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Materials Chemistry and Physics 84 (2004) 14–19
MATERIALS CHEMISTRY AND PHYSICS
www.elsevier.com/locate/matchemphys

Epitaxial lattice matching between epi-n-IZO thin films and ⟨1 0 0⟩ Si, GaAs and InP wafers with out any buffer layers by L-MBE technique: a novel development for III–V opto-electronic devices

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Received 23 April 2003; received in revised form 21 August 2003; accepted 3 September 2003

Abstract

We have optimised and deposited epitaxial indium zinc oxide (epi-IZO) ($In_2Zn_2O_5$) thin films on ⟨1 0 0⟩ oriented Si, GaAs and InP by laser-molecular beam epitaxy (L-MBE) technique, i.e., pulsed laser deposition (PLD). Optimised growth conditions have been obtained for the deposition of high quality epi-IZO thin films. To our knowledge, this is the first time that the PLD deposited indium zinc oxide thin films on semiconductor wafers have been applied to semiconductor–insulator–semiconductor (SIS) iso- and hetero-type junction solar cell structures as wide band gap transparent conducting front electrode-window layers. We have carried out X-ray diffraction (XRD) and energy dispersive chemical analysis (EDAX) to determine the Structural and compositional properties of as-grown thin films. The crystalline quality of the obtained thin films is similar to that of the bulk single crystals. Increasing the deposition temperature leads the thin films to fine nano-structure nature. In the present work, the effects of various substrate temperatures, substrates and heavy indium oxide doping on indium zinc oxide thin film growth, structural and compositional properties were analysed. As well as our main aim, the feasibility of developing high quality transparent conducting oxide (TCO) thin films for opto-electronic devices was also studied simultaneously. Our novel achievement in this work is without any buffer layers, we have obtained good epitaxial lattice matching between the highly oriented IZO functional layers and the substrate materials suitable for III–V based high-speed opto-electronic and micro-electronic devices.

PACS: 68.55; 81.15.G; 73.60.F; 72.20; 72.80.E

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

1. Introduction

The transparent conducting oxide (TCO) materials must be developed with lower resistivities than previously achieved and with optical properties superior to those of the present generation of TCOs [1–15]. Improving the mobility of the charge carriers leads to superior performance of both optical and transport phenomena. The TCO thin films were prepared by so many techniques such as spray pyrolysis, metal organic chemical vapour deposition (MOCVD), jet vapour deposition (JVD), atomic layer epitaxy (ALE) and molecular beam epitaxy (MBE). Among this laser-MBE technique, i.e., pulsed laser deposition (PLD) produces a pure thin film with high conductivity and good step coverage. PLD now emerged as a new technique for thin film growth technology. The sophisticated technology and design of L-MBE system for the growth of high quality epitaxial layers are becoming increasingly important for the development of the electronic industries [6,7]. Due to adopting some unique properties, TCO thin films are used in so many commercial applications such as in solar cells, flat panel displays, Polymeric light emitting diodes, micro-electronics and micro-machining technologies.

Generally, the detailed and systematic study of correlation between the film structural properties and the device qualities is believed to gives a better understanding of the

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doi:10.1016/j.matchemphys.2003.09.001

film growth and a more 'scientific control' of a deposition process [3]. On the basis of referred literature, we framed the chemical and thin film strategies for the development of high quality TCOs. Modern integrated circuit devices require the production and Structural characterisations of state-of-the-art-ultra thin films. In the present work, we optimised and deposited epi-IZO ($In_2Zn_2O_5$) thin films on ⟨1 0 0⟩ oriented Si, GaAs and InP single crystal wafers by laser-MBE, i.e., PLD technique and studied their structural and compositional properties.

There are so many extrinsic varieties of zinc oxide thin films like $A1_2O_3$:ZnO, B_2O_3:ZnO, Ga_2O_3:ZnO, In_2O_3:ZnO, fluorine:ZnO and Tb:ZnO thin films [9]. Among this, In_2O_3:ZnO thin film seems to be suitable for our purpose, since In_2O_3 and ZnO both are exact candidates responsible for conductivity and transparency in TCO technology. On the basis of this conclusion, we prepared epitaxial indium zinc oxide (epi-IZO) thin films as a commercial competitor for indium tin oxide (ITO) thin films with ITO composition. So we took In_2O_3 as a suitable dopant for our study.

