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Epi-n-ZnO/⟨100⟩ Si, GaAs and InP by L-MBE: a novel approach for III–V devices

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Abstract

Highly textured zinc oxide (ZnO) thin films have been optimized and deposited by pulsed laser deposition (PLD), i.e., laser-molecular beam epitaxy technique on ⟨100⟩ Si, GaAs and InP wafers compatible with current semiconductor processing techniques. To our knowledge this is the first time that the PLD deposited zinc oxide thin films on semiconductor wafers have been applied to semiconductor–insulator–semiconductor type multi junction (homo and hetero) solar cell structures as wide band gap transparent conducting oxide (TCO) front electrode-emitter layers. In this present work, the effects of various substrate temperatures and substrates on ZnO thin film growth, structural and compositional properties were analyzed and the feasibility of developing high-quality TCO thin films for opto-electronic devices was also studied simultaneously. Increasing the deposition temperature leads the thin films to fine nano-structures. Our achievement in this work is elimination of any buffer layer like GaN and we have obtained good epitaxial lattice matching between the ZnO functional layers and the ⟨100⟩ substrates suitable for III–V-based high-speed opto- and micro-electronic devices.

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

1. Introduction

Pulsed laser deposition (PLD) technology is a relatively novel method having advantages in reproducing the structural morphology and stoichiometry of multi-component oxide thin films. PLD technique may be used to deposit both the buffer and functional layers in commercial grade electronics application compared to metal organic chemical vapour deposition (MOCVD) and molecular beam epitaxy (MBE) [1]. To our knowledge this is the first time that the PLD deposited zinc oxide thin films on semiconductor wafers have been applied to semiconductor–insulator–semiconductor (SIS)-type multi-junction solar cells as wide band gap transparent conducting oxide (TCO) front electrode layers. Due to their unique properties, ZnO, Si, GaAs and InP are appropriate materials for opto-electronic applications, micro-electronic monolithic circuit industries and micro machining technologies.

On the basis of the referred literature [2], we framed the chemical and thin film strategies for the development of high-quality TCOs. Oxides cannot be epitaxially deposited by physical methods directly on to the bare

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semiconductor crystal wafers, since high quality, commercially valid deposition would require heating the semiconductor crystal substrate to high temperature in an oxygen atmosphere. Both the oxygen pressure and the substrate temperature are responsible parameters for obtaining stoichiometric and oriented thin films. Even under such optimized conditions, the crystallinity of the wafer surface degrades due to oxidization. This problem can somewhat be minimized by buffer layers grown on substrate at low oxygen pressure and temperature [3]. Moreover, the buffer layers help to minimize the epitaxial lattice mismatching and the inter-diffusion processes between substrates and the functional layers. Such buffer layers should have inter-planar distance (d) value just between the 'd' values of substrate and the functional layer. Also, the crystalline morphology of that buffer layer should be analogous to the functional layer. In the present work, the effects of various substrate temperatures and substrates on ZnO thin film growth and on structural and compositional properties was analyzed. The feasibility of developing high-quality TCO thin films for opto-electronic devices was also studied simultaneously. Our novel approach does not use any buffer layers like GaN and we have obtained good epitaxial lattice matching between the ZnO functional layers and $\langle 100 \rangle$ substrate materials. The nano-structural characteristics identified from epitaxial ZnO thin films on wafers are significant from reports so far [2–14].

