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Development of a novel high speed (electron-mobility) epi-n-ZnO thin films by L-MBE for III–V opto-electronic devices

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Abstract

Intrinsic epitaxial zinc oxide (epi-ZnO) thin films were grown by laser-molecular beam epitaxy (L-MBE), i.e., pulsed laser deposition (PLD) technique using Johnson Matthey "specpure"-grade ZnO pellets. The effects of substrate temperatures on ZnO thin film growth, electrical conductivity (σ), mobility (μ) and carrier concentration (n) were studied. As well as the feasibility of developing high quality conducting oxide thin films was also studied simultaneously. The highest conductivity was found for optimized epi-ZnO thin films is $\sigma = 0.06 \times 10^3$ ohm^{-1} cm^{-1} (n-type) (which is almost at the edge of semiconductivity range), carrier density $n = 0.316 \times 10^{19}$ cm^{-3} and mobility $\mu = 98$ cm^2/V s. The electrical studies further confirmed the semiconductor characteristics of epi-n-ZnO thin films. The relationship between the optical and electrical properties were also graphically enumerated. The electrical parameter values for the films were calculated, graphically enumerated and tabulated. As a novelty point of view, we have concluded that without doping and annealing, we have obtained optimum electrical conductivity with high optical transparency ($\geqslant$95%) for as deposited ZnO thin films using PLD. Also, this is the first time that we have applied PLD made ZnO thin films to iso-, hetero-semiconductor–insulator–semiconductor (SIS) type solar cells as transparent conducting oxide (TCO) window layer. We hope that surely these data be helpful either as a scientific or technical basis in the semiconductor processing.

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Keywords: Laser epitaxy; Semiconducting materials; Thin film structure and morphology; Buffer layer on InP; Solar cells

1. Introduction

We know that, recently pulsed laser deposition (PLD) technique was used to deposit both the buffer and functional layers in commercial grade electronics application comparative to the metal organic chemical vapour deposition (MOCVD) and molecular beam epitaxy (MBE). Also at present, coatings of intrinsic and extrinsic varieties of zinc oxide (ZnO) are employed on a massive scale for opto-electronic devices [1–6]. The optimum electrical conductivity with superior optical transparency window is needed for current envisaged applications.

On the basis of referred literature [1–15], we framed the chemical and thin film strategies for the development of high quality transparent conducting oxides (TCOs).

For zinc oxide thin film growth, several deposition techniques have been utilized including electron beam evaporation, spray pyrolysis, rf magnetron sputtering, metal organic chemical vapour deposition (MOCVD), recently molecular beam epitaxy (MBE). Among these, PLD offers high attraction of in situ growth under a variety of atmospheres, easy control of composition.

In this work, we described the application of pulsed laser deposition technique to deposit high quality

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conducting oxide thin films (i.e., ZnO thin films) with the goals of defining appropriate precursors, growth conditions, the relationship of film processing on thin film quality, microstructures and what has been left from bulk studies.

Extra-mural studies also extended towards various factors, which influencing the electrical properties of epi-ZnO thin films were carried out. The effects of substrate temperatures on zinc oxide thin film growth, electrical conductivity (σ), mobility (μ) and carrier concentration (n) were studied. As well as the feasibility of developing high quality conducting oxide thin films was also studied simultaneously. The electrical parameters were calculated, graphically enumerated and tabulated. The relationship between optical and electrical characteristics was also graphically emphasized.

2. Experimental techniques

Pulsed laser deposition system, i.e., laser-molecular beam epitaxy is employed to optimize, deposit highly oriented, high speed (electron-mobility) epi-n-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, good crystalline metal oxide epitaxial thin films in combinatorial synthesis of materials. Before 'metal oxide on semiconductor wafer deposition for the fabrication of semiconductor–insulator–semiconductor (SIS) type solar cells', the deposition of ZnO thin films was optimized with float glass substrates. 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, cleaned with trichloroethylene (3 min), acetone (4 min), methanol (3 min) and dried. The targets were Johnson Matthey 'specpure'-grade ZnO pellets, i.e., ZnO powders were mixed with polyvinyl alcohol binder and hot water. Then stirred, slurred, crushed into powder, dye palletized, kept in a 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, 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.