The structural properties of thin films are known to depend considerably on the state of the surface on which they are deposited. The crystallographic form also depends on substrate surface conditions. Dealing of film properties is one of the interesting area in surface physics. The film growth characteristics of laser deposited IZO thin films on to glass, Si, GaAs and InP are very novel and significant from reported so for. The physical properties of TCO films are sensitive to the mode of preparation In this present work, the effect of various substrate temperatures, substrates and heavy indium oxide incorporation on structural and compositional properties of epi-IZO thin films were analysed. As well as our main aim, the feasibility of developing high quality TCO thin films was also studied simultaneously.

Our novel achievement in this work is without using any buffer layers, we have obtained good epitaxial lattice matching between the epi-IZO functional layers and substrate materials. From the structural analysis of epitaxial indium zinc oxide thin films, we come to a conclusion that heavy indium oxide incorporation in to the zinc oxide thin films improves the intrinsic zinc oxide thin films oriented epitaxial lattice matching quality as explored in the previous work.

2. Experimental techniques

In the present work, highly oriented, epitaxially lattice matched n-type indium zinc oxide (epi-n-IZO) ($In_2Zn_2O_5$) thin films were grown on float glass and ⟨1 0 0⟩ oriented Si, GaAs and InP semiconductor single crystals substrates held at room temperature (RT), 350 and 450 °C by laser-MBE (L-MBE) technique, i.e. PLD.

PLD technique is a good technique to produce crystalline quality and stoichiometric thin films. PLD has been shown to be superior to sputtering and conventional MBB 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. Si, GaAs, and InP single crystal wafers (grown at Hebei Semiconductor Research Institute (HSRI), Ministry of Informatics, Hebei, PR China) are lapped, polished with HBr–$K_2Cr_2O_7$–H_2O solution. Also degreased, cleaned with trichioroethylene (3 mm), acetone (4 mm), methanol (3 mm) and dried. In order to eliminate the native oxide layer of the as-grown wafers, the substrates were heated up to 500 °C for 3 mm. Before 'metal oxide on semiconductor deposition', the deposition of IZO was optimised with float glass substrates using oxygen ambient at different substrate temperatures, i.e. room temperature, 350 and 450 °C. The Jhonson-Matthey 'specpure' grade 10% ZnO and 90% In_2O_3 powders (similar to commercial ITO composition, 10% SnO_2 and 90% In_2O_3) were mixed with polyvinyl alcohol binder and hot water. Then stirred, slurred crushed into powder, dye palletised, kept in furnace at 600 °C for 3 h and sintered at 900 °C for 3 h. The IZO target was ablated with third harmonic of "Quantel, YG 930, 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. Through out the deposition period, the target holder is rotated for uniform deposition of the ablated material. The epi-n-IZO thin films depositions were optimised using float glass plates, ⟨1 0 0⟩ SI-InP and ⟨1 0 0⟩ p-InP wafers as substrates. The optimum substrate temperature for epi-n-IZO thin films was found at 450 °C. The subsequent depositions on ⟨1 0 0⟩ oriented n-Si, p-Si, n-GaAs and n-InP wafers were carried out at $T_{sub} = 450$ °C for high quality optimised epi-n-IZO thin films.

The crystallinity of the as-grown epi-IZO thin films was characterized by X-ray diffraction (XRD) (Philips X-PERT-MPD X-ray diffractrometer), using Cu Kα radiation. The composition of the ZnO thin films was analysed by EDAX (Philips, ESEM-TMP + EDAX) [7,10].

3. Results and discussion

3.1. Structural properties

Before metal oxide on semiconductor deposition the process was optimised on float glass substrates, since the crystallite orientation appears to be influenced by the deposition technique. As a matter of fact, TCO texture is a key issue.

