

Electrical and optical properties of ITO films grown at room temperature on glass substrates using pulsed electron deposition

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Sn-doped In₂O₃ (ITO) films ~70nm were deposited on glass substrates using pulsed electron deposition (PED). A series of films were prepared by varying oxygen pressure (3.1 mTorr to 20 mTorr) in growth chamber during deposition and characterized for structural, electrical and optical properties. Resistivity as low as $2.94 \times 10^{-3} \Omega\text{-cm}$ and an average transmittance ~ 80% in the visible spectrum were achieved in films after annealing. As deposited films have a roughness of 2.17 nm and roughness (rms) was seen to increase with increasing oxygen pressure, these values are comparable to films achieved by other methods and better than the roughness of commercially available polycrystalline ITO films indicating that films prepared by PED technique are smoother. The results suggest that PED is a viable technique for exploring ITO films.

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1. Introduction

Indium tin oxide (ITO) is a transparent conducting material that has been extensively studied for its applications in the optoelectronic industry. ITO films find use in a wide variety of applications, such as transparent electrodes in liquid crystal displays, organic light emitting diodes (OLEDs), solar cells, plasma display panels, transparent heat reflecting windows and surface heaters for cameras, lenses, mirrors, car windows, gas sensors, and ohmic contacts for surface emitting diodes [1-9]. These applications require the films to be highly transparent and conducting. The mechanism of electrical conduction and optical transmission are interdependent [10]. Achieving high values of conductivity without compromising the transparency is still a major challenge especially when the films are prepared at room temperature without intentional heating of the substrate. Temperature and oxygen pressure during growth are seen to have a significant impact on the electrical and optical properties of ITO films, which is attributed mainly due to the effect of micro structural changes in the films [11-13]. In addition, properties of ITO films are also seen to be strongly dependent on the growth methods used. Techniques employed to prepare these films include chemical vapor deposition [14], RF and DC and magnetron sputtering [15-19], e-beam evaporation [20-21], spray pyrolysis [22], pulsed laser deposition (PLD) [23-25] and nano cluster deposition [26].

In this work, we explore a relatively new technique known as pulsed electron deposition (PED) for preparing polycrystalline ITO films deposited at room temperature. PED is a technique very similar to the popular pulsed laser deposition method (PLD), except that PED uses

energetic electrons to ablate the target material instead of a laser beam. PED technique provides the ability to deposit smooth thin films of oxide materials with a control over particulates generally present in PLD deposited films.

Details of PED are given previously that show the feasibility of using PED to grow 30 nm ITO films on Si (100) substrates achieving films with resistivity as low as $2 \times 10^{-4} \Omega\text{-cm}$ [27]. However, for practical optoelectronic applications, the films should be transparent in the visible portion of the electromagnetic spectrum which was not studied in our previous work. Here, we report growth of ITO films on transparent glass substrates by PED and characterization of these films including their transmission properties. This is, to the best of our knowledge, the first report of ITO deposition on glass substrates by PED.

2. Experimental

Glass substrates were cleaned prior to deposition in an ultrasonic bath using standard cleaning procedure (Acetone, Isopropanol, deionized water sequence) followed by blow drying with nitrogen gas. Commercially obtained Indium Tin Oxide (90:10) target one inch diameter and 0.25 inch thickness was used as a source. During all depositions the system was first pumped down to a base pressure of $< 3 \times 10^{-6}$ Torr before high purity (99.999 %) oxygen gas was introduced into the chamber to maintain a desired growth pressure. The electron accelerating voltage was 18 kV, frequency of the pulse 3 Hz, distance between the source and target ~ 3 mm and substrate to target distance ~ 7 cm. A shadow mask was used during deposition to create an edge,

which was later used to measure the film thickness. Each film was deposited using 5000 pulses which produced films with thickness of ~ 70 nm (deposition rate of 0.14 Å per pulse).

To study the electrical, structural, morphological and optical properties of the grown films, a number of characterization techniques were employed. Film thickness was measured using a profilometer. Resistivity was measured using 4 point van der Pauw configuration. Mobility and carrier concentrations were measured at room temperature with an applied magnetic field of 0.5 T using a standard Hall measurement unit. An atomic force microscope (AFM) from Digital Instruments (Veeco) was used to examine the surface roughness. A Kratos Axis 165 XPS system with an Al mono X-ray source (12 mA, 12 KV) was used for XPS analysis in the range of 500-1000 eV. Optical properties were examined using UV-Visible spectrophotometry (Cary 3C). The source light was incident normal to the ITO grown on glass substrate, air was reference for all the measurements which means that the data reported here for ITO includes the transmittance of the glass substrate. Commercially available ITO was purchased from Sigma Aldrich and used as received.