In order to increase the performance of the present day state-of-the-art of hetero-junction solar cells, the electrical conductivity, mobility and carrier concentration of TCO thin films have to be investigated. Both, Van der Pauw four probe resistivity and Hall effect experiments were performed for the detailed study of electrical properties of the epi-ZnO thin films/float glass substrates. The Van der Pauw and Hall effect electrical characterizations were carried out at Solid State Electronics (SSE) Laboratory, Tata Institute of Fundamental Research (TIFR), Bombay, a reputed research institute in frontier areas of science and technology.

3. Results and discussions

3.1. Electrical properties

Extra-mural studies on various factors, which influencing the electrical properties of zinc oxide thin films were carried out. The transport phenomena, related electrical conductivity in zinc oxide films were successfully explained on the basis of 'controlled valence verwey principle'. The effects of substrate temperatures on zinc oxide thin film growth and electrical properties were studied. As well as the feasibility of developing high quality conducting oxide thin films (of the order of 10^3 $\Omega^{-1}\,cm^{-1}$) was also studied simultaneously. The conductivity and mobility of the films were measured by using Van der Pauw type four probe and Hall effect setups [16–20]. As a novelty point of view, we have concluded that without doping and annealing, we have obtained optimum electrical conductivity with high optical transparency ($\geqslant$95%) for as deposited ZnO thin films using PLD. Also, this is the first time that we have applied PLD made ZnO thin films to iso-, hetero-semiconductor–insulator–semiconductor (SIS) type solar cells as transparent conducting oxide (TCO) window layer. The pulsed laser deposited ZnO thin films have good epitaxial lattice matching with $\langle 1\,0\,0\rangle$ oriented Si, GaAs and InP without using any buffer layers like GaN. This is our novel achievement. Also, the films have stoichiometric approachment; the respective work was published [21]. Beyond this, the films have better surface morphology, nanostructural characteristics, maximum optical transparency (T) ($\geqslant$95%) and anti-reflection nature. The high electrical conductivity of ZnO thin films was also confirmed by low photoluminescence intensity. The respective works were also communicated [22,23].

The Van der Pauw and Hall effect electrical characterizations were carried out at Solid State Electronics (SSE) Laboratory, Tata Institute of Fundamental Research (TIFR), Bombay, a reputed research institute in frontier areas of science and technology.

Point contacts at four corners of the samples were made by soldering 40 gauge copper wire with highly pure indium solder. The entire specimen was fastened to

Table 1
Electrical parameters of optimized epi-n-ZnO thin films

Epi-n-ZnO thin films	Conductivity, σ (ohm^{-1} cm^{-1})	Carrier concentration, n (cm^{-3})	Mobility, μ (cm^2/V s)
RT	0.256×10^{-3}	0.196×10^{15}	8.163
200 °C	8.33×10^{-1}	0.276×10^{18}	18.856
300 °C	0.06×10^{3}	0.316×10^{19}	98

the gold block. The complete set up was held between the two pole pieces of electromagnet (2.5 kG), current (I) 10 mA was passed by means of "dc aplab" constant power supply between the two diagonally opposite contact points of the sample. The values of electrical parameters for intrinsic ZnO thin films were calculated, tabulated (refer Table 1) and graphically emphasized (refer Figs. 1–5). The relationship between electrical and optical parameters was graphically enumerated (refer Figs. 6 and 7). As a merit on structural characteristics point of view, we have emphasized the words 'epitaxial' and 'epi-n-ZnO thin films' on the basis of epitaxial lattice matching nature of pulsed laser deposited ZnO thin films with single crystalline ⟨1 0 0⟩ oriented Si, GaAs and InP substrates, since glass substrates are amorphous in nature. We have utilized the float glass substrates solely for optimization of better quality condition. In this regard, we have also included proofs, i.e., Figs. 8–10: Epitaxial lattice matching of ZnO thin films with ⟨1 0 0⟩ SI-InP, n-InP and p-InP substrates (without using any buffer layers like GaN) deposited at room temperature (RT). Exact coincidence and merging of peaks of thin films with the substrates confirmed the epitaxial lattice matching.