Highly oriented, epitaxially lattice matched epi-IZO ($In_2Zn_2O_5$) thin films were grown on float glass and ⟨1 0 0⟩ oriented Si, GaAs and InP semiconductor single crystals substrates held at room temperature, 350 and 450 °C by L-MBE, i.e. PLD. From XRD experiment, the material,

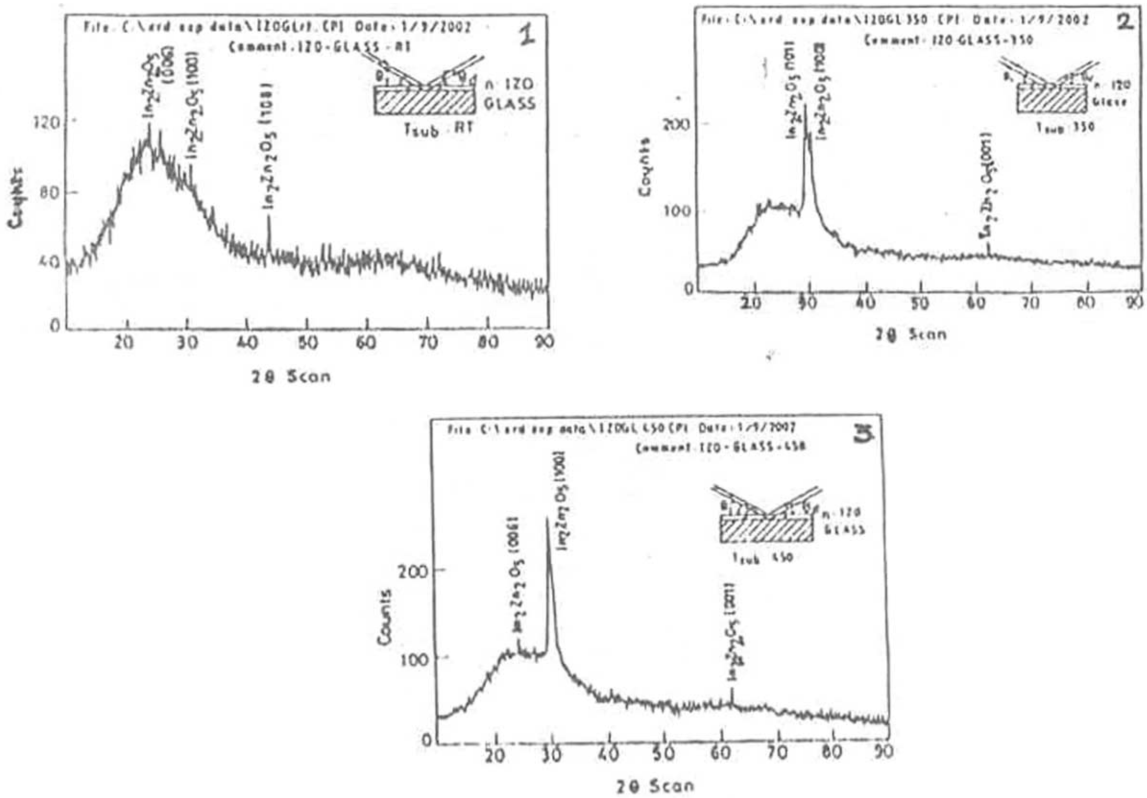

Fig. 1. The X-ray diffractograms "θ–2θ'' scan of the epi-n-IZO thin films on float glass deposited at room temperature (RT) of 350 and 450 °C, respectively.

hexagonal crystal system, cubic crystal structure and crystalline quality of the thin films were confirmed. Single, stable phase IZO thin films were confirmed.

From the X-ray diffractogram respective phase for epi-IZO thin films was indexed by using ASTM (card no. 20-1442) standard data as $In_2Zn_20_5$. From literature, we know that $In_2Zn_2O_5$ is a very stable phase. The XRD reflections are sharp and strong. The films are found to be highly textured with structure assignable to cubic In_2O_3 with low Zn levels. Also the films exhibit better micro structures, similar to the results of MBE derived films. The preferential growth was oriented towards (1 0 0), i.e. "*a*" axis orientation, when we go from room temperature to high temperature 450 °C. The preferential orientation of that epitaxial thin films is due to adsorption and thermal accommodation of impinged atoms with respect to growth parameters and nature of substrates. The initial orientation is then followed by the preferred growth of the oriented nucleation or cluster of atoms and continuously leads to the preferential growth of thin films. The requirement for preferential orientation is that this particular orientation should give lower interfacial free energy and a much higher nucleation rate than any other orientations. Generally epitaxial relationship between thin films and substrate was discussed on the basis of nucleation. The presence of epitaxy usually indicates that the nucleation rate is a maximum for the preferential orientation. Some times homogenous and coherent nucleation leads to the epitaxial nature. The crystalline quality of the obtained thin films is similar to that of the bulk single crystals. Single crystalline approachment was increased for high temperature thin films.

