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Development of a novel high optical quality ZnO thin films by PLD for III–V opto-electronic devices

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Abstract

A novel highly transparent intrinsic zinc oxide (ZnO) thin films (without adding any dopants and annealing) were grown by pulsed laser deposition (PLD) technique using Johnson Matthey "specpure"- grade ZnO pellets. The effects of substrate temperatures on zinc oxide thin film growth, optical transmission, absorption, reflection and photoluminescence properties were studied. As well as the feasibility of developing high quality transparent oxide thin films was also studied simultaneously. The optical transmission window of such obtained films, i.e., $T\%$ (max) $\geqslant 95\%$ is broader than those of other transparent conducting oxides such as indium tin oxide (ITO) and absolute rivals that of the most transparent conducting oxides (TCOs). Also as a novelty merit, we want to emphasize as a interesting, significant and novel physical effect that the average optical transmittance of ZnO thin films rivals that of the most transmittive TCO films reported to date for this conductivity level (of the order of $10^3\ \Omega^{-1}\ \mathrm{cm}^{-1}$). Also this is the first time that we have applied these PLD prepared ZnO thin films to iso and hetero semiconductor–insulator–semiconductor (SIS) type solar cells as transparent conducting oxide (TCO) coatings. From optical studies, we know that the films were act as highly anti-reflective coatings. From photoluminescence study, we confirmed the purity and high electrical conductivity of the deposited thin films of ZnO. The optical parameter values for the films were calculated, tabulated and graphically emphasized. Supplementary studies on surface, electrical, structural and internal morphological properties of zinc oxide thin film growth correlated with optical transmission, absorption, reflection and photoluminescence properties gives added advantages to this work. We hope that surely these data should be helpful either as a scientific or technical basis in the semiconductor processing and technology.

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Keywords: Laser epitaxy; Semiconducting materials; Thin film structure and morphology; Optical materials; Solar cells

1. Introduction

Transparent conducting oxide (TCO) films have been actively studied for applications in numerous solid state opto-electronic devices (such as displays, solar cells) [1–16]. At present, coatings of intrinsic and extrinsic or doped varieties of zinc oxide are employed on a massive scale for display devices. The optimum electrical conductivity and also superior optical transparency window is needed for current envisaged applications.

For zinc oxide thin film growth, several deposition techniques have been utilized including electron beam

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evaporation, spray pyrolysis, metal organic chemical vapour deposition (MOCVD), molecular beam epitaxy (MBE) and pulsed laser deposition (PLD). Among these, PLD offers the attraction of in situ growth under a variety of atmosphere, easy control of composition.

In this paper, we described the application of pulsed laser deposition technique to optimize and deposit high quality transparent oxide thin films (i.e., zinc oxide thin films) with the goals of defining appropriate precursors, growth conditions, the relationship of film processing on thin film quality, micro structures and what has been left from bulk studies. On the basis of referred literature [1–5], we framed the chemical and thin film strategies for the development of high quality TCOs.

The effects of substrate temperatures on the intrinsic zinc oxide thin film growth, optical transmission, absorption, reflection and photoluminescence properties were studied. As well as the feasibility of developing high quality transparent oxide thin films were also studied simultaneously. Supplementary studies on surface, electrical, structural and internal morphological properties of zinc oxide thin film growth correlated with optical transmission, absorption, reflection and photoluminescence properties gives added advantages to our TCO work [17–22]. Also this is the first time that we have applied these PLD prepared ZnO thin films to iso and hetero semiconductor–insulator–semiconductor (SIS) type solar cells as transparent conducting oxide (TCO) coatings.