3. Results and discussion

Electrical, optical and structural properties of ITO films show strong dependence on the film composition, substrate temperature, oxygen pressure, and film thickness [28]. In this work, we have investigated effect of oxygen pressure and post annealing on electrical, structural and optical properties of the grown films. A set of films was prepared at room temperature at five different oxygen pressures viz., 3.1, 6.5, 10, 15, 20 mTorr (20 mTorr being the limit of the technique). Films grown with oxygen pressures greater than 10 mTorr were highly resistive and electrical properties could not be measured on those samples. Results from those samples are not included here.

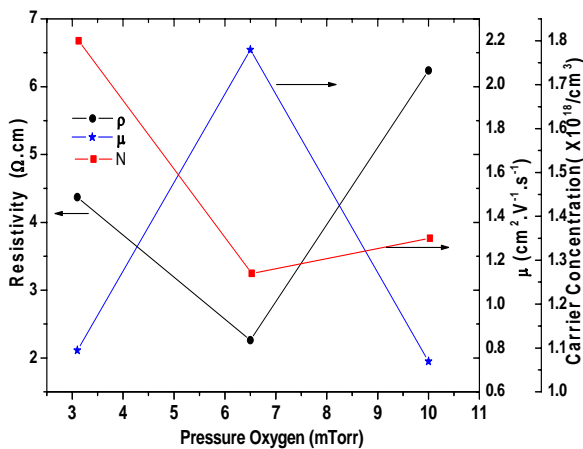


Fig. 1. (Color online) Resistivity (solid circle), Mobility (star) and Carrier concentration (square) with varying Oxygen pressure for as-deposited ITO films grown at room temperature.

Fig. 1 illustrates the electrical resistivity, carrier concentration and mobility of 70 nm as grown ITO films deposited at three oxygen pressures. The resistivity of the films decreases with reducing the oxygen pressure from 10 to 6.5 mT. As-deposited films with minimum resistivity of 2.2 Ω·cm were achieved at 6.5 mTorr oxygen pressure. In general, bands of oxygen defects (reported as vacancies /interstitials) or substitutional Sn-doping have been reported to affect the electrical properties of ITO films [29-30]. An increase in the number of oxygen vacancies/interstitial leads to an increase in free electrons (carrier density) and a consequent decrease in resistivity. A similar trend is seen in Figure 1 for the films deposited in the pressure range of 10 - 6.5 mT where the resistivity of the films was seen to decrease with decreasing oxygen pressure.

However, as seen in Fig. 1, films deposited by PED show an increase in resistivity with further decrease in oxygen pressure to 3.1 m Torr. Such increase in resistivity can be attributed to severe oxygen deficiencies at such low pressures. A similar observation has been reported by Kim et al., for films deposited by PLD where resistivity of ITO films increased for pressures below 10 m Torr [24]. As is clear resistivity of ITO films is sensitive to the oxygen pressure during deposition and films with low resistivity are only achieved in a short range of oxygen pressures, this range is seen to vary with the film preparation method. Thus the key is to obtain high conductivity without compromising the transmission of the films through optimization of oxygen pressure. This pressure is determined to be ~ 6.5 mTorr for the PED technique. For PLD method ITO films deposited in the oxygen pressure range of 0 -100 mT, lowest resistivity was achieved at 10 mT [24]. Dekkers et al., have also reported a similar trend in films grown by sputtering method, in the same pressure range [23].

The optical transmittance as a function of wavelength (300-900 nm) for 70nm ITO films deposited at room temperature at three different oxygen pressures is shown in Fig. 2. For comparison, the transmission of a bare glass substrate and commercially-available ITO is also shown in Fig. 2. Films deposited at 3.1 mTorr exhibit a low transmission (60 %) and the transmission is seen to improve with oxygen pressure. Highest transmission of 80% in the visible region was obtained for films deposited at 10.0 mTorr. The inset of Figure 2 shows the optical absorption coefficient showing that significant optical absorption occurs at wavelengths below 350 nm. The optical gap [31] was calculated by extrapolating the linear region of the absorption coefficient to zero using a previously reported procedure [31]. The optical gap increases from 3.88 eV to 3.94 eV as the pressure increases from 3.1mTorr to 10mTorr. The relationship between carrier concentration and bandgap does not follow the Burnstein-Moss model, which is valid only for heavily doped n-type semiconductors ($n > 10^{22}$ cm⁻³).