The results of the XRD experiments were diagrammatically presented in Fig. 1. The grain size, full width half maximum (FWHM) and cell constant were calculated and tabulated (refer Table 1). The average grain size for room

Table 1
Structural parameters of epi-n-IZO thin films deposited on float glass and ⟨1 0 0⟩ semiconductor substrates at RT, 350 and 450 °C

Structures	FWHM (β, rad)	Grain size (r, nm) with ⟨preferential peaks⟩	Cell constants (C, Å)
epi-n-IZO/glass/RT	0.0087	9.03 ⟨0 0 6⟩	22.44
epi-n-IZO/glass/350 °C	0.0174	4.57 ⟨1 0 1⟩	23.17
epi-n-IZO/glass/450 °C	0.01918	4.16 ⟨1 0 0⟩	–
epi-n-IZO/⟨1 0 0⟩ n-Si/450 °C	0.017	4.58 ⟨1 0 0⟩	–
epi-n-IZO/⟨1 0 0⟩ p-Si/450 °C	0.0087	9.15 ⟨1 0 0⟩	–
epi-n-IZO/⟨1 0 0⟩ n-GaAs/450 °C	0.0174	4.58 ⟨1 0 0⟩	–
epi-n-IZO/⟨1 0 0⟩ n-InP/450 °C	0.0174	4.58 ⟨1 0 0⟩	–
epi-n-IZO/⟨1 0 0⟩ p-InP/RT	0.0087	9.15 ⟨1 0 0⟩	–
epi-n-IZO/⟨1 0 0⟩ p-InP/350 °C	0.0174	4.58 ⟨1 0 0⟩	–
epi-n-IZO/⟨1 0 0⟩ p-InP/450 °C	0.0174	4.59 ⟨1 0 0⟩	–
epi-n-IZO/⟨1 0 0⟩ SI-InP/RT	0.0087	9.17 ⟨1 0 0⟩	–
epi-n-IZO/⟨1 0 0⟩ SI-InP/350 °C	0.0174	4.58 ⟨1 0 0⟩	–
epi-n-IZO/⟨1 0 0⟩ SI-InP/450 °C	0.0261	3.059 ⟨1 0 0⟩	–

temperature, 350 and 450 °C thin films were 9, 4.5 and 3 nm, respectively as estimated by the Scherrer method. From this, we observed that, we will get good confined nano-structure material, when we deposit IZO thin films beyond the deposition temperature 450 °C. From above we know that increasing the deposition temperature leads the thin films to fine nano-structure nature.

The growth rates for room temperature, 350 and 450 °C thin films were 21.6, 13.3 and 1.1 nm s^{-1}, respectively. The process was optimised and the optimum deposition temperature was found as 450 °C. Especially, the epitaxial lattice matching of epi-IZO thin films on ⟨1 0 0⟩ GaAs substrate at $T_{sub} = 450\,°C$ is highly appreciated. $T_{sub} \geq 450\,°C$, inter facial insulator oxide layer growth begins between the functional TCO thin films and substrate. Highly epitaxial nature with substrates was enhanced when we go from room temperature to higher substrate temperature 450 °C. Low grain size indicates the high quality crystalline nature of as-grown thin films (refer Fig. 2).

The quality of epi-IZO thin films also varies with various substrates and substrate temperatures, at which the films were deposited. Generally, the films are uniform and film growth was insensitive to substrate surface irregularities. Deposition occurs equally well on to well-treated surfaces. High intense and sharp peaks in XRD spectrum further confirmed the crystalline quality of the films. Thus from the above we found that the critical parameter determining the crystal quality of epi-IZO thin films is the substrate temperature. The best crystalline quality film was obtained at a substrate temperature of 450 °C. Higher substrate temperature enhances the single crystalline approachment, orientation and nano-structure growth of thin films. Similarly, the surface homogeneity and epitaxial lattice matching of thin films with the substrates was increased when we approached higher T_{sub}. Our novel achievement in this work is without using any buffer layers, we have obtained good epitaxial lattice matching between the functional layers and substrate materials. Since without an interfacial buffer layer between thin films and substrates, this lattice matching was achieved. Among ⟨1 0 0⟩ Si, GaAs and InP substrates, indium phosphide gives high quality epitaxial lattice matching to thin films. Both grain size and oriented crystalline quality no were affected by substrates. Similarly, better surface architecture was observed for thin films on indium phosphide than silicon and gallium arsenide. The effect of heavy indium oxide incorporation in to the intrinsic zinc oxide thin films was also analysed. We observed that due to this heavy doping, highly oriented epitaxial lattice matching with substrates and the approachment of single crystalline quality of intrinsic zinc oxide thin films were improved. As a result of study, we say that due to the heavy incorporation of

