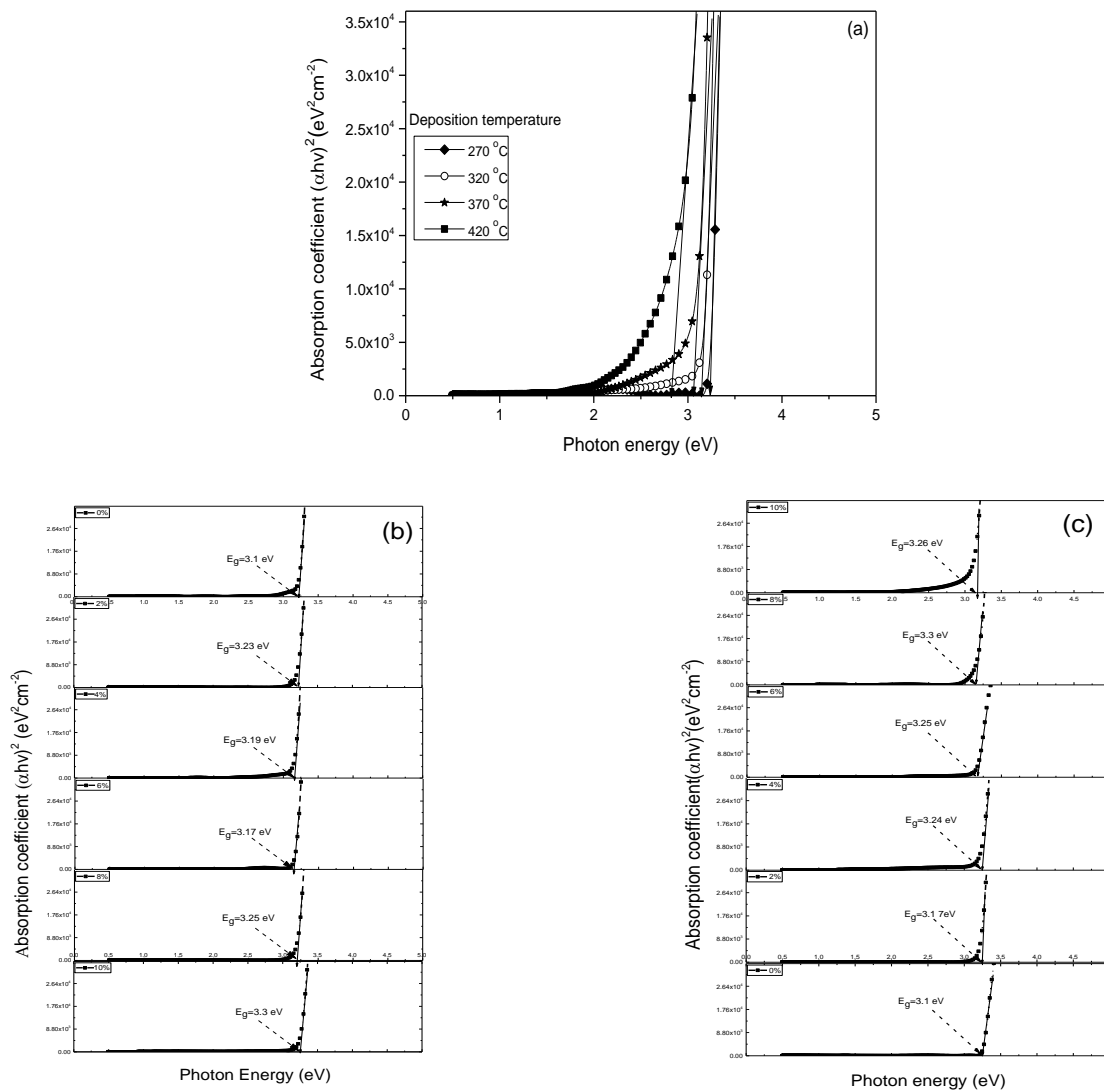


Fig 3: Graph showing absorption coefficient against photon energy for undoped ZnO at various deposition temperatures (a), Sb-doped ZnO and P-doped ZnO at various doping concentrations at a temperature of 420 °C (b) and (c) respectively.