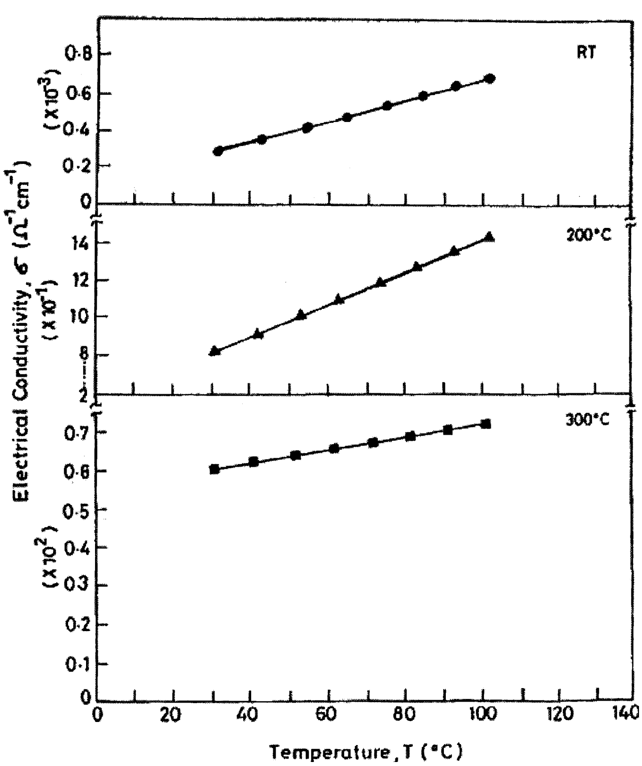

Fig. 1. The plot between electrical conductivity, σ of epi-n-ZnO thin films deposited at RT, 200 and 300 °C versus heating temperature, T (°C).

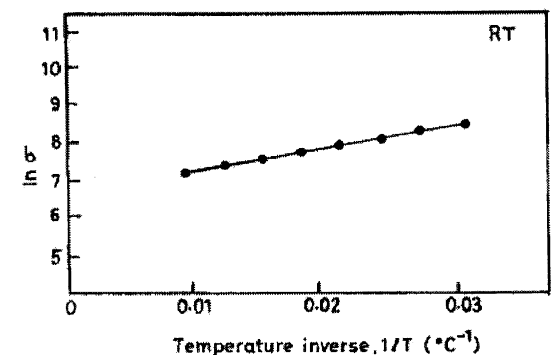

Fig. 2. Arrehenius plot of epi-n-ZnO thin films deposited at RT, i.e., $\ln\sigma$ versus heating temperature inverse, $1/T$ (°C^{-1}).

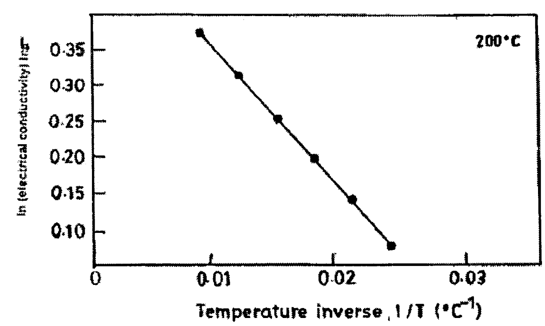

Fig. 3. Arrehenius plot of epi-n-ZnO thin films deposited at 200 °C, i.e., $\ln\sigma$ versus heating temperature inverse, $1/T$ (°C^{-1}).

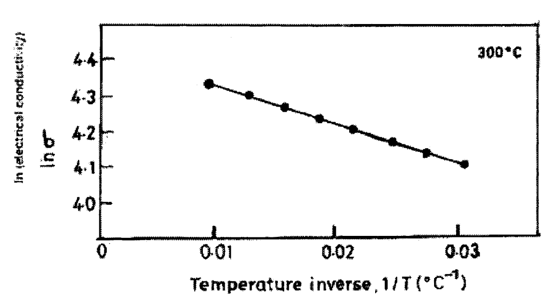

Fig. 4. Arrehenius plot of epi-n-ZnO thin films deposited at 300 °C, i.e., $\ln\sigma$ versus heating temperature inverse, $1/T$ (°C^{-1}).

