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Investigation on tin concentration dependence of solution processed indium oxide thin film

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Abstract
Indium tin oxide (ITO) thin films have been prepared by spray pyrolysis using a very low concentration of indium precursor. The spray process parameter like the concentration of SnO precursor in spray solution, have been optimized for obtaining optically transparent, structure and device-quality ITO films.
The material properties are reported by studying the structural and optical properties of the ITO films prepared at a relatively lower temperature of 574K. The surface morphology has been studied by atomic force microscopy it was found ITO films have nanostructured. The grain size and the roughness of the films doping concentration 2%, 4% and 6% was (76, 87 and 127)nm and (0.969, 2.56 and 1.61)nm respectively. The concentration rate 2% produces an overall shift to lower photon energies of the optical constant spectra and the optical transmission of greater than 85%, which is related to the increase in electrical resistivity. Characterization of ITO on glass and silicon has shown that increasing the concentration rate will increase in the optical band gap of the ITO films. Samples deposited at doping concentration 2%, 4% and 6% the optical gaps of 3.74 eV, 3.9 eV and 3.73 eV respectively.
Keyword: Indium tin oxide, spray pyrolysis, optical properties and nanostructure properties

1. Introduction

Indium tin oxide (ITO) is a commonly used transparent conducting oxide (TCO) with applications as a transparent electrode for flat panel displays (Nomura 2004), photovoltaic devices (Iwasaki 2007) and as an infrared mirror in energy saving windows (Park 2007). ITO offers the best combination of electrical conductivity and visible light transmission with excellent environmental stability, reproducibility and surface morphology (Fortunato 2008 and Brewer 2004). ITO is based on indium oxide (In_2O_3), a wide optical gap (≈3.6 eV) semiconductor material which, as a result of being n-type degenerate, is electrically conducting. Two explanations given in the literature for the source of the free carriers in indium oxide are (a) oxygen vacancies (Yeadon 2011) and (b) a hydrogen doping mechanism (Kim 2005, Kim 2008 and Kim1999). In ITO, the free charge carrier (electron) concentration is further increased by substitutionally doping In^{3+} sites with Sn^{4+} . The doping efficiency is related to the energy delivered to the growing film during deposition. To effectively dope the ITO, commercial films are deposited at high temperature (Aoki 2006 and Yoon 2007). The recent interest in flexible electronic devices has increased demand for processes offering low temperature deposition of high quality ITO films onto large area polymeric substrates (Thanikai 2012). The move to polymeric substrates is driven by their relatively low cost, mechanical flexibility, and light weight (Song 2010). These properties not only make flexible devices attractive to the end customer, but also enable efficient mass manufacturing using ‘roll to roll’ processes. However, due to the thermal sensitivity of polymers, sputter deposition of high quality ITO remains an area of intense research (Armstrong 2009).
Thin films of ITO can be prepared by a variety of techniques such as chemical vapour deposition (Jung 2012), spray pyrolysis (Kim 2009), evaporation of indium followed by oxidation (Betz 2006), vacuum evaporation (Kiju 2010), and magnetron sputtering (Yeadon 2011 and Kim 2010). Among these techniques, spray pyrolysis provides an easy route to fabricate thin films at low cost. It can be easily modified for mass production and device quality oxide films can be obtained over a large area.
Spray pyrolysis involves optimization of many process parameters. Definite control on the optoelectronic properties and growth mechanism of the films can be realized only if one investigates thoroughly the influence of every process parameter on the film properties. This procedure helps in preparing high-quality conducting oxide films, which are useful for the development of photovoltaic solar cells and TCO films (Kim2009 and Li 2004).

Transparent heaters have been developed in an attempt to keep track with the remarkable progress made in liquid crystal display (LCD) technologies, due to their crucial importance in defrosting or maintaining LCD displays at optimum operating temperatures. Moreover, transparent heaters have attracted considerable attention in the automotive industry owing to their defrosting capability. Indium tin oxide (ITO) films have been utilized world wide as a heat generating material for the construction of transparent heaters, since these films possess environmental stability and high transparency to visible light (Choi 2009, Lewis 2000, Chiu 2009 and Chang 2013). Recently, an attempt was made to use single-walled carbon nanotubes (SWCNTs) as an alternative to ITO films for the fabrication of transparent electrodes and heaters. Nevertheless, ITO films are still regarded as being a more suitable material for transparent heaters, because of the degradation problems of SWCNTs and the complex separation processes of bundles of SWCNTs. Commercial ITO-based transparent heaters have been constructed through relatively expensive deposition processes such as vapor deposition methods (Shin 2010).