One possible explanation for the band gap narrowing would be the increase in interatomic spacing with temperature increase which in turn makes the electron potential smaller leading to a narrower band gap. Besides, phonon–electron interaction is enhanced at higher temperatures^[41]. A narrower band gap would mean more light harvesting in the visible range hence the suitability of the materials in solar cell light harvesting. Temperature treatment is therefore key for enhanced light absorption for solar cell applications. On the other hand our work revealed that doping ZnO with

antimony generally widened the energy band gap from 3.10 eV to 3.33 eV as the doping levels were increased from 0%-10% while similar doping levels with phosphorous produced a minimum band gap of 3.10 eV and a maximum of 3.30 eV, another increase. It can be argued that there isn't significant difference in the maximum energy band gap for Sb- and P-doped as 3.33 eV is simply 3.30 eV when rounded off. More specifically, the energy band gap versus doping level in both antimony appears as a smoothened capital 'N' (Fig 4a) below. This is due to the Burstein-Moss effect and the band renormalization due to many body effects. The band gap widening can be explained as follows: As a material is increasingly doped, higher occupation of the donor states near the conduction band takes place. Thus more stationary states are created widening the conduction band gap

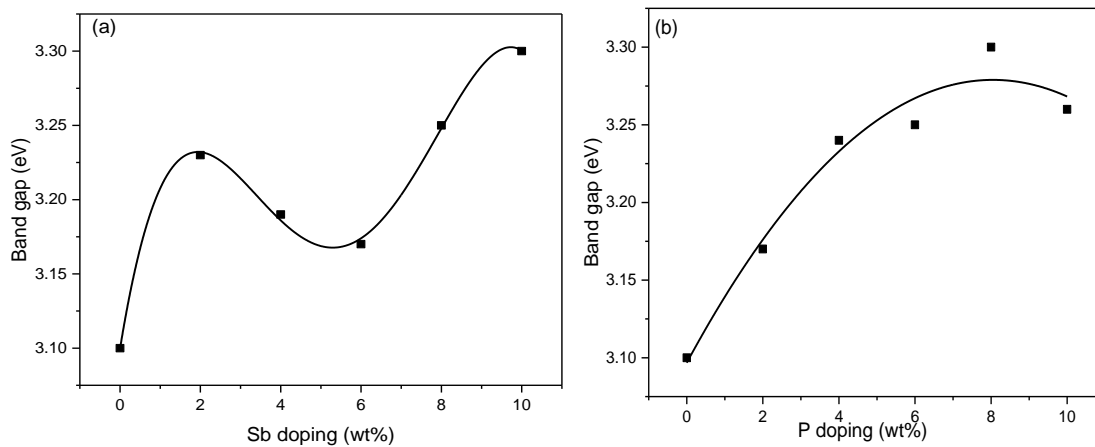


Figure 4: Energy band gap against doping concentrations for Sb (a) phosphorous (b)

This in essence is the Burstein-Moss (B-M) effect. Other researchers have explained the effect as also being as a result of band gap renormalization due to many body effects and an increase in the Fermi level of the degenerate semiconductors in the conduction band as well as pushing of conduction band edge to higher energies leading to high density of states near the conduction band and high electron carrier concentration^[43,44]. The band gap widening is particular of interest in transparent conducting oxides (TCOs) when applied as back contact in solar cell electrodes.

IV. CONCLUSION

Undoped ZnO, antimony-and Phosphorous-doped ZnO thin films have been deposited by spray pyrolysis and their structural and optical characterization done. Structurally, Raman spectroscopy showed the presence of the main peak for ZnO at 437 cm^{-1} for all the films. Antimony-doped films showed other peaks associated with the doping but phosphorous doping did not show extra peaks. Optical characterization indicated that at the visible region, the average transmittance of the pure ZnO films was ~62% while it was ~85% and ~80% for Sb- and P-doped films respectively, an increase of ~23 % and ~18 % respectively. For the undoped ZnO films, high deposition temperatures led to band gap narrowing from 3.25 eV to 3.10 eV while doping resulted in band gap widening from 3.1 eV to 3.3 eV (for P-doped) and 3.1 eV to 3.33 eV (for Sb-doped), an observation confirmed by the increased transmittance on doping. The band gap narrowing for ZnO films makes the film become a better materials for visible light absorption which is good for photovoltaic applications. The wide gap broadening on doping makes the film more transparent to solar radiation making it suitable for transparent conducting oxide applications.

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