Table I. Resistivity (ρ), mobility (μ), carrier concentration (N), and band gap (E_g) of as deposited and annealed ITO films, all films were deposited at room temperatures.

O ₂ pressure (mTorr)	Resistivity (ρ) ($10^{-3} \Omega\text{-cm}$)		Mobility (μ) ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)		Carrier Concentration (N) ($\text{cm}^{-3} \times 10^{18}$)		Optical gap E_g (eV)	
	As Deposited	Annealed	As Deposited	Annealed	As Deposited	Annealed	As Deposited	Annealed
3.1	4370	2.94	0.789	5.44	1.8	390	3.8837	3.86872
6.5	2260	7.6	2.159	13.2	1.27	61.8	3.93541	3.76929
10	6240	7.22	0.739	7.34	1.35	117	3.9397	NA

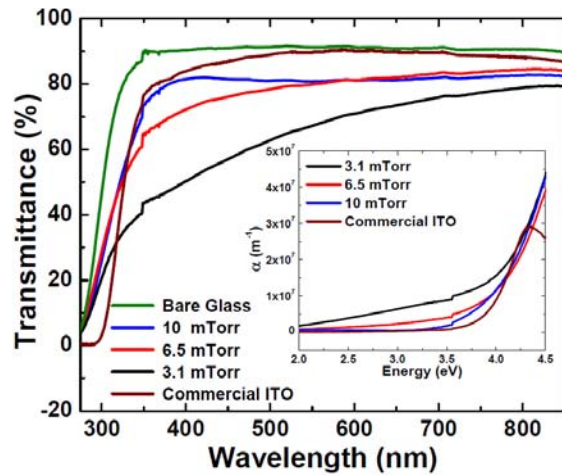


Fig. 2. (Color online) Optical transmittance spectra of as-deposited 70 nm ITO films grown at room temperature at various oxygen pressures. The inset shows the plot for $(h\nu)$ versus $(\alpha)^2$ which was used for calculating the estimated band gap.

The surface roughness (rms) of these films was obtained from the AFM images. The roughness (rms) increased from 2.17 to 5.28 nm with increasing oxygen pressure, as shown in Figure 3. Films grown at 3.1 mTorr oxygen pressure have a roughness of 2.17 nm which is comparable to films achieved by other methods [26]. However, these values are better than the roughness of commercially available polycrystalline ITO films (7 nm) [34] indicating that films prepared by PED technique are smoother.

3.1 Effects of post annealing

Post annealing effect on various properties of as-deposited films was studied by annealing the films at various temperatures in flowing oxygen.

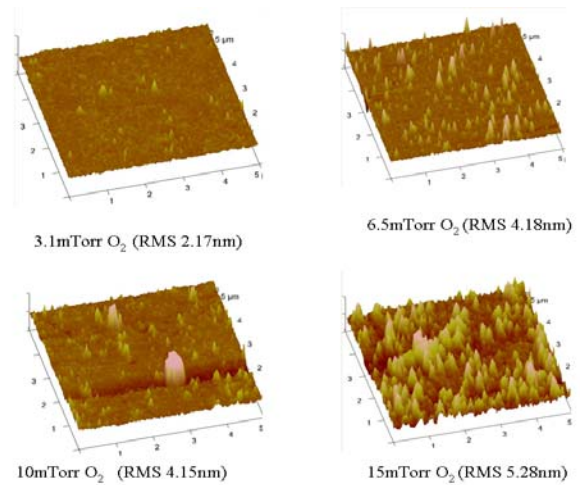


Fig. 3. (Color online) AFM scan (40 nm x 5 μm) of the ITO films deposited at (a) 3.1 mTorr, (b) 6.5 mTorr, (c) 10 mTorr, (d) 15 mTorr

Films deposited at 3.1 mTorr and post-annealed at 200 °C and 400 °C, showed a dramatic reduction in the electrical resistivity from 4.370 ($\Omega\text{-cm}$) to 2.94 $\times 10^{-3}$ ($\Omega\text{-cm}$). These films also showed a significant improvement in the mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$) from 0.789 to 5.44, and carrier concentration (cm^{-3}) from 1.8 $\times 10^{18}$ to 390 $\times 10^{18}$ after annealing (Table 1). However, beyond 400 °C, no appreciable change in resistivity was seen. Further, to optimize the post annealing time, films deposited at room temperature were annealed at 400 °C for 120, 180, 300 and 420 minutes. An appreciable decrease in resistivity was observed with annealing time, the change being more significant for annealing time of 420 minutes. So annealing time of 420 minutes and temperature of 400 °C in oxygen ambient was used for the remaining films.