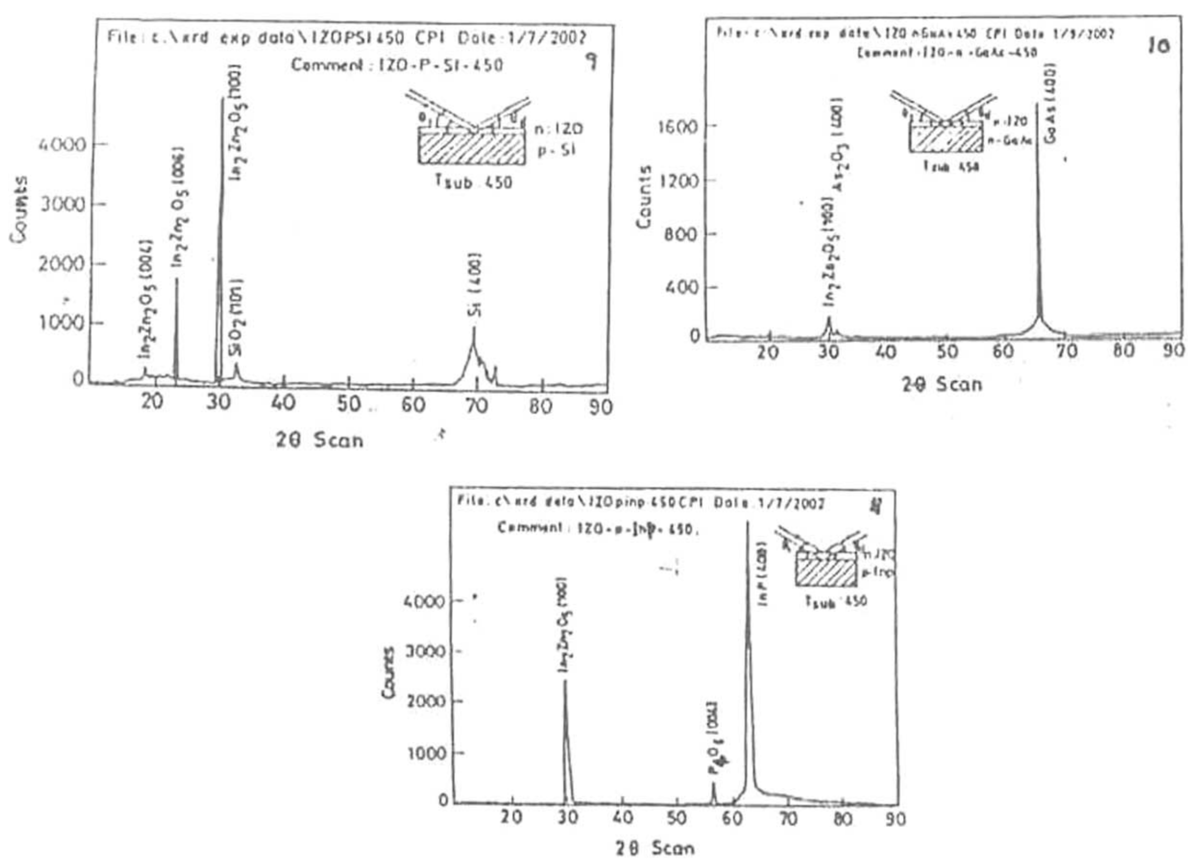

Fig. 2. The X-ray diffractograms "θ–2θ" scan of the epi-n-IZO thin films/⟨1 0 0⟩ p-Si, n-GaAs and p-InP structures prepared at 450 °C, respectively.

indium oxide as dopant in to the zinc oxide thin films, the structural properties of intrinsic zinc oxide was improved. By combining the results of XRD (θ–2θ scan) Philips X-PERT-MPD, we know that the epitaxial and lattice matching relationship between epi-IZO thin films and ⟨1 0 0⟩ oriented semiconductor single crystals substrates is very good and well appreciated, i.e. $\langle 1\,0\,0\rangle_{\text{epi-IZO functional thin films}} \| \langle 1\,0\,0\rangle_{\text{semiconductor single crystals substrates}}$. This would be an useful data to fabricate high speed micro-electronics and opto-electronics devices based on III–V compound hetero-structures.