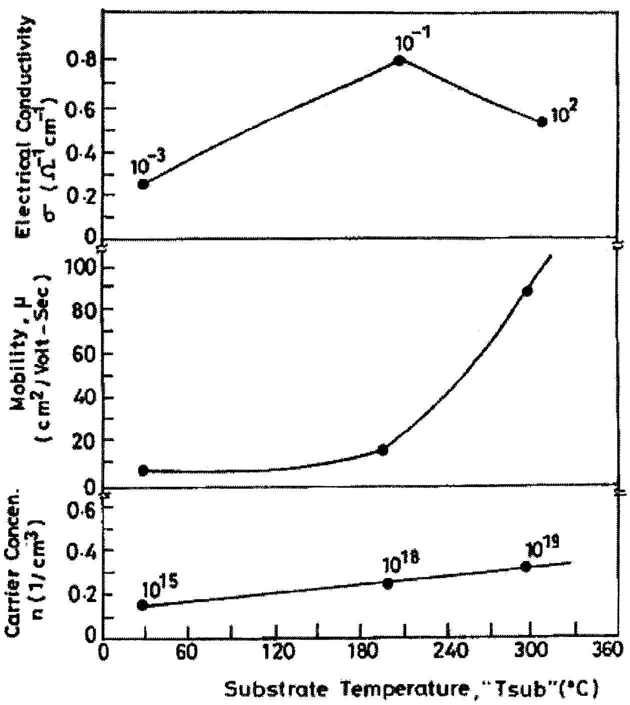

Fig. 5. Electrical conductivity σ, mobility μ and carrier concentration, n of epi-n-ZnO thin films deposited at RT, 200 and 300 °C versus substrate temperature 'T_{sub}' (°C).

The highest conductivity was found for epitaxial zinc oxide thin films is $\sigma = 0.06 \times 10^3\ \Omega^{-1}\,\mathrm{cm}^{-1}$ (n-type) (which is almost at the edge of semiconductivity range), carrier density $n = 0.316 \times 10^{19}\ \mathrm{cm}^{-3}$ and mobility $\mu = 98\ \mathrm{cm^2/V\,s}$. The electrical studies further confirmed the semiconductor characteristics of both epi-n-ZnO thin films. The gradual decrease in the film resistivity on raising the heating temperature, i.e., negative temperature coefficient of resistivity confirmed the semiconductor characteristics of deposited films. The elevated graph line observed in Fig. 1 and declined graph line observed in Figs. 2–4 confirmed the above characteristics. Beyond this obtained conductivity order ($10^3\ \Omega^{-1}\,\mathrm{cm}^{-1}$), TCO lose its semiconductor nature and changed to metallic nature. The n-type carrier transport (as predicted by theory) was confirmed by (−ve) value of Hall voltage (V_H). These results were further shown to be better and comparable with the values of MBE derived TCO thin films. The changes in mobility, carrier concentration and electrical conductivity with substrate temperature is most probably due to the changes in the crystalline orientation and size. The oxygen vacancies and interstitial zinc atoms were act as donors and defects in grain boundaries, lattice sites, interstitial sites were act as acceptors in the zinc oxide thin films. The quantitative treatment of these donors and acceptors is rare in analyzing the electrical conduction of the films, although this is a key to estimate the film quality.

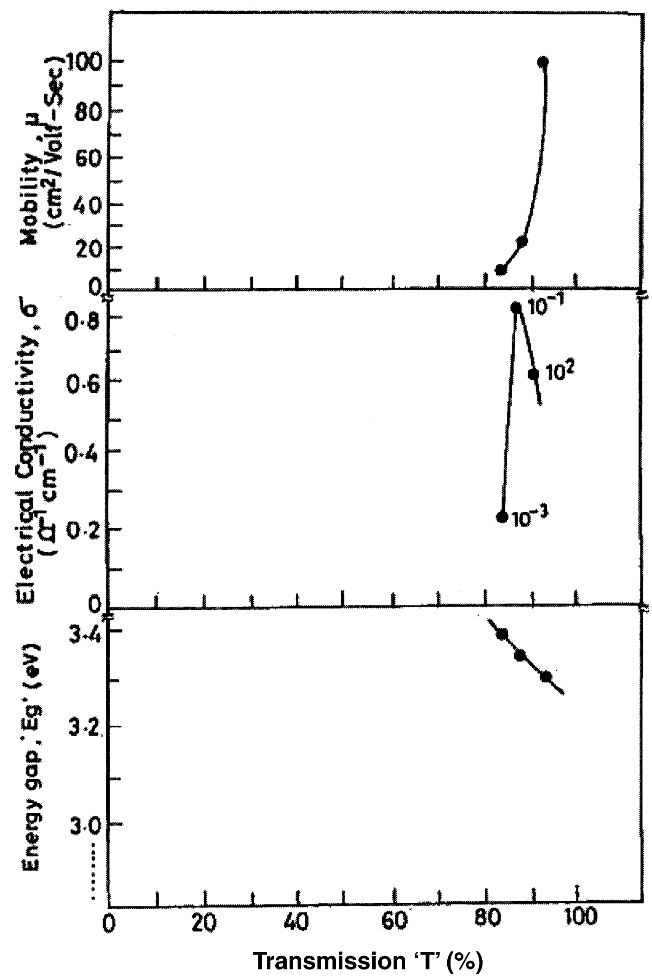

Fig. 6. Correlation between electrical conductivity σ, mobility μ and energy gap E_g of epi-n-ZnO thin films deposited at RT, 200 and 300 °C versus transmission T (%).

High resistivity of the ZnO thin films deposited at room temperature is may be due to the inactive 'Zn' atoms segregated at the grain boundaries, stronger carrier scattering (due to non-crystalline, irregular arrangement of atoms, related constituents) and trapping centres, which affect the transport mechanism of conduction carriers. The above concept was confirmed by the amorphous nature of ZnO thin films deposited at room temperature. The scattering of charge carriers by high angle grain boundaries may limits the mobility of the charge carriers. According to the current semiconductor transport theory, scattering of lattice vibrations, crystalline defects, dislocations and trapping centres are the factors, which influenced the 'electrons and holes transport' drastically and thereby led to the high resistivity. These factors were minimized when the higher substrate temperature (T_{sub}) was approached.

The higher carrier concentration, mobility and electrical conductivity were observed in optimized higher substrate temperature epi-n-ZnO thin films were due to

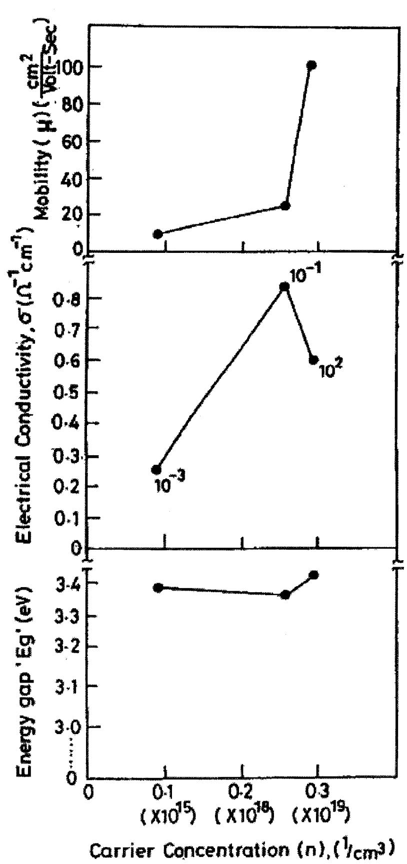

Fig. 7. Correlation between electrical conductivity σ, mobility μ and energy gap E_g of epi-n-ZnO thin films deposited at RT, 200 and 300 °C versus carrier concentration (n).

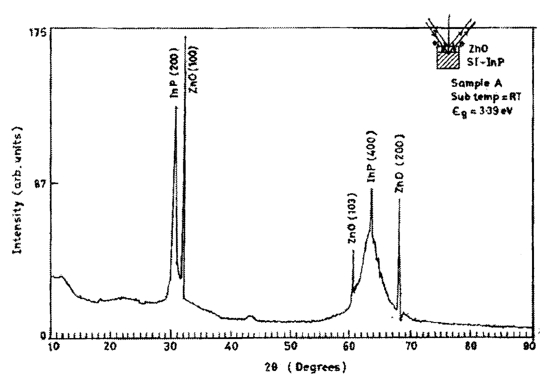

Fig. 8. Epitaxial lattice matching of ZnO thin films with ⟨1 0 0⟩ SI-InP substrates (without using any buffer layers like GaN) deposited at room temperature (RT).

oxygen vacancies and interstitial zinc atoms. The observed small increase in conductivity with increasing T_{sub} suggested the decreased lattice scattering. The formation of an electron accumulation layer within the epitaxial TCO thin films gives rise to the observed rise in carrier concentration (n), mobility (μ) and electrical conductivity (σ). The best results were obtained for thin films deposited at $T_{sub} = 300$ °C. The reduction in resistivity may also be attributed to the high packing density of the grains. While the increase in mobility was attributed to crystallinity improvement and homogeneous distribution of grains. The above concepts were clearly revealed from Fig. 5.

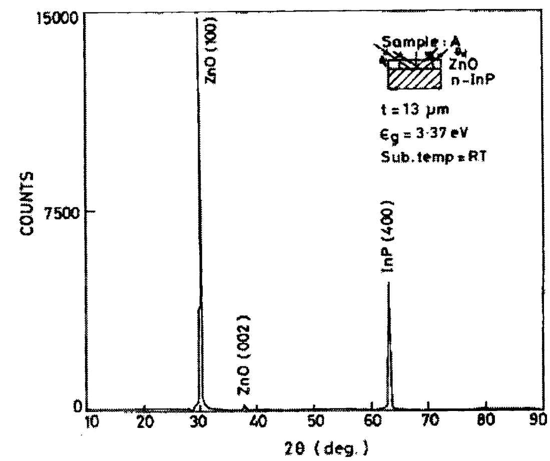

Fig. 9. Epitaxial lattice matching of ZnO thin films with ⟨1 0 0⟩ n-InP substrates (without using any buffer layers like GaN) deposited at room temperature (RT).

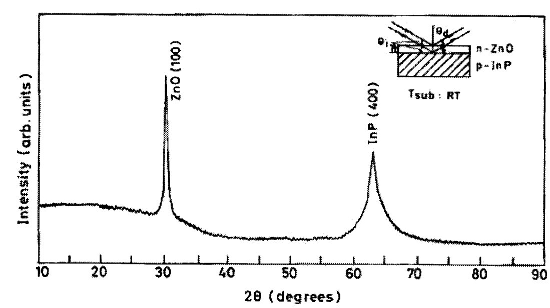

Fig. 10. Epitaxial lattice matching of ZnO thin films with ⟨1 0 0⟩ p-InP substrates (without using any buffer layers like GaN) deposited at room temperature (RT).

We knew that the 'figure of merit' (Φ_{TCO}) of TCO thin film is $\Phi_{TCO} = T^{10}/R_{sh} = \sigma t \exp(-10\alpha t)$, where T is the numerical value of the optical transmission, R_{sh} sheet resistance and α is the absorption coefficient of the thin films. The 'figure of merit' Φ_{TCO} is maximum for high transparency with high mobility TCO thin films. The observed raising of transmission, electrical conductivity and mobility on raising of substrate temperature combined with decrement in energy gap was clearly revealed from Fig. 6. Similarly, the observed raising of electrical conductivity on raising of carrier concentration back by raising of substrate temperature and mobility was also revealed from Fig. 7.

4. Conclusions

As a summary, we have stated that we have optimized and developed high quality conductive zinc oxide thin films by using L-MBE, i.e., PLD considerably comparable with the state-of-the-art of indium tin oxide (ITO) and other commercially valid TCO's.

Extra-mural studies on various factors, which influencing the electrical properties of zinc oxide thin films were carried out. The effects of heating temperatures and substrate temperatures on zinc oxide thin film growth, electrical properties were studied. As well as the feasibility of developing high quality conducting oxide thin films were also studied simultaneously. The electrical conductivity and carrier mobility of ZnO thin films were increased for higher heating and substrate temperature. Also the correlation study between electrical and optical properties was carried out. As a novelty point of view, we have concluded that without doping and annealing, we have obtained optimum electrical conductivity with high optical transparency ($\geqslant 95\%$) for as deposited ZnO thin films using PLD. Also, this is the first time that we have applied PLD made ZnO thin films to iso-, hetero-SIS type solar cells as TCO window layer. We hope that surely these data be helpful either as a scientific or technical basis in the semiconductor processing.

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