Indium tin oxide, a transparent conducting oxide, is an important coating material for use in energy saving lamp, solar cells, liquid crystal display, automobile measuring instrument due to its excellent electro-optical properties such as high electrical conductivity and transparency to light, etc. In recent years, much effort has been made on the synthesis of ITO nanoparticles, especially on the preparation of ITO films. It has been shown that the electrical, catalytic and optical properties of nanoparticles depend sensitively on its shape and size. Hence, shape-controlled synthesis of nanoparticles has been reported (Armstrong 2009 and Fung 2011).

In the present work, thin films of ITO have been deposited on glass substrates at various doping concentration of SnO. Atomic force microscopy has been carried out to determine the structural properties of the deposited films. The structural parameters such as crystallite size, root mean squar (rms) and roughness. The effect of solution doping concentration morphological and optical properties of the deposited films are studied and the results are reported.

2. The experimental work

In this research ITO thin films were deposited by spray pyrolysis technique on glass substrates. The carrier gas used in all the experiments was filtered air, which was supplied by an air compressor. Before deposition, glass substrates were ultrasonically cleaned in acetone, ethanol and deionized water for 5 min each and blown dry. The distance among substrate and nozzle has been fixed at 30 cm. To prevent precipitation, a few droplets of acetic acid were added to precursor solution. Air flow rate was 18 Lit/min. The technique of active spray pyrolysis from aqueous $InCl_3.4H_2O$ solution was used for deposition of ITO films. The In_2O_3 :Sn were deposited by spray pyrolysis. Afine spray consisting of a certain quality of indium chloride ($InCl_3.4H_2O$) and tin chloride ($SnCl_5.4H_2O$) was dissolved in pure deionized water. Variations in deposition parameters such as recursor concentration (2% - 6%), temperature of pyrolysis (*T=573K*), and volume of sprayed solution 20 ml were used for controlling the structure of the deposited films. The flow rate of sprayed solution was 0.15 ml/s for all experiments. The film thickness (d) was varied in the range of 100–450 nm. The surface morphology and the structural properties of the ITO films were examined by atomic force microscopy (AFM) (Seiko Instruments SPA 400). The optical properties of ITO films were analyzed by UV/VIS/ NIR spectrometer (Varian, Cary5000) in a range of (200-900)nm.

3. Results

An analysis of the AFM pictures of ITO films prepared at the doping concentration 2%, 4% and 6% has been made. It is clearly seen from the pictures that the surface smoothness, uniformity and grain size increase with increase in doping concentration to 4% and then deteriorates. Fig. 1.a shows the AFM picture of ITO film prepared at 2% doping concentration. The surface is covered with grains of uniform size and the grain size is found to be the maximum of about 76nm. The average grain size calculated using the standard statistical averaging technique is ≈76nm. A smooth and uniform surface morphology is evident from the AFM picture.

The roughness of the grown films was found to be in the range 0.969 - 2.56 nm (Fig. 1). It can be noted that RMS increases with film at doping concentration 2% up to 200 nm. However, for films over 4% Cp, an irregular increase in the RMS with values over 3.12 nm was observed (shown in Fig. 1), a behavior related to the presence of nano- or micro-features on the surface of the films, as it can be seen in Fig. 1 a to f.

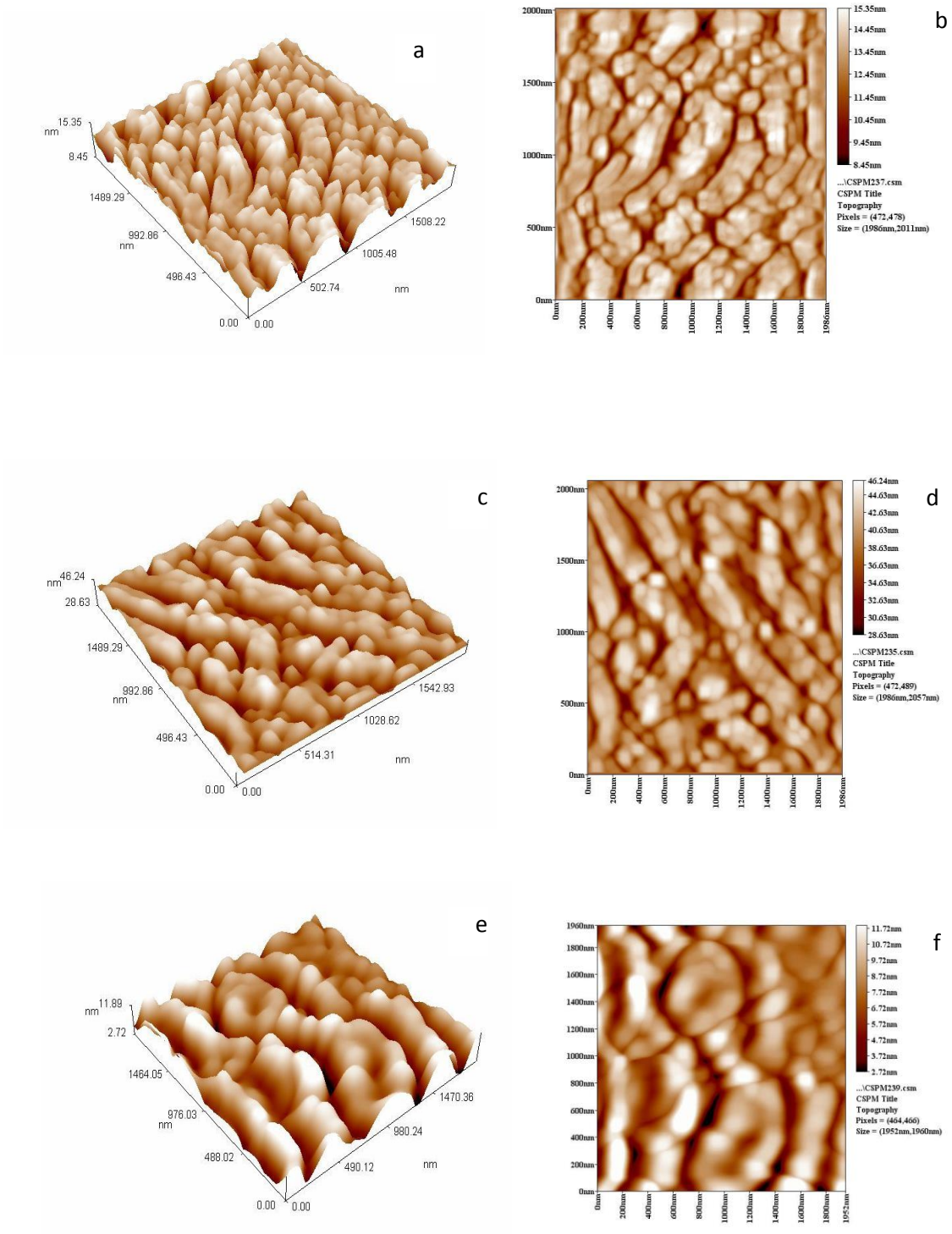

Fig .1 AFM picture of ITO thin film deposited at different doping concentration a) 2%, b) 4% and c) 6%.

The absorbance spectra recorded in the range of (300-900) nm are shown in figure 2 as a function of doping concentration (SnO) in In_2O_3. This indicates that the film is active in the visible region of the spectrum. Thus, there is good possibility to employ the film it as a visible light energy conversion material.

The absorbance spectra of ITO thin layers in Fig. (2), show significant influence of the doping concentration on spectrum absorbance. The absorbance decreases with increase the Cp. These samples present an abrupt absorbance edge around 350 nm corresponding to a gap of 3.6 eV. Films deposited at Cp appeared lightly dark due to the low wavelength absorption at low doping concentration for deposition. The decreases in the optical absorbance (high transmittance) could be attributed to the improved structure coupled with reduction in the number of charge carriers.

Optical parameters such as absorption coefficient, band gap are determined from optical absorption and transmittance measurements. The value of absorption coefficient for strong absorption region of thin film is calculated using the following Eq. (1) (Choi 2009, Chiu 2009 and Chang 2013).

$$\alpha h\nu = A(h\nu - E_g)^n \qquad 1$$

where α is the absorption coefficient in cm-1, *hv* is the photon energy, A is an energy dependent constant and n is an integer. The value of 'n' determines the type of transition present in the material. In this case n=1/2 indicates that the transition present in the ITO thin films obtained at various Cp values is shown in Fig. 3.

This is consistent with the Burstein-Moss effect which predicts a widening of the optical band gap as more low energy states in the conduction band are filled by free carriers. With regard to electrical properties.

Extrapolation of linear portion of the graph to energy (hv) axis gives the band gap value of the material. The band gap value of the material obtained in the present work is found to be in the range between 3.7 and 3.9 eV for films obtained at various solution Cp values.

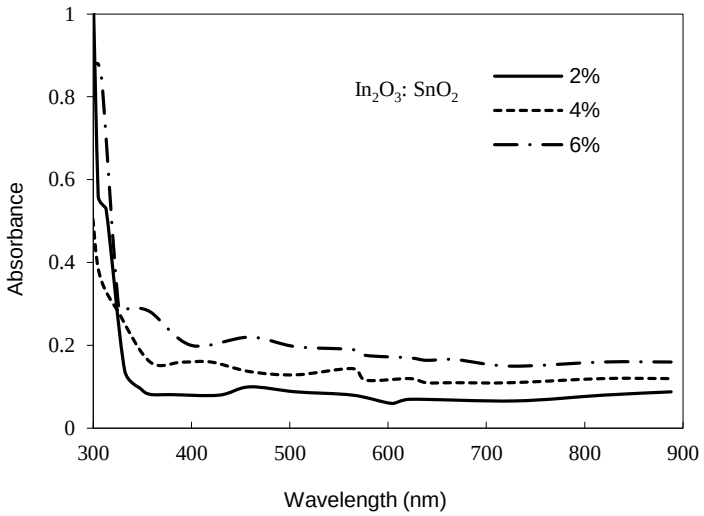

Fig. 2. Influence of the fabrication doping concentration Cp on the ITO absorbance.

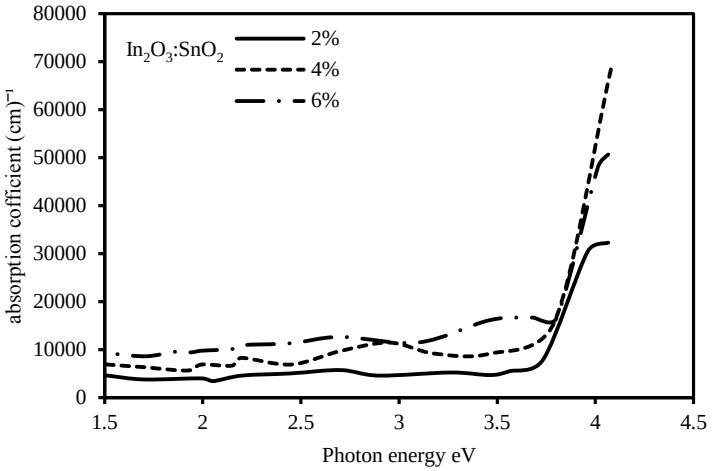

Fig. 3: α vs *hv* plot for ITO thin film with different Sn doping concentration.

Refractive index (n) and extinction coefficient (k) are determined using the following Eq. (2) and Eq. (3) (Armstrong 2009 and Fung 2011). Fig. 4 shows the variation of refractive index (n) with wavelength (λ) for films obtained at various Cp values. It is observed that there is sudden decrease of dispersion (n) at 730 nm shows the presence of characteristic absorption at that wavelength. On the other hand, the extinction coefficient (k) is found to decrease with wavelength (λ) and attained almost constant value after 730 nm (Fig. 4. a and b). The value of (n) is found to be almost constant at wavelength greater than 730 nm. The very strong absorption exhibited for photon energies above Eg value is very likely due to high density of cadmium ion within the lattice.