3.2. Compositional characterisation

For a detailed study of compositional analysis of the epi-IZO thin films/Glass substrates and epi-IZO thin films/⟨1 0 0⟩ oriented single crystal semiconductor substrate structures prepared at room temperature to 450 °C, the energy dispersive analysis by X-rays (EDAX) compositional profile measurements were applied. The experiment was done by using the instrument "Philips, ESEM-TMP + EDAX" at Sophisticated Instrumentation Center for Applied Research and Testing (SICART), Department of science and technology, Government of India. The effects of various substrate temperatures and various substrates on compositional properties of epi-IZO thin films were analysed. The effect of heavy indium oxide doping was also analysed.

The results of the EDAX experiments were diagrammatically presented in Fig. 3. The elemental peaks for In, Zn, O, Si, Ga, As, In and P were identified by EDAX. High intense peak of In and O confirmed the heavy indium oxide doping. High intense peaks of Si, As, P and O may due to the mixing and overlapping of the same elemental peaks having same binding energy present in the different depth profile. The EDAX results further confirm the materials, their purity and quality of our epi-IZO thin films on Si, GaAs and InP structures.

In the EDAX composition profile, the more number of high intense peaks of Si, As, P and O may be indicate the presence of very thin SiO_X, As_xO_x and P_xO_x (where x = 1, 2, 3) interfacial insulator layers present in the semiconductor–insulator–semiconductor (SIS) structures of epi-IZO/⟨1 0 0⟩ oriented Si, GaAs and InP single crystal wafers respectively. A shift of the Si, As and P elemental core levels towards higher binding energy may also be due to the formation of their respective insulator-oxide compounds [7]. To the best of our knowledge and on the basis of