2. Experimental techniques

In the present study, a single target pulsed laser deposition system is employed to optimize, deposit highly oriented, transparent ZnO thin films on float glass substrates held at room temperature (RT), 200, 300 °C. PLD technique is a good technique to produce crystalline quality and stoichiometric thin films. Pulsed laser deposition has been shown to be superior to sputtering and conventional MBE for growing highly pure and good crystalline metal oxide epitaxial thin films in combinatorial synthesis of materials. A critical step to achieving high quality thin films was the treatment of the substrate surface. The float glass substrates were treated with hot chromic acid and cleaned with trichloroethylene (3 min), acetone (4 min), methanol (3 min) and dried. Before 'metal oxide on semiconductor deposition' for iso and hetero type multi-junction solar cell fabrication, the deposition of ZnO thin films was optimized with float glass substrates. The targets were made by Johnson Matthey 'specpure'- grade ZnO powders for zinc oxide thin film optimization and deposition. The powders were mixed with poly vinyl alcohol binder and hot water. Then stirred, slurred, crushed into powder, dye palletized, kept in furnace at 600 °C for 3 h. And sintered at 1200 °C for 3 h for ZnO targets. The targets were ablated with third harmonic of "Quantel, Yg 980, France, Nd:YAG laser" (355 nm, 6 ns, and 10 Hz) with energy density of 5 J/cm^2. Throughout the experiment, the laser was set at pulse energy of 250 mJ and repetition rate of 10 Hz. Deposition chamber was initially evacuated up to 1×10^{-6} Torr pressure using a turbo molecular pump and O_2 was introduced during deposition and kept constant at 1×10^{-5} Torr. Substrate to target distance was kept at 6 cm. Throughout the deposition period, the target holder is rotated for uniform deposition of the ablated material. The optimum substrate temperature for ZnO thin films was found at 300 °C. In order to increase the performance of the present day state-of-the-art of multi-junction solar cells, the optical transmission, absorption, reflection and photoluminescence properties of TCO thin films have to be investigated [10–16]. UV–VIS–NIR spectrophotometry (using Schimadsu; UV-160 and Hitachi; V.3400 UV–VIS–NIR spectrometers), Photoluminescence (Hitachi; 650-10S fluorescence spectrophotometer) studies were performed for the detailed study of optical properties of the ZnO/Glass substrates.

3. Results and discussions

3.1. Optical properties

The effects of substrate temperatures on zinc oxide thin film growth and optical transmission, absorption, reflection and photoluminescence properties were studied. The optical transmission, absorption and reflection spectra for a wavelength range between 300 and 1100 nm of the optimized epitaxial zinc oxide thin films for various substrate temperatures were illustrated graphically as in Figs. 1–3. As well as the feasibility of developing high quality transparent oxide thin films

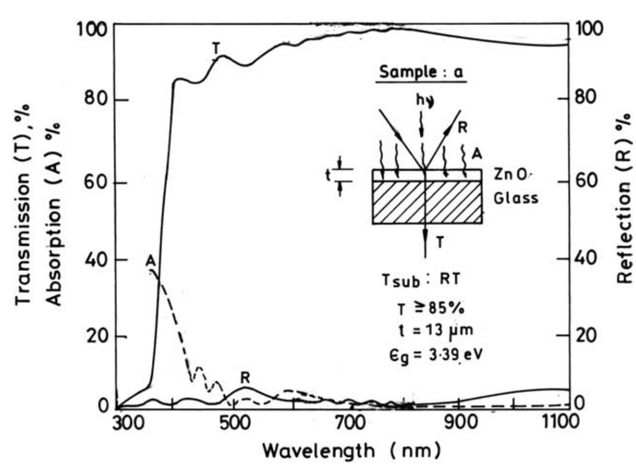

Fig. 1. Optical transmission, absorption and reflection spectra of ZnO thin films deposited at RT.

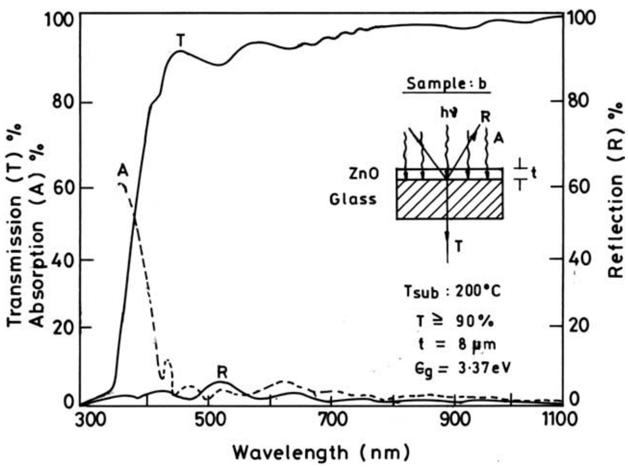

Fig. 2. Optical transmission, absorption and reflection spectra of ZnO thin films deposited at 200 °C.

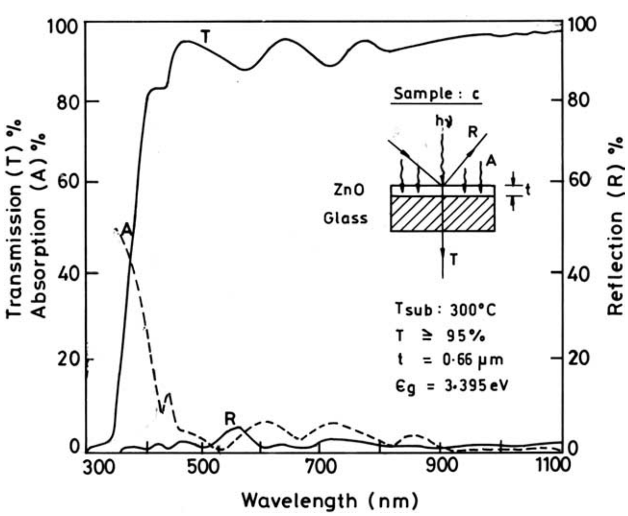

Fig. 3. Optical transmission, absorption and reflection spectra of ZnO thin films deposited at 300 °C.

was also studied simultaneously. Supplementary studies on surface, electrical, structural and internal morphological properties of zinc oxide thin film growth correlated with optical transmission, absorption, reflection and photoluminescence properties gives added advantages to this work.

3.2. Optical transmission properties

The average optical transmission window of such obtained films, i.e., T% (max) $\geqslant$ 95% for optimized zinc oxide thin films is broader than those of other transparent conducting oxides such as indium tin oxide (ITO) and absolute rivals that of the most transparent conducting oxides (TCOs) (as illustrated in Figs. 1–3). The optical parameter values were calculated and tabulated. Also, the results were graphically enumerated. The superior optical transmission of the ZnO thin films was due to high mobility of the charge carriers and the reduction of free carrier absorption. Also attributed to the ability of the film surface roughness to reduce reflectivity, an increase of a structural homogeneity, fine texturing, a decrease of the diffuse scattering and the approach of the film composition to the stoichiometry. Coloured interference patterns, it is a common concept for optically transparent film by naked eye. By this way, we have used optical interference method to measure film thickness. The thickness of optimized ZnO thin films deposited at RT, 200 and 300 °C are 13 μm, 8 μm and 0.66 μm or 6600 Å respectively (as illustrated in Fig. 4). From the results of surface morphological, micro and nano structural characterizations by scanning electron microscope (SEM) and atomic force microscope (AFM), it is well known that deposited ZnO films with textured better aligned micro structures have superior transmission to randomly oriented once suitable for most optical, electrical and opto-electronic applications. From X-ray diffraction study, it is revealed that better aligned epitaxially lattice matched films are suitable one to improve conductivity and light transmittance. From optical studies, we know that the highly oriented intrinsic zinc oxide films have enhanced light transmission perpendicular to the surface with less scattering. Higher substrate temperature enhanced the transparency of the deposited TCO thin films. It is observed that the average transmission of the ZnO thin films improves from $\geqslant$85% to $\geqslant$95% with increasing in the substrate temperature from RT to 300 °C. Table 1 clearly explained optical parameters of optimized ZnO thin films.

Thus the transparency window is considerably greater than that of typical TCO film and comparable to that MBE derived thin films and also, rivals that of the most transmittive TCO films reported to date [6–15]. The increment in transmission with increasing substrate temperature is related with improvements in

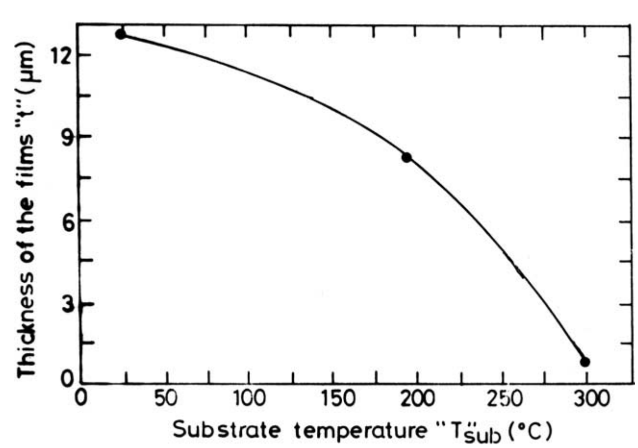

Fig. 4. The plot of thickness of ZnO thin films deposited at RT, 200 °C and 300 °C versus substrate temperature 'T_{sub}' (°C).

Table 1
Optical parameters of optimized ZnO thin films

ZnO thin films	T (%) (at particular wave length λ)	E_g (eV)
RT	$\geqslant$85 (λ = 400 nm)	3.39
200 °C	$\geqslant$90 (λ = 450 nm)	3.37
300 °C	$\geqslant$95 (λ = 475 nm)	3.395

crystallinity and mobility of carriers. Also as a novelty merit, we want to emphasize as a interesting, significant and novel physical effect that the average optical transmittance of ZnO thin films rivals that of the most transmittive TCO films reported to date for this conductivity level (of the order of $10^3\ \Omega^{-1}\ cm^{-1}$).

3.3. Optical absorption properties

The optical band gap widening or shrinkage was generally attributed to Moss–Burstein shift. The optical band gap widening is due to the optical band filling effect. The optical shrinkage is due to electron–electron interaction and higher carrier concentration, i.e., in this case, donor level approaches the conduction band. The low absorption observed in the films can be reconciled with the high dc conductivity according to the recent electrical transport theories of wide band gap semiconductors (as illustrated in Figs. 1–3). The typical plots of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for zinc oxide thin films deposited on glass substrate at RT, 200, 300 °C were also plotted. When the linear portion of the graph is extrapolated to zero, the intercept of '$h\upsilon$' axis gives the optical band gap (E_g). Generally for direct band gap n-type TCOs, the optical band gap (E_g) is accurately found by plotting the square of $(\alpha h\upsilon)^2$ versus $h\upsilon$. This plot is known as 'Tauc' plot (as illustrated in Figs. 5 and 6). For optimized zinc oxide thin films, the band gap energy varies from 3.39 eV to 3.395 eV, when we increase the substrate temperature from RT to 300 °C. The values were coinciding with the previous values. Increasing in substrate temperature yields slight widening in optical band gap. The effect of slight band gap widening is attributed primarily to the Moss–Burstein shift in semiconductors. The band gap values derived from optical absorption studies of films were coincide with the previous values reported so far. The intrinsic absorption in zinc oxide semiconductor thin films occurs for wavelengths in the vicinity of the energy gap. The absorption coefficient has its maximum value at a high optical energy and decreases with decreasing optical energy in a manner similar to the absorption edge of semi conductors. The optical band gap as a function of incident photon energy is defined as $\alpha h\upsilon \propto (h\upsilon - \epsilon_g)^{1/2}$. In intrinsic zinc oxide thin films inter band or selective absorption (200–400 nm) occurred. The micro formation of elemental zinc, any other sub-oxides, high carrier concentration and free-carrier absorption may give rise to shift in the optical-band gap (Moss–Burstein shift), there by decreases the current density (I_{sc}) of the solar cells. The lower binding energy peak of zinc in EDAX spectra (as evidenced from compositional analysis) may indicates the micro-formation of elemental Zn due to the reduction process takes place in TCO thin films. The most opto-electronic applications required the films to have low absorption in the visible region and high dc conductivity.

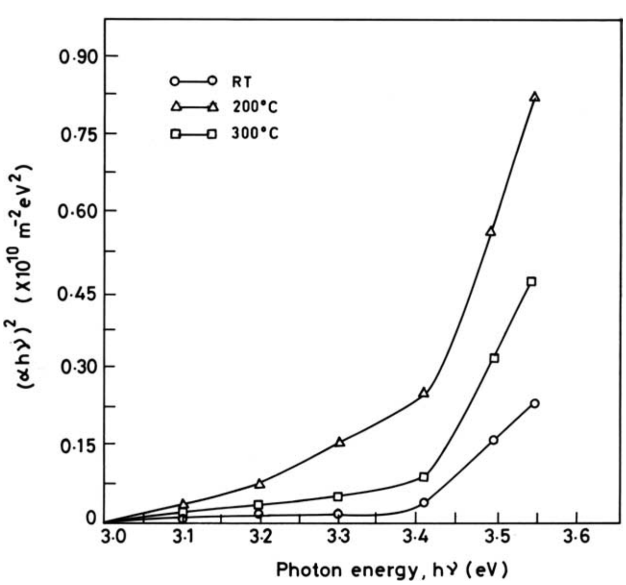

Fig. 5. The 'Tauc' plot of ZnO thin films deposited at RT, 200 °C and 300 °C.

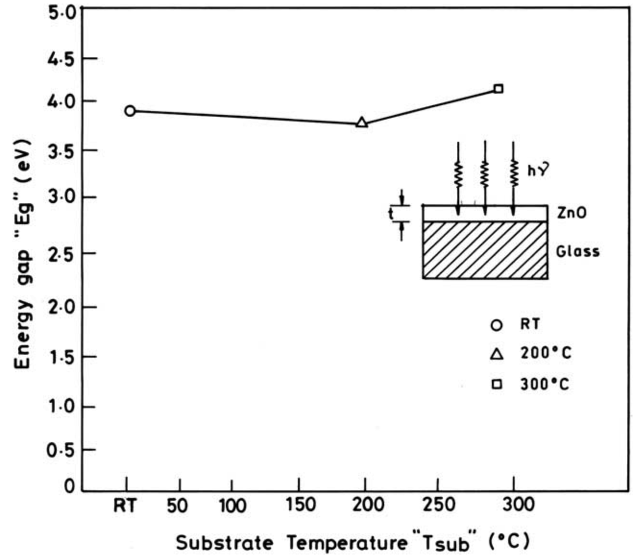

Fig. 6. The plot of energy gap 'E_g' of ZnO thin films versus substrate temperature T_{sub} (°C).

3.4. Optical reflection properties

The anti-reflection (AR) property of optimized high substrate temperature ZnO thin films was confirmed by the poor reflection spectra (as illustrated in Figs. 1–3). Low cost anti-reflection (AR) coating technology is a currently envisaged field. The important consideration of a very thin insulation layer between the TCO thin film and the substrate has lead the structure to low reflection loss. Generally TCO greatly increases light diffusion and reduces optical reflection loss. In the past few years, improvement of the optical properties has been a dominating factor in increasing the commercial quality of opto-electronic devices. Light trapping or confinement effect of TCOs is a very important property to obtain high collection of incident photons in solar cells.

3.5. Photoluminescence properties

In order to reveal additional optical characteristics of the deposited thin films and for in-depth study, the thin films were undergone to photoluminescence characterization. The photoluminescence (PL) studies were carried out on optimized epi-ZnO thin films/glass substrates deposited at RT, 200 °C and 300 °C using the Hitachi; 650-10S fluorescence spectrophotometer (as illustrated in Fig. 7). The photoluminescence properties of obtained ZnO thin films were significant from reported so far [15,16]. From photoluminescence study, we confirmed the purity of the deposited ZnO thin films. Also the low photoluminescence (PL) intensity of zinc oxide thin films confirmed that the obtained films have high electrical conductivity (of the order of $10^3\ \Omega^{-1}$ cm^{-1}). The effects of substrate temperatures on zinc oxide thin films photoluminescence properties were studied. Higher substrate temperature decreases the photoluminescence intensity of ZnO thin films, there by increases the electrical conductivity (of the order of $10^3\ \Omega^{-1}\ cm^{-1}$) which was evidently shown from electrical studies.

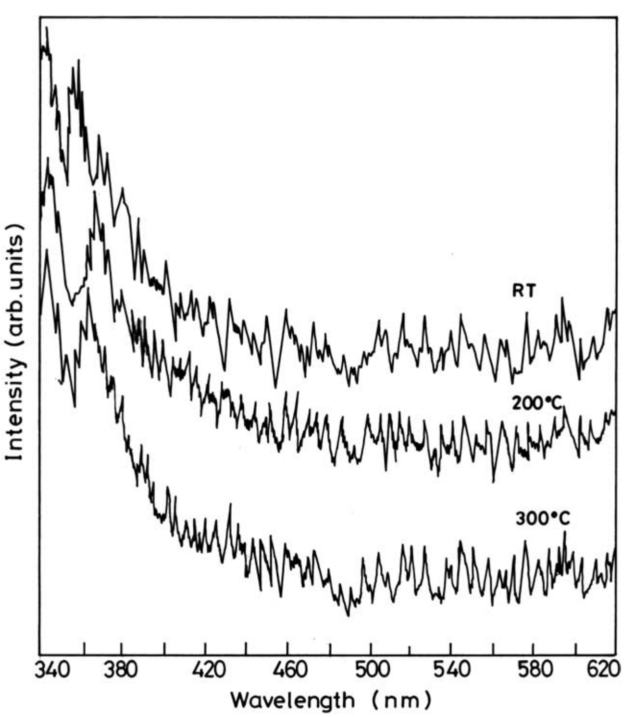

Fig. 7. Photoluminescence spectra of ZnO thin films deposited on float glass substrates at RT, 200 °C and 300 °C.

As a result of study, we observed that due to the increment in substrate temperature the optical transmission, low absorption, anti-reflection and needful low intense photoluminescence properties of intrinsic zinc oxide were improved.

4. Conclusions

In summary, we have optimized and developed a novel high quality transparent intrinsic zinc oxide thin films without adding any dopants considerably greater than that of state-of-the-art of indium tin oxide (ITO) and other commercially valid TCO's by using L-MBE i.e., PLD.

The effects of substrate temperatures on zinc oxide thin film growth, optical transmission, absorption, reflection and photoluminescence properties were studied. As well as the feasibility of developing high quality transparent oxide thin films was also studied simultaneously. Higher substrate temperature enhances the transparency and anti-reflection property of ZnO thin films. Higher substrate temperature decreases the photoluminescence intensity of ZnO thin films, there by increases the electrical conductivity which was evidently shown from electrical studies. From photoluminescence study, we confirmed the purity and high electrical conductivity of the deposited ZnO thin films. Supplementary studies on surface, electrical, structural and internal morphological properties of zinc oxide thin film growth correlated with optical transmission, absorption, reflection and photoluminescence properties gives added advantages to this work. Also as a novelty merit, we want to emphasize as a interesting, significant and novel physical effect that the average optical transmittance of ZnO thin films rivals that of the most transmittive TCO films reported to date for this conductivity level (of the order of $10^3\ \Omega^{-1}\ cm^{-1}$). Also this is the first time that we have applied these PLD prepared ZnO thin films to iso and hetero semiconductor–insulator–semiconductor (SIS) type solar cells as transparent conducting oxide (TCO) coatings.

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