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \tag{2}$$

$$k = \frac{\alpha\lambda}{4\pi} \tag{3}$$

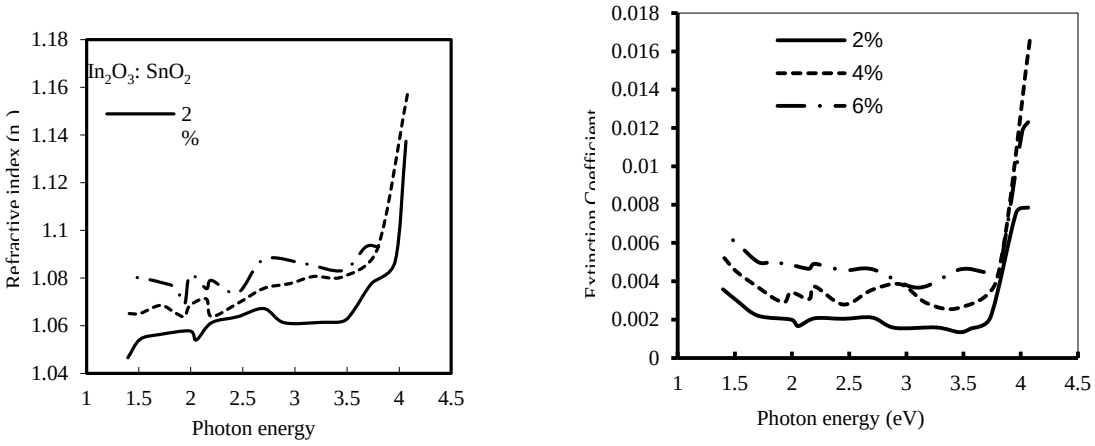

Fig. 4: Variation of a) extinction coefficient b) refractive index with the photon energy.

Real and imaginary dielectric constants are determined by using the following Eqs. (4) and (5) (Lewis 2000). Fig. 5 (a and b) shows the variation of real dielectric constant (ε1) with wavelength (λ) for films obtained at various dioping concentration values. It is observed that the value of (ε1) indicated a similar variation as that of (n). The value of (ε2) decreases with increasing wavelength just like (k) which is shown in Fig. 4 (b). It is observed from above Figures that all of them such as n, k, ε1, ε2 shows decreasing dependence withwavelength (λ).

This may be due to inter band transition for photon energy smaller than the smallest band gap. The value of n, k, ε1, ε2 are found to be 3.3, 0.64, 10.60, 4.32 correspond to the band gap value of the material.

$$\varepsilon_1 = n^2 - k^2 \tag{4}$$

$$\varepsilon_2 = 2nk \tag{5}$$

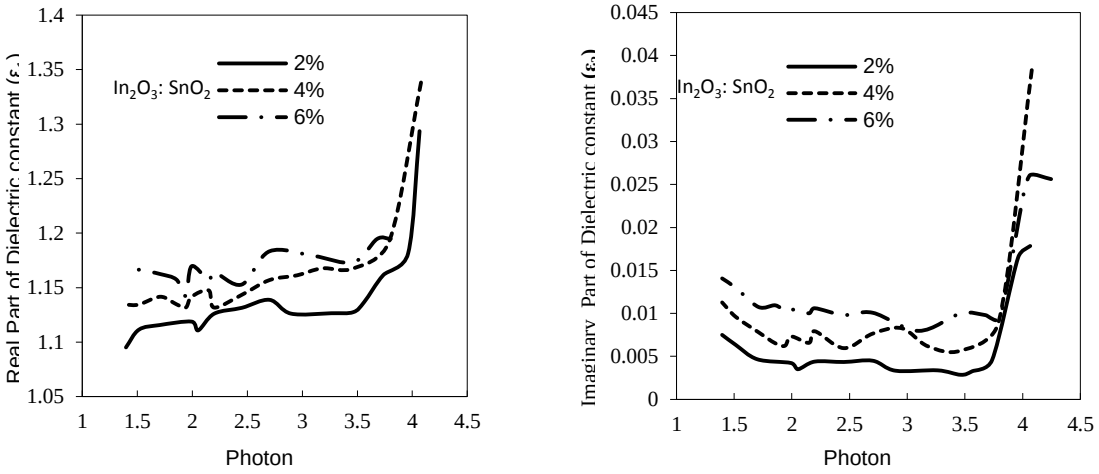

Fig. 5: Variation of a) real part of dielectric constant b) imaginary part of dielectric constant with the photon energy for ITO thin film with different Sn doping concentration.

4. Conclusion

Indium oxide films have been successfully prepared using the spray pyrolysis technique. The influence of various process parameters on the film properties has been carried out and the spray pyrolysis parameters have been optimized to give good quality films. The optimized process parameter for the preparation of device-quality ITO films are: concentration of SnO in In_2O_3 was 2%, air-flow rate is 15 lpm, substrate–nozzle distance is 25 cm and the substrate temperature is 574K. The best ITO film prepared in this set of optimized conditions has a band gap value of 3.74 eV with a transmission of ≈87%. The surface morphology of thin films have uniformity and grain size increase with increase in doping concentration to 4%.

References

Aoki Y., Huang J. and Kunitake T (2006), J. Mater. Chem., **16**, 292.

Armstrong N.R., Veneman P.A., Ratcliff E., P D. lacencia , Brumbach M. (2009), Acc. Chem. Res., **42**, 1748.

Betz U., Kharrazi M.O., Marthy J., Escola M. F. and Atamny F. (2006), Surf. Coat. Tech., **200**, 5751.

Brewer S.C.and Franzen S. (2004), Chem. Phys., **300**, 285.

Chiu C.H., Yu P.C., Chang C.H., Yang C.S., Hsu M.H., Kuo H.C., Tsai M.A. (2009), Opt. Express, **17**, 21250.

Choi K. H., Jeong J. A., Kang J. W., Kim D. G., Kim J.K., Na S. I., Kim D. Y., Kim S. S., Kim H. K. (2009), Sol. Energy Mater. Sol. Cells, **93**, 1248.

Dong W. K., Dong W. P. (2010), Surface & Coatings Technology, **205**, S201–S205.

Fortunato E., Pereira L., Barquinha P., Rego A., Goncalves G., Vila A., Morante J. and Martins R.(2008), Appl. Phys. Lett., **92**, 222103.

Fung M.K. Sun Y,C., Ng A.M.C., Djuri A.B. , Chan W.K.(2011), Current Applied Physics, **11**, 594-597.

Iwasaki T., Itagaki N., Den T., Kumomi H., Nomura K, Kamiya T., Hosono H. (2007) Appl. Phys. Lett., **90**, 242114.

Jung C.H., Lee J.Y., Pu L.S., Lee K. S., Yoon D. H. (2012), Thin Solid Films, **520**, 4726–4729.

Kiju Im, Kyoungah Cho, Jonghyun Kim, Sangsig Kim (2010), Thin Solid Films, **518**, 3960–3963.

Kim H., Pique A., Horwitz J.S., Mattouss H., Murata H., Kafafi Z.H. and Chrisey D.B. (1999), Appl. Phys. Lett., **74**, 3444.

Kim J. H., Ahn B.D., Kim C.H., Jeon K.A., Kang H.S. and Lee S.Y. (2008), Thin Solid Films, **516**, 1330.

Kim S.I., Cho S.H., Choi S.R., Yoon H.H. and Song P.K. (2009), Curr. Appl. Phys., **9**, S262.

Kim Y. N., Shin H.G., Song J.K., Cho D.H., Lee H.S. and Jung Y.G., J. (2005), Mater. Res., **20**, 1574.

Lewis B.G. and Paine D.C. (2000), MRS Bull., 23.

Li Z.Q. and Lin J.J. (2004), J. Appl. Phys., **96**, 5918.

Nomura K., Ohta H., Takagi A., Kamiya T., Hirano M., Hosono M. (2000), Nature **432**, 488.

Park J.S., Jeong J. K., Mo Y. G., Kim H. D., and Kim S. D. (2007), Appl. Phys. Lett., **90**, 262106.

Rwei Ch. Ch., Tsai F. T and Chin H. T. (2013), Thin Solid Films, **540**, 118–124

Song J.O., Ha J.S. and Seong T.Y. (2010), IEEE Trans. Electron Devices, 57, 42.

Shin H., Boyeon S., Myeongkyu L. (2010), Optics and Lasers in Engineering, **48**, 816–820.

Thanikaikarasana S. and Mahalingam T. (2012), Journal of Alloys and Compounds, **511**, 115– 122.

Yeadon A.D., Wakeham S.J., Brown H.L., Thwaites M.J., Whiting M.J. and Baker M.A. (2011), Thin Solid Films, **520**, 1207–1211.

Yoon Y.H., Song J.W., Kim D., Kim J., Park J. K., Oh S. K. and Han C.S. (2007), Adv. Mater., **19**, 4284.