2. Experimental techniques

In the present work, highly oriented, epitaxially lattice matched ZnO thin films were grown on semiconductor single-crystal substrates (Si, GaAs and InP) held at room temperature (RT), 200°C and 300°C by laser molecular beam epitaxy technique (L-MBE) i.e. PLD. Si, GaAs and InP single crystals having different types [semi-insulating (SI), n, p] and $\langle 100 \rangle$ orientations are used as substrates for preparation of ZnO thin films. PLD is a good technique to produce crystalline quality and stoichiometric thin films. It has been shown to be superior to sputtering and conventional MBE for growing highly pure and good crystalline metal oxide epitaxial thin films for opto-electronic devices and 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, Hebei, P.R. China) are lapped, polished with $HBr–K_2Cr_2O_7–H_2O$ solution, and also degreased, cleaned with trichloroethylene (3 min), acetone (4 min), methanol (3 min) and dried. Before "metal oxide on semiconductor deposition", the deposition of ZnO was optimized with float glass substrates using O_2 ambient at different substrate temperatures i.e., RT, 200°C and 300°C, since deposition above 300°C has yielded low-photovoltaic efficiency. The pure (99.9%) ZnO powder is mixed with polyvinyl alcohol binder and hot water, then stirred, slurred, crushed into powder, dye pelletized, kept in furnace at 600°C for 3 h and sintered at 1200°C for 1 day. The ZnO target was 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 was found at 300°C. The subsequent depositions on $\langle 100 \rangle$ oriented n-Si, p-Si, n-GaAs and n-InP wafers were carried out at $T_{sub} = 300$°C. The crystallinity of the as-grown epi-ZnO thin films was characterized by X-ray diffraction (Philips; X-PERT-MPD, X-ray diffractrometer), using Cu-Kα radiation. The composition of the ZnO thin films was analyzed by energy dispersive analysis by X-rays (EDAX) (Philips, ESEM-TMP + EDAX) [6,7].

3. Results and discussion

3.1. Structural characterization

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. The quality of epi-ZnO thin films also varies with various substrates and substrate temperatures, at which the films were deposited. Generally, the films are uniform and film growth is insensitive to substrate surface irregularities. Deposition occurs equally well on to well-treated surfaces. The XRD crystalline peaks of the epi-ZnO/Glass and epi-ZnO/$\langle 100 \rangle$ oriented single-crystal semiconductor substrate structures were indexed by using ASTM data (card no: 3-0888), through which, the material, quality, crystalline nature, the hexagonal crystal system and the wurtzite crystal structure of ZnO thin films were confirmed. In this study (refer Figs. 1(a–e)), high-quality thin films without existence of any other combinatorial phases of ZnO were confirmed by X-ray diffraction studies.

The X-ray diffraction (Philips, X-pert-MPD; using Cu-Kα radiation) of epi-ZnO thin films on float glass substrates indicates that low T_{sub} (25°C), (i.e., at RT) films are amorphous in nature. Generally, the growth of

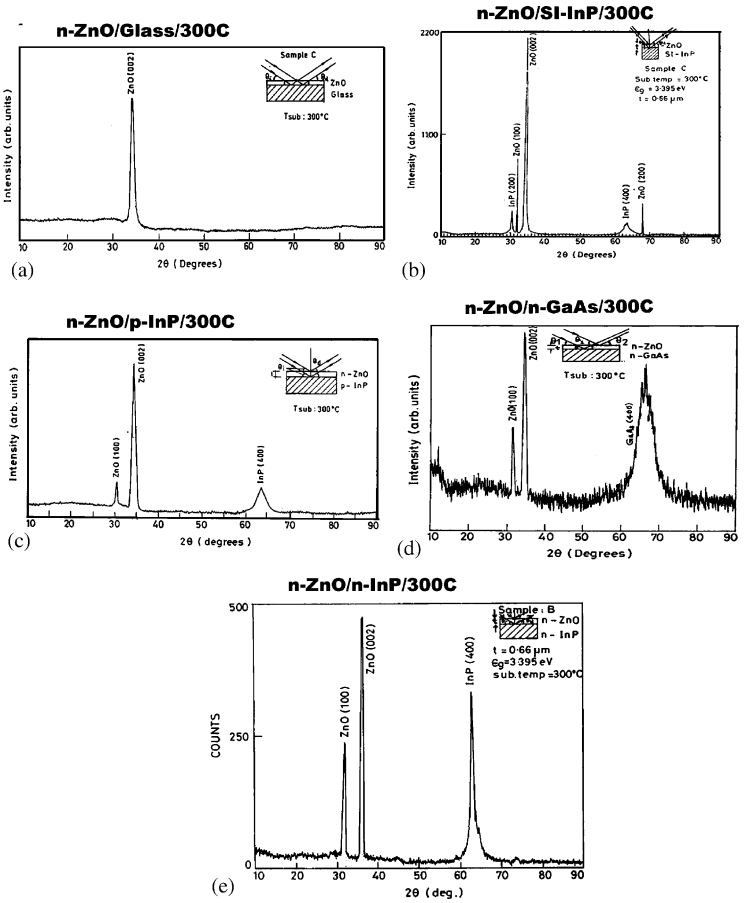

Fig. 1. (a–e) The X-ray diffractograms Θ–2Θ scan of the epi-ZnO thin films on float glass and $\langle 100 \rangle$ GaAs and InP structures prepared at 300°C.

the thin films varies from granular nature to columnar, when we travel from low substrate temperature to high. At lower substrate temperatures, amorphous films were formed presumably due to the incomplete formation of ZnO crystalline lattices on glass substrates. Amorphous nature of thin films vanishes and the formation of crystalline peaks occurs by keeping the substrate temperature at 200°C and above. High T_{sub} (200°C and 300°C) films demonstrate the enhancement of crystalline peaks, implying preferential orientation of the crystallites with the "*c*"-axis normal to the glass surface.

While for epi-ZnO thin films/$\langle 100 \rangle$ Si, GaAs and InP semiconductor single-crystal wafers, the XRD diffractograms indicates that low T_{sub} (25°C) films are polycrystalline in nature, high T_{sub} (200°C and 300°C) films demonstrate enhancement of the [100] and [002] peaks, implying preferential orientation of the crystallites with the "*c*"-axis normal to the substrate surface. Also, the ZnO polycrystalline thin films approaches single-crystalline nature, when we travel from T_{sub} : RT to 300°C. The relative intensity of the (100) and (002) diffraction peaks is greater than that given by the ASTM 3 – 0888 card. Thus, the intensity of the peak increases with increase in the substrate temperature, indicating an improved crystalline nature of the ZnO thin films. ZnO is an interesting material in that even with low substrate heating, Zn and O atoms follow vertical packing, resulting in a single "*c*"-axis orientation. From the XRD diffractograms, we know that the smaller the range over which the diffracted beam emerges indicates the more perfect orientation of the thin films. High intense and sharp peaks in X-ray diffraction spectrum further confirmed the stoichiometric form and the crystalline quality of the films.

The preferential orientation of the thin films on semi-substrates varies from '*a*'-axis to '*c*'-axis, when we go from RT to 300°C. The cell constant '*c*' = 5.207 Å corresponding to the preferential orientation (102) of ZnO thin films deposited on glass plates at 200°C was calculated and tabulated (refer Table 1). The cell constant value '*c*' = 5.270 Å corresponding to the

Table 1
Structural parameters of epi-n-ZnO thin films deposited on float glass and ⟨100⟩ substrates at RT, 200°C and 300°C

Structures	FWHM (β) (rad)	Grain size (r) (nm) with ⟨preferential peaks⟩	Cell constants (C) (Å)
Epi-ZnO/Glass/RT	Amorphous nature	Amorphous nature	—
Epi-ZnO/Glass/200°C	0.009345	8.96 ⟨102⟩	5.2077
Epi-ZnO/Glass/300°C	0.013418	6.02 ⟨002⟩	5.2700
Epi-ZnO/n-Si/300°C	0.021803	3.71 ⟨002⟩	5.2700
Epi-ZnO/p-Si/300°C	0.017444	4.69 ⟨002⟩	5.2700
Epi-ZnO/n-GaAs/300°C	0.013460	6.0 ⟨002⟩	5.2700
Epi-ZnO/n-InP/RT	0.008177	9.76 ⟨100⟩	—
Epi-ZnO/n-InP/300°C	0.013955	5.70 ⟨002⟩	5.2700
Epi-ZnO/p-InP/RT	0.008722	9.15 ⟨100⟩	—
Epi-ZnO/p-InP/200°C	0.009768	8.18 ⟨100⟩	—
Epi-ZnO/p-InP/300°C	0.016048	5.04 ⟨002⟩	5.2700
Epi-ZnO/SI-InP/RT	0.008722	9.19 ⟨100⟩	—
Epi-ZnO/SI-InP/200°C	0.010466	7.60 ⟨100⟩	—
Epi-ZnO/SI-InP/300°C	0.017444	4.60 ⟨002⟩	5.2700

preferential orientation (002) of ZnO thin films deposited on glass plates, SI- InP, p-InP, n-InP, n-GaAs, p-Si and n-Si at 300°C was also calculated and tabulated. The full-width at half-maximum (FWHM) (rad) values of preferential orientation of ZnO thin films were calculated and tabulated (refer Table 1). It is shown that FWHM values increase with increasing substrate temperature from RT to 300°C. The ZnO films grown on glass and ⟨100⟩ Si, GaAs and InP semiconductor single-crystal substrates at RT, 200°C, and 300°C have an average grain sizes of about 9, 7 and 5 nm, respectively, as estimated by the Scherrer method. The values were calculated and tabulated. The grain sizes decrease for higher substrate temperatures, i.e., nano-structure nature of the material is enhanced, when we deposit from RT to 300°C. From this, we know that we get good confined nano-structure material, when we deposit ZnO thin films beyond the deposition temperature 300°C. From the above we know that increasing the deposition temperature leads the thin films to nano-world.

Thus, from the above, we found that the critical parameter determining the crystal quality of ZnO is the substrate temperature. The substrate temperature is critical in that low substrate temperature results in a low surface migration of ad atoms while too high substrate temperature causes the ad atoms to re-evaporate from the film surface. Higher substrate temperature enhances the single-crystalline approach, orientation and nano-structure growth of thin films. Similarly, the surface homogeneity and epitaxial lattice matching of thin films with the substrates were increased when we approached higher $T_{sub.}$ The best crystalline quality film was obtained at a substrate temperature of 300°C. The optimal deposition temperature was found to be about 300°C and the deposition process was optimized. The films deposited at a substrate temperature 300°C show the epitaxial lattice matching and stoichiometric nature with ⟨100⟩ oriented semiconductor single-crystal wafers. Among ⟨100⟩ Si, GaAs and InP substrates, InP gives high-quality epitaxial lattice matching to the thin films. Both the grain size and oriented crystalline quality were not affected by the various substrates used. Similarly, better surface architecture was observed for thin films on InP than Si and GaAs. Especially, ZnO thin films on InP lattice matching was highly appreciated. Since, without GaN as an interfacial matching layer between thin films and substrates, this lattice matching was achieved. By combining the results of XRD (θ–2θ scan) Philips X-pert –MPD, we know that the epitaxial and lattice matching relationship between ZnO and SI–InP is very good, i.e.; $\langle 100 \rangle_{ZnO}$ ll $\langle 100 \rangle_{InP}$. This would be a useful data to fabricate high-speed micro-electronics and opto-electronics devices based on III–V compound hetero-structures.

3.2. Compositional characterization

For a detailed study of compositional analysis of the epi-ZnO thin films/glass substrates and epi-ZnO thin films/⟨100⟩ oriented single-crystal semiconductor substrate structures prepared at RT, 200°C and 300°C, the EDAX compositional profile measurements were applied. The experiment was carried out 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 substrates on ZnO thin film growth and compositional properties were analyzed.

The results of the EDAX experiments are presented in the Figs. (2(a–e)). The elemental peaks for Zn, O, Si, Ga, As, In and P are identified by EDAX. 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-ZnO thin films on Si, GaAs and InP structures. EDAX spectrum shows the stoichiometric approach of the ZnO thin films. When we go from RT to 300°C, the stoichiometric nature of the thin films increases., i.e., approach of stoichiometric nature was observed for higher substrate temperature epitaxial ZnO thin films. Stoichiometry was nowhere affected by the various substrates used.

In the EDAX composition profile, the higher number of high-intense peaks of Si, As, P and O may indicate the presence of very thin SiO_x, As_xO_x and P_xO_x (where $X=1, 2, 3,\ldots.$) interfacial insulator layers present in the SIS structures of epi-ZnO/$\langle 100 \rangle$ 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 indicate the formation of their respective insulator-oxide compounds [8]. To the best of our knowledge and on the basis of referred literature [8], which contains more insights into the TCO/substrate interface, we state that there may be some complex interfacial insulator region between TCO functional layer and substrate ($\langle 100 \rangle$ wafers) materials. This shows that the epi-ZnO thin film growth proceeds through a strong chemical interaction with the crystal wafers, which may lead to the formation of insulator oxides regions between them.

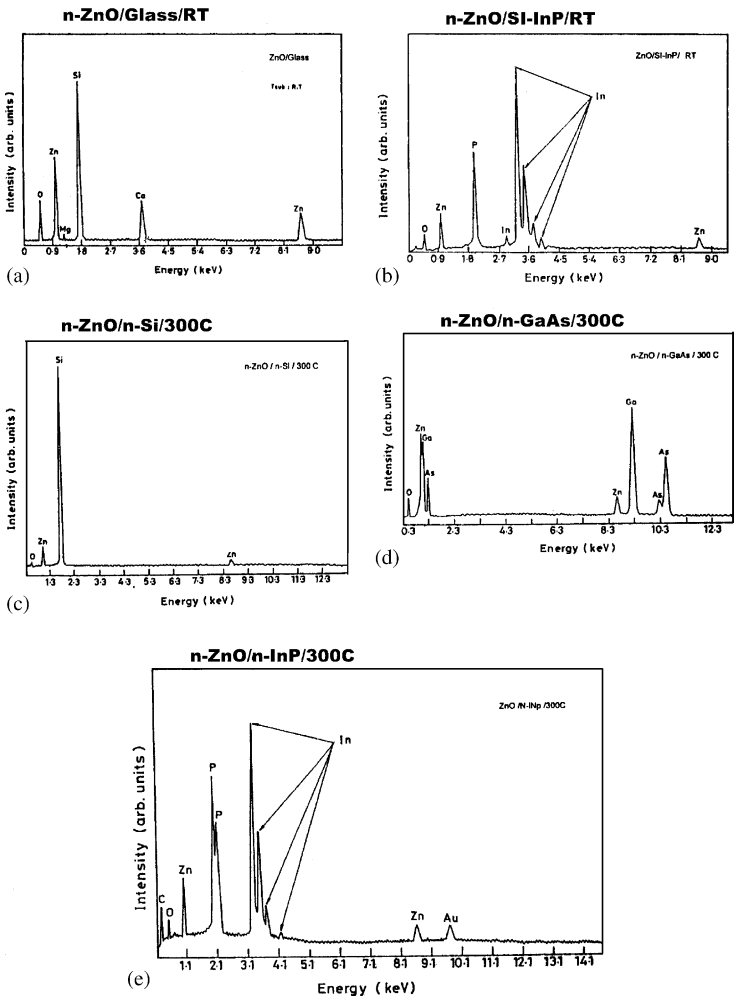

Fig. 2. (a–e) The EDAX spectrums of the epi-ZnO thin films on float glass and $\langle 100 \rangle$ Si, GaAs and InP structures prepared at RT and 300°C.

4. Conclusions

High-quality ZnO thin films were epitaxially grown on ⟨100⟩ Si, GaAs and InP semiconductor single-crystal substrates by L-MBE, i.e., PLD method. These structures are suitable for SIS-type multi-junction solar cells. In this present work, the effect of various substrate temperature and substrate on ZnO thin film growth and on structural and compositional properties was analyzed and the feasibility of developing high-quality TCO thin films for opto-electronic devices was also studied simultaneously. Higher substrate temperature enhances the single-crystalline approach, 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}. Approach of stoichiometric nature was observed for higher substrate temperature epitaxial ZnO thin films. Among ⟨100⟩ Si, GaAs and InP substrates, InP gives high-quality epitaxial lattice matching to the thin films. Both grain size and oriented crystalline quality were not affected by the substrates. Similarly, better surface architecture was observed for thin films on InP than Si and GaAs. Structural properties including epitaxial lattice matching were analyzed. Compositional measurement showed the stoichiometric nature of the high-temperature thin films. Increasing the deposition temperature enhanced the nano-structure nature of thin films. These results and the understanding should be helpful to fabricate high-speed micro- and opto-electronics devices based on III–V compