CHAPTER 6

SUMMARY, CONCLUSION AND SUGGESTIONS FOR FUTURE PROGRESS

6.1 Summary

6.2 Conclusion

6.3 Suggestions for future work
CHAPTER 6

SUMMARY, CONCLUSION AND SUGGESTIONS FOR FUTURE PROGRESS

Thin film technology is developing very fast in order to meet the needs of the human life where as the development of high quality TCOs for opto-electronic applications is still an evergreen field of investigations. In order to give some contributions to the present day state of the art of developing high quality TCOs for opto-electronic applications like solar cells, the author has made some attempts using suitable precursor materials (ZnO, In$_2$O$_3$). On the basis of referred literature, we have framed chemical and thin film strategies for preparing TCOs. In order to meet the needs of commercial device, TCO films not only must have the high transparent conductive properties, but also should be easily processed through the standard processing technology with out any complication.

6.1 Summery

A detailed study on the properties of pulsed laser deposited epitaxial zinc oxide and indium zinc oxide thin films was carried out for the purpose of opto-electronic applications like solar cells. In the previous chapters, the authors have described the properties of the zinc oxide and indium zinc oxide thin films and established optimum preparation conditions for the films. Even though, upon subsequent aging, the qualities of the films were found to be stabilized. High quality ZnO and IZO thin films were confirmed by compared with other related works, published so far, also referred in this thesis.

The over all present thesis comprises the growth kinetics and properties of PLD deposited ZnO, IZO thin films changes with deposition parameters, substrate temperatures, substrates, heavy indium oxide doping and annealing at different temperatures through various characterization and studies. In addition with fabrication and application of these films to SIS type solar cells was also emphasized. Emphasis is laid on the understanding of the junction formation mechanism and the role of interfacial layer in these junctions. To minimize experimental errors, several readings are taken at each required stage on different samples deposited in different conditions. The absolute
values reported in the present thesis are reproducible. The impetus for the work is derived from the published literature of data on device quality TCOs and their practical applications.

As a preliminary step for the understanding of the device qualities of prepared TCO thin films structural, compositional, surface morphological, optical and electrical characterizations have been carried out as function of various growth and deposition parameters. Highly oriented ZnO and IZO thin films were deposited on float glass and semiconductor substrates held at room temp. (RT), 200, 300°C and RT, 350, 450°C respectively by pulsed laser deposition. The substrates were selected so as to satisfy our aim of specialized criteria. Especially for solar cells, the substrate materials should have optimum energy gap (≈ 1.35 eV) for photovoltaic conversion, long minority carrier life time and high radiation resistance. <100> Si, GaAs, and InP (including SI, n, p) wafers were utilized as substrates. Semi-insulating (SI) substrates were used for preliminary device quality optimization, like wise, both n, p types were used for device fabrication. Similarly, float glass substrates were used for study the optical and electrical qualities of deposited thin films. <100> Si, GaAs, and InP single crystal wafers (grown at Hebei Semiconductor Research Institute (HSRI), Ministry of Informatics, Hebei, P.R.China) were lapped, polished with HBr-K2Cr2O7-H2O solution. Also degreased, cleaned with trichloroethylene (3 min), acetone (4 min), methanol (3 min) and dried. 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 powders for ZnO thin films and In2O3, ZnO powders (as per commercial ITO composition) i.e., 90% In2O3 + 10% ZnO for IZO thin films were mixed with polyvinyl alcohol binder and hot water. Then stirred, slurried, crushed into powder, dye palletized, kept in a furnace at 600°C for 3 hours. And sintered at 1200°C for ZnO targets and 900°C for IZO targets for 3 hours. 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/cm². Throughout the experiment, the laser was set at pulse energy of 250mJ and repetition rate of 10 Hz. Deposition chamber was initially evacuated up to 1x10⁻⁶ torr pressure using a turbo molecular pump, O₂ was introduced during deposition and kept constant at 1x10⁻⁵ 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.

Before 'metal oxide on semiconductor wafer deposition for the fabrication of semiconductor-insulator-semiconductor (SIS) type solar cells', the depositions of thin films were optimized with float glass substrates. The optimized deposition conditions for both of these films were explained in detail. Optimized ZnO and IZO thin films were highly oriented, uniform, single crystalline approachment, nano-crystalline, anti-reflective (AR), epitaxially lattice matched with <100> Si, GaAs and InP semiconductor single crystal wafers with out any buffer layers like GaN. The optimized ZnO films showed stoichiometric approachment. Both the ZnO and IZO films were uniform, homogeneous irrespective of the substrate surface, showed salient features and nano crystalline architecture. Both the ZnO and IZO thin films have higher transparency (≥95%) with anti-reflective nature. Both the films were highly conducting in nature. The enhancement in nano-structure nature gives rise to high conductivity. The increase in mobility is attributed to crystallinity improvement and homogeneous distribution of grains. The highest conductivity was found for optimized ZnO thin films, \( \sigma = 0.06 \times 10^3 \text{ ohm}^{-1} \text{ cm}^{-1} \) (n - type) (which is almost at the edge of semi-conductivity range), carrier density \( n = 0.316 \times 10^{19} \text{ cm}^{-3} \) and mobility \( \mu = 98 \text{ cm}^2/\text{volt-sec} \). The highest conductivity was found for optimized epitaxial IZO thin films, \( \sigma = 0.47 \times 10^3 \text{ ohm}^{-1} \text{ cm}^{-1} \) (n - type) (almost at the edge of semi-conductivity range), carrier density \( n = 0.168 \times 10^{20} \text{ cm}^{-3} \) and mobility \( \mu = 123 \text{ cm}^2/\text{volt-sec} \). The electrical studies further confirmed the semiconductor characteristics of both thin films. The photovoltaic solar cell (I-V) characteristics of fabricated TCO/substrate structures using epi-n-ZnO and epi-n-IZO thin films as TCOs and <100> Si, GaAs and InP as substrates paved way for possible usage and have value in iso and hetero SIS type solar cell fabrication efforts. Development of photovoltaic solar cells is one of the thrust areas of research especially in non-conventional energy production. Various approaches in device structures and fabrication techniques were adopted for the same. Among these, SIS type is also an advantageous one.

Extra-mural studies are also extended towards various factors, which influencing the above characteristic properties of both ZnO and IZO thin films were carried out. The effects of substrate temperatures, various substrates and heavy incorporation of indium
oxide as efficient dopant on both the thin film (deposited on glass and <100> Si, GaAs, InP wafers) growth, internal material properties, characteristics such as structural, compositional, surface morphological, nanostructural, optical, photoluminescence, electrical and photovoltaic were studied in detail. Correlation studies among material characteristics were carried out. As well as the feasibility of developing high quality transparent conducting oxide thin films (from both ZnO and IZO work) was also studied simultaneously. The characteristic parameter values for the films were calculated, graphically emphasized and tabulated. Supplementary studies on relationship between various characteristic properties gives added advantages to the both ZnO and IZO work. Beyond all of these we have carried out a feasibility study which comprises the possible usage of epi-n-TCO/<100> Si, GaAs and InP structures (in which both ZnO and IZO utilized as TCOs) for solar cell application, also as a contribution to the present day state-of-the-art of iso and hetero SIS type hetero junction solar cells. Annealing effects on photovoltaic characteristics of fabricated SIS solar cells and their parameters under various temperatures were studied in detail. The results were presented in cleared, detailed manner.

The thesis comprises six chapters. The chapter 1 outlines the various stages, steps involved in the thin film formation and techniques for the preparation of thin films, various factors which affect the film properties, like deposition parameters, characteristics of substrate, complete details of pulsed laser deposition technique, Scope and Aim of the thesis. The thesis also describes the objective and approach of the present work.

The chapter 2 describes the complete outline of transparent conducting oxides, importance of TCO coating in solar cells, Survey of literature on material properties and applications of ZnO and indium zinc oxide (IZO), complete characterizations of transparent conducting oxide thin films viz structural (XRD), compositional (EDAX), surface morphological (SEM, AFM), Optical (absorption, transmission, reflection), photoluminescence and electrical (four probe resistivity, hall effect measurements).

The chapter 3 deals with the preparation of epitaxial ZnO thin films by pulsed laser deposition, important results and discussion of characterizations. Also it comprises the conclusion which explained the novel merits of the ZnO thin film work. This chapter
also covered extramural studies on the effects of substrate or deposition temperatures and various substrates on thin film growth, quality and material characteristics. Supplementary studies on various factors, which influencing the characteristic properties of ZnO thin films were carried out. Correlation studies on comparative relationship among material characteristics were carried out. As well as the feasibility of developing high quality zinc oxide transparent conducting oxide thin films was also studied simultaneously. All of these studies give added advantages to the ZnO material processing.

The chapter 4 deals with the deposition and characterization of epitaxial IZO thin films by pulsed laser deposition, important discussion, novel merits and conclusion. The remaining progress of studies on thin film growth, quality and material characteristics were followed as already explained in chapter 3.

The chapter 5 describes the Photo voltaic solar cell phenomenon, various types of Solar cells particulars emphasize on iso and hetero semiconductor-insulator-semiconductor type hetero - junction solar cells with energy band diagrams, energy conversion process in a solar cell and fabrications process. Photovoltaic studies of epi-n-ZnO thin films/ <100> Si, GaAs and InP wafers and epi-n-IZO thin films/ <100> Si, GaAs and InP wafers as novel feasibility studies for iso and hetero type hetero junction solar cell models were explained in detail with particular emphasize on role of interfacial insulator oxide layer on solar cell characteristics. Conclusion part of this chapter covered extramural studies on the effects of substrate or deposition temperatures, various substrates and heavy indium oxide incorporation on solar cell characteristics of these structures. Supplementary studies on various factors, which influencing the solar cell characteristics, Also correlation studies on comparative relationship between various characteristics parameters and solar cell characteristics were analysed.

The chapter 6 comprises summery, conclusion and suggestions for future work.

6.2 Conclusion

Higher substrate temperature enhanced the single crystalline approachment, orientation, nano-crystalline growth of both ZnO and IZO thin films. Stoichiometric nature of ZnO thin films was improved with higher T_sub. Similarly, the surface
homogeneity, uniformity and epitaxial lattice matching with substrates of both the films were improved when we have approached higher $T_{\text{sub}}$. The transparency and anti-reflection of both the films were improved by higher temperature deposition. The optical energy gap and thickness of both the films were slightly decreased with increasing in substrate temperature. The photoluminescence intensity of the both the films was also decreased for higher temperature deposition. The electrical conductivity, carrier concentration and carrier mobility of both the films were enhanced for higher substrate temperature. A slight improvement in the photovoltaic solar cell characteristics of epi-n-TCO /<100> Si, GaAs and InP structures (in which both ZnO and IZO utilized as TCOs) for high substrate temperature deposition indicates the improvement in cell performance. Optimum substrate temperature was found as 300°C and 450°C respectively for ZnO and IZO thin film growth, quality and related photovoltaic response respectively.

The growth and physical properties of prepared ZnO and IZO thin films depend strongly on the substrate materials. The nature of growth kinetics, oriented nucleation and epitaxial lattice matching of the films are observed and controlled by the substrate materials. Among <100> Si, GaAs and InP substrates, InP gives high quality epitaxial lattice matching to both ZnO and IZO thin films. Oriented crystalline quality no were affected by substrates. Similarly better surface architecture was observed for both the films on InP than Si and GaAs. Improved photovoltaic solar cell characteristics were observed for InP based SIS structures (in which both ZnO and IZO utilized as TCOs). InP was observed to be the optimum substrate suitable for deposition of both films and also for SIS solar cell application, since InP additionally have high radiation resistance and optimum energy gap for solar energy conversion.

Due to heavy indium oxide doping, highly oriented epitaxial lattice matching with substrates is improved than pure ZnO thin films. Approachment of single crystalline nature was also improved. Due to heavy doping, stoichiometric approachment of intrinsic ZnO thin films was perturbed. Both nano crystalline nature and grain size of pure ZnO thin films were refined. Similarly the surface uniformity, homogeneity optical transparency with anti-reflection, needful low photoluminescence intensity, electrical conductivity, carrier concentration and carrier mobility of intrinsic zinc oxide thin films were also prominently enhanced. Due to heavy doping, optical energy gap of intrinsic
zinc oxide thin films was slightly decreased. Also a slight improvement in the solar cell characteristics of epi-n-TCO /<100> Si, GaAs and InP structures (in which IZO was utilized as TCO) was observed. As a result of study, we have stated that due to the heavy incorporation of indium oxide as efficient dopant needful structural, compositional, surface morphological, optical, needful photoluminescence, electrical and photovoltaic solar cell characteristics of intrinsic zinc oxide were improved. The study also confirmed that commercial ITO composition (i.e., 90% In2O3 + 10% ZnO) or (Zn content should be ≤ 5-10 %) is an optimum one for making new TCO competitors.

We may also stated that the material science or physics behind the slightly improved photovoltaic performance of 200°C vacuum annealed SIS structures than 300°C,100°C vacuum annealed SIS structures and as-prepared structures is that vacuum annealing at 200°C may leads to a combined process. The above combined process may covered i) perfect crystalline arrangement, ii) perfect internal morphological modification and iii) minute optimum oxidation or growth of interfacial insulator oxide layer between respective base substrates and TCO thin films. These three effects may further leads to disappearance of obstacles, dislocations for charge carrier mobility and minute rise in carrier density in base substrate so as to create slight decrement in Rsh , Rs and slight increment in output power through generated photo current respectively.

Improved photovoltaic performance of vacuum annealed SIS structures than as-prepared structures may be attributed to the possible existence of buried hetero type homojunction on respective n-type substrate and heavily Zn doped hole concentrated p⁺ layer on p-type substrate by interdiffusion or penetration of Zn (acceptors) into n-type and p-type substrate respectively. Also attributed to ablation process induced surface modifications

The performance of the solar cell characteristics of fabricated SIS structures can be improved by using technological steps in i, fabrication, ii, electronic contact of the TCO with substrate i.e., reduction of insulator layer width with-in the fruitful limit (< 22Å) and iii, electronic grade of base substrates since higher carrier concentration of a heavily doped substrate reduces the insulator layer width resulting in a reduced series resistance, an improved fill factor (FF) and open-circuit voltage (Voc).
The aim, novelty, motive, point of view, findings and validity of data of this thesis were accepted and published in various highly reputed field specialized international journals, conferences, workshops, topical meetings, symposiums, seminars, schools... The work carried out in this thesis have value in material science in semiconductor processing and related practical device fabrication efforts either as a technical or scientific basis especially in III-V based hetero-junction opto-electronics. As a novelty point of view we may stated that

i, With out any buffer layer like GaN, we have obtained good epitaxial lattice matching between epi-n-ZnO and epi-n-IZO thin films and <100> Si, GaAs and InP wafers as value in practical opto and micro-electronic device fabrication efforts. Author proposed that the observed lattice matched epitaxial growth was due to the effect of heating on the substrate surface by the repeated impingement of high-energy particulates emerging from the target under the action of impulse collision of every subsequent laser pulse. Lattice matching in semiconductor device structure is important in the sense that lattice mismatch with lattice imperfection leads to dominant recombination loss associated with other interface loss. For example in solar cells, it causes a several drop in conversion efficiency.


ii, With using various substrate temperature and substrate as controlling tools, we have fabricated novel nano architecture for ZnO and IZO thin films on <100> Si, GaAs and InP wafers as value in practical nano-electronics and nano machining technological efforts The surface morphology of the films comparable to MOCVD and MBE films

\[( \text{Surface Engineering} \, 20, \, 3 \, (2004) \, 1-6., \text{ Material science in semiconductor processing}, \text{ vol.8, issue 4, to be published in next available issue} \]

iii, With out doping and annealing, we have obtained high electrical conductivity (i.e., high electron-mobility) and high optical transparency ($\geq 95\%$) with anti-reflective nature for as deposited ZnO and IZO thin films by using PLD as value in producing commercial
competitors for Indium Tin Oxide (ITO) efforts so as to viable for current envisaged applications. The ZnO and IZO thin films proved that they are innocuous materials manifesting high optical transparency and electrical conductivity. As a result of long period optimization, better results were observed for ZnO thin films at substrate temperature $T_{\text{sub}}$: 300°C and for IZO thin films at $T_{\text{sub}}$: 450°C. Also the high transparency thin films were observed even at room temperature. The electrical and optical properties of the ZnO and IZO films deposited at $T_{\text{sub}}$: 300°C and 450°C respectively are preferable for application to high efficient optical and opto electronic device fabrication efforts.


iv. We have developed some novel models using epi-n-ZnO and epi-n-IZO thin films as TCOs and <100> Si, GaAs and InP wafers as substrates for the state of the art of iso and hetero SIS type hetero junction solar cells for possible usage in solar cell application.


v. With the best of our knowledge and belief on the basis of referred literature, which contains more in-sights into the TCO/substrate structures, we have stated that this the first time that we have applied these PLD prepared ZnO and IZO thin films to iso and hetero semiconductor-insulator-semiconductor (SIS) type solar cells as transparent conducting oxide (TCO) coatings.

(Material Chemistry and Physics 84, 1(2004) 14-19.)

6.3 Suggestions for future work

Further research can be made in future to initiate improvement steps for the favour of practical application of prepared TCOs. Improvement steps will be taken to form a basis for possible commercial wide range usage of epitaxial ZnO and IZO, initially as commercial competitor to indium tin oxide (ITO) in addition with adopting some technologies for increasing conversion efficiency of fabricated SIS solar cells suitable for practical applications.
Citation

Based on the published work (*J. Cryst. Growth* 226 (2001) 281), a citation was referred in the highly reputed international journal, Material Science and Engineering B

Contributions to world literature

The published work (*Current Applied Physics* 4 (2004) 1) was referred as a scientific literature for a diploma thesis by a student Miss. Maria Sidarova, Belarusian College, Russia

The published work (*Material Chemistry and Physics, 85 (2004) 257*) was selected as a technical literature for *Solid State Lighting Devices* by Sandia national laboratory, Department of Energy, USA.

The published work (*Material science in semiconductor processing 6 (2003) 219*) was selected as a 7th rank highly downloaded scientific article under subject: Materials science by *Science Direct®* (Elsevier, Amsterdam).

The published work (*Material Chemistry and Physics, 85 (2004) 257*) was selected as a 12th rank highly downloaded scientific article under subject: Materials science by *Science Direct®* (Elsevier, Amsterdam).