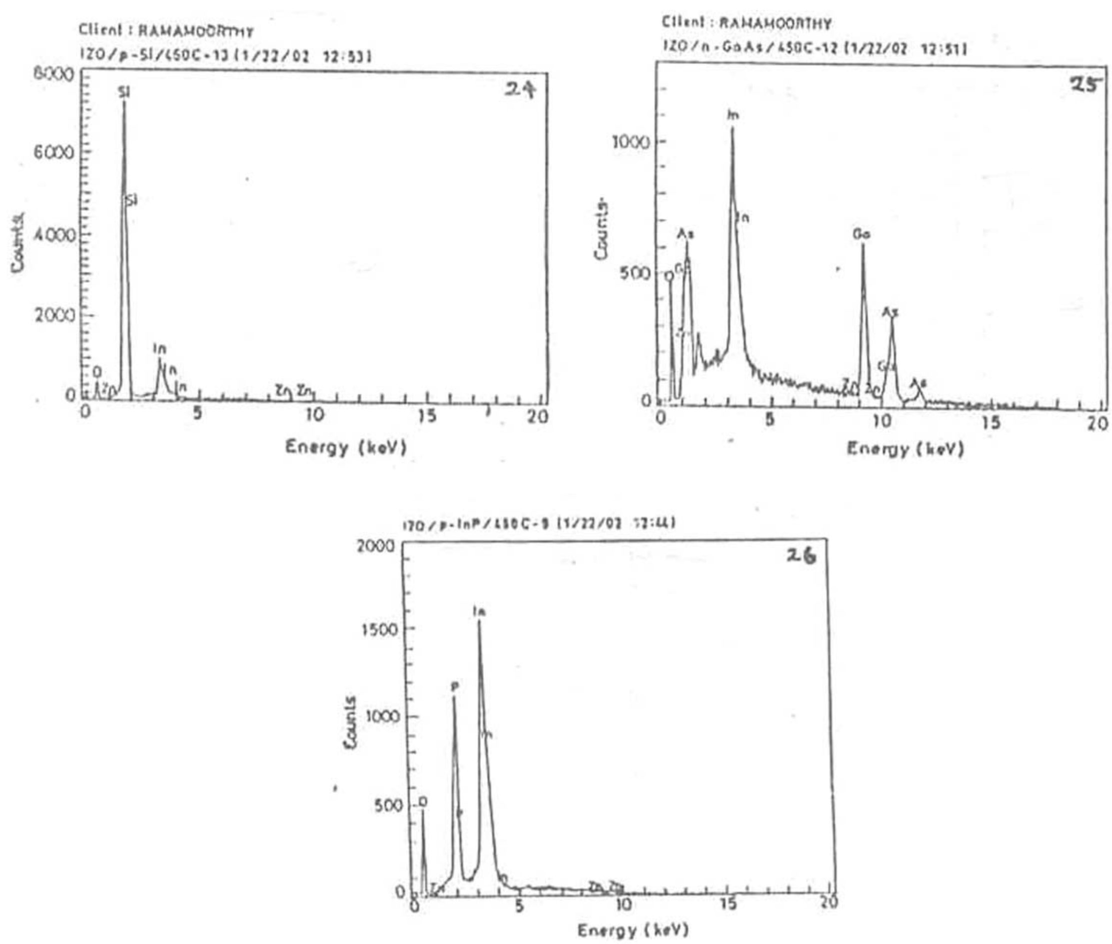

Fig. 3. The EDAX spectrums of the epi-n-IZO thin films/⟨1 0 0⟩ p-Si, n-GaAs and p-InP structures prepared at 450 °C, respectively.

referred literature [7], which contains more in-sights into the TCO/substrate interface, we stated that there may be some complex interfacial insulator region between TCO functional layer and substrate (⟨1 0 0⟩ wafers) materials. This shows that the epi-IZO thin film growth proceeds through a strong chemical interaction with the crystal wafers, which may be leads to the formation of insulator oxides regions between them.

4. Conclusions

High quality epi-IZO thin films were epitaxially grown on ⟨1 0 0⟩ Si, GaAs and InP semiconductor single crystal substrates by L-MBE, i.e., pulsed laser deposition method. These structures are suitable for SIS type multi-junction solar cells. To our knowledge this is the first time that the PLD deposited indium zinc oxide thin films on semiconductor wafers have been applied to SIS iso- and hetero-type junction solar cell structures as wide band gap transparent conducting front electrode-window layers. Structural properties including epitaxial lattice matching were analysed. Compositional measurement showed the high purity nature of the thin films. The crystalline quality of the obtained thin films is similar to that of the bulk single crystals. Increasing the deposition temperature leads the thin films to fine nano-structure nature. In the present work, the effect of various substrate temperature and substrate on indium zinc oxide thin film growth and on structural and compositional properties were analysed. As well as our main aim, the feasibility of developing high quality transparent conducting oxide thin films was also studied simultaneously. Higher substrate temperature enhances the single crystalline approachment, orientation and nano-structure growth of thin films. Similarly, the surface homogeneity and epitaxial lattice matching of thin films with the substrates was increased when we approached higher T_{sub}. Among ⟨1 0 0⟩ Si, GaAs and InP substrates, indium phosphide gives high quality epitaxial lattice matching to both the thin films. Both grain size and oriented crystalline quality no were affected by substrates. Similarly better surface architecture was observed for thin films on indium phosphide than silicon and gallium arsenide. Due to the effect of heavy indium oxide incorporation in to the intrinsic zinc oxide thin films, highly oriented epitaxial lattice matching with substrates and approachment of single crystalline quality were improved. As a result of study, we say that due to the heavy incorporation of indium oxide as dopant in to the zinc oxide thin films, the structural and compositional properties of intrinsic zinc oxide were improved. Our novel achievement in this work is without any buffer layers, we have obtained good epitaxial lattice matching between the IZO functional layers and the substrate materials suitable for III–V based high-speed opto-electronic and micro-electronic devices.

Acknowledgements

The authors would like to acknowledge the supports provided by the Sophisticated Instrumentation Centre for Applied Research and Testing (SICART), sponsored by Department of Science and Technology (DST), Government of India, Vallabh Vidhyanagar 388120, Gujarat, India.

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