In addition to an improvement in electrical properties with annealing, an improvement in transmission was observed with annealing. The effect was prominent for films grown at lowest oxygen pressure

deposited at 3.1 mTorr, as shown in Figure 4. The optical transmittance for the 70nm film deposited at room temperature and 3.1 mTorr oxygen pressure changes from 60 % for as-deposited films to 80 % for annealed ITO in the 400-600 nm range. The optical gap decreases slightly from 3.883 eV to 3.869 eV after annealing for the ITO deposited at 3.1 mTorr (Table 1).

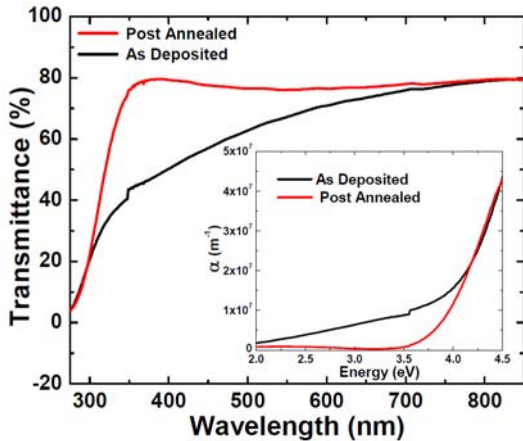


Fig. 4. (Color online) Transmittance spectra as a function of wavelength for as-deposited and post annealed ITO films grown at 3.1 mTorr oxygen pressure. The inset shows the plot for $(h\nu)^2$ versus $(\alpha)^2$ which was used for calculating the estimated band gap.

3.2 XPS Analysis

To understand the effect of change in oxygen pressure during deposition a set of films grown at room temperature and 3.1 mTorr pressure were chosen for analysis using XPS. All samples were subjected to ion milling with 3.7kV, 15mA at a pressure of 1×10^{-7} Torr (in XPS system) for 4 etch cycles of 60 seconds each. The high resolution XPS spectra of as deposited and annealed samples (O 1s, Sn 3d and In 3d) are shown in figures 5(a, b, c, respectively). For as deposited (un annealed) films, the O1s peak was observed at 530.5 eV, shifted from 531 eV. A similar shift has been reported indicating an oxygen deficiency in the film that comes from In_2O_3 – like oxygen [26, 35, 36], which can be expected for the films grown at lowest pressure. This corroborates well with the electrical measurements that indicate higher carrier concentration for 3.1 mTorr ITO deposited at room temperature. A broad shoulder peak near O1s was observed at ~ 533 eV in both as deposited and annealed films, which can be attributed to hydroxyl groups as observed in films prepared by other deposition methods [35]. The peak disappeared after a fourth etching cycle (240 seconds), indicating it may be a surface effect which is present only in the top layers due to moisture adsorption and is not seen towards the bulk of the sample. ITO films are reported to darken due to trapping of a Sn_3O_4 like phase in the bulk [35].

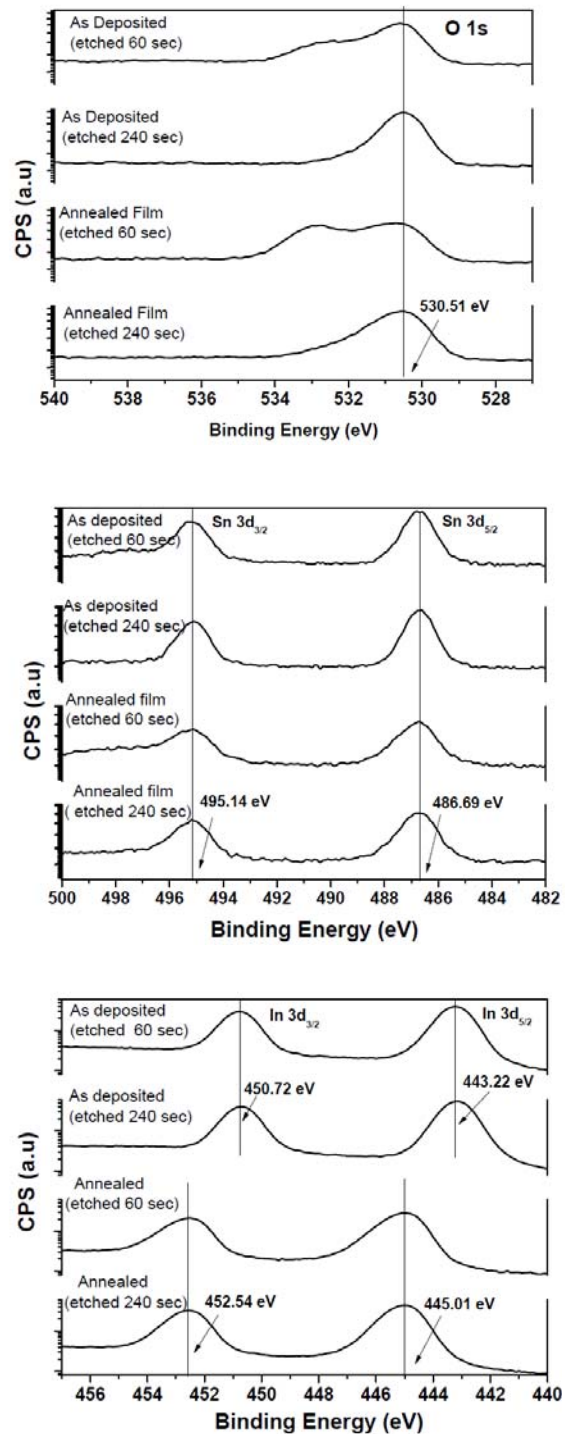


Fig. 5. (a,b,c). The XPS spectra of In 3d, Sn 3d and O1s of films deposited at 3.1 mTorr oxygen pressure for as deposited and post annealed film.

The depth profiles of annealed and un annealed films for Sn 3d (Figure 5b) gives a clear indication of presence of SnO_2 phase in the bulk of the film, with no shift in the Sn 3d peaks upon etching. Thus the XPS results show the absence of Sn_3O_4 impurity phases in both as deposited and annealed films.

For post annealed films it is observed that the In 3d peaks shifted towards higher binding energies compared to as deposited films, the shift in peaks being from 450.72 eV to 452.54 eV for In 3d_{3/2}, and 443.22 to 445.01 eV for In 3d_{5/2}, indicative of In₂O₃ [36]. These results match with the binding energy shifts reported with increase of oxygen content in literature for the In₂O₃ films grown at different O₂ flow rates [26]. The shift of the peak at 443.22 eV in the as deposited film suggests the presence of metallic phases in the bulk [37]. After annealing this peak shifts to 445.01 eV which indicates that metallic indium is converted to In₂O₃ phase after annealing. The suggested increase in oxygen content in annealed samples seen in XPS results matches well with a similar trend in electrical and optical properties in annealed films where a decrease in resistivity with a corresponding increase in mobility and increase in transmission is seen compared to the unannealed samples.

4. Conclusions

Pulsed electron deposition has been used to deposit thin films of ITO on glass substrates at room temperature for the first time. By investigating the effects of deposition conditions on the electrical and optical properties, the optimum pressure for obtaining conductive ITO films by PED was identified. Transparency in the visible region was found to increase as deposition pressure increased. Additionally, ITO deposited at 3.1 mTorr and room temperature showed marked improvement in resistivity and transparency after annealing under flowing oxygen, with resistivity decreasing to $2.94 \times 10^{-3} \Omega\text{-cm}$ and transparency increasing to 80%. Films deposited at room temperature have rms roughness values below commercial ITO indicating the PED technique may provide tighter control over deposition conditions leading to higher quality films. Thus PED is well suited for deposition of ITO films at room temperature and should be explored further to obtain high quality films at lower growth temperatures for device applications.

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References

- [1] C. W. Tang and S. A. VanSlyke, *Applied Physics Letters* **51**, 913 (1987).
- [2] D. K. Dhar, Reddy V S, S K Ray, *Semicond. Sci. Technol.* **21** (12), 1747 (2006).
- [3] C. Chu, W. Shrotriya, V. Huang, J. Li, Y. Yang, *Appl. Phys. Lett.* **88** (25), 253503 (2006).
- [4] K. W. Whang and J. K. Kim, *J. Display Technol.* **1**, 295 (2005).
- [5] G. Brauer, *Surf. Coat. Technol.* **112**, 358 (1999).
- [6] M. Rottmann and K. H. Heckner, *J. Phys. D: Appl. Phys.* **28**, 1448 (1995).
- [7] L. Zhao, Z. Zhou, H. Peng, R. Cui, *Applied Surface Science* **252**, 3884 (2005).
- [8] F. G. Comini, G. Sberveglieri, *Sensors Actuators* **78**, 385 (2001).
- [9] P. Chan, C. H. Sharma R. K. Yan, G. Hsing, Tang Z and J. K. O. Sin, *Sensors Actuators* **79** (1), 39 (2001).
- [10] J. L. Vossen, *Thin Solid Films* **9**, 1 (1977).
- [11] F. Hanus, A. Jadin, and L.D. Laude, *Appl. Surf. Sci.* **96-98**, 807 (1996).
- [12] H. Kim, J.S. Horwitz, A. Pique, C.M. Gilmore, D.B. Chrisey, *Appl. Phys. A: Materials Science. Process.* **69**, S447 (1999).
- [13] S. H. Kim, N.M. Part, T. Y. Kim, G. Y. Sung, *Thin Solid Films* **475**, 262 (2005).
- [14] T. Maruyama, K. Fukui, *Thin Solid Films* **203**, 297 (1991).
- [15] C.H. Yang, S.C. Lee, T.C. Lin, S.C. Chen, *Thin Solid Films* **516**, 1984 (2008).
- [16] Y. Sato, M. Taketomo, N. Ito, A. Miyamura, Y. Shigesato, *Thin Solid Films* **516**, 4598 (2008).
- [17] M. Bender, W. Seelig, C. Daube, H. Frankenberger, B. Ocker, J. Stollenwerk, *Thin Solid Films* **326**, 72 (1998).
- [18] B. S. Chiou, W. F. Wu, S. T. Hsieh, *Semicond. Sci. Technol.* **9** (6), 1242 (1994).
- [19] O. Tuna, Y. Selamat, G. Aygun, L. Ozyuze, *Journal of Physics D: Applied Physics* **43**, 055402 (2010).
- [20] P. Nath, R. F. Bunshah, B. M. Basol, O. M. Staffsud, *Thin Solid Films* **72**, 463 (1980).
- [21] H. R. Fallah, M. Ghasemi, A. Hassanzadeh, H. Steki, *Materials Research Bulletin* **42**, 487 (2007).
- [22] S. M. Rozati and T. Ganj, *Renewable Energy* **29**, 1671 (2004).
- [23] J. M. Dekkers, G. Rijnders, D. H. A. Blank, *Applied Physics Letters* **88**, 151908 (2006).
- [24] H. Kim, C. M. Gilmore, A. Pique, J. S. Horwitz, H. Mattoussi, H. Murata, Z. H. Kafafi, D. B. Chrisey, *Journal of Applied Physics* **86**, 6451 (1999).
- [25] C. Viespe, I. Nicolae, C. Sima, C. Grigoriu, R. Medianu, *Thin Solid Films* **515**, 8771 (2007).

- [26] S. V. N. Pammi, A. Chanda, N.-J. Seong, S.-G. Yoon, *Chemical Physics Letters* **490**, 234 (2010).
- [27] H. V. Nampoore, V. Rincon, M. Chen, S. Kotru, J. *Vac. Sci. Technol. A* **28**, 671 (2010).
- [28] Wen-Fa and C. Bi-Shiou, *Semiconductor Science and Technology* **11**, 196 (1996).
- [30] X. Yin, W. Tang, X. Weng, L. Deng *J. Phys. D: Appl. Phys.* **42**, 025104 (2009).
- [31] J. Ederth, A. Hultåker, P. Heszler, G. A. Niklasson, C.G. Granqvist, A. Doorn, C. Haag, M. J. Jongorius D. Burgard, *Smart Mater. Struct.* **11**, 675 (2002).
- [32] W. Du, F. Zong, H. Ma, J. Ma, M. Zhang, X. Feng, H. Li, Z. Zhang, P. Zhao, *Crystal Research and Technology* **41**, 889, (2006).
- [33] E. Burstein, *Phys. Rev.* **93**, 632 (1954).
- [34] T.S. Moss, *Proc. Phys. Soc. London B* **67**, 775 (1954).
- [35] D. Kato, G. Xu, Y. Iwasaki, Y. Hirata, R. Kurita, O. Niwa, *Langmuir* **23**, 8400 (2007).
- [36] J. C. C. Fan and J. B. Goode nough, *Journal of Applied Physics* **48**, 3524 (1977).
- [37] R. W. Hewitt, N. Winograd, *J. Appl. Phys.* **51**, 2620 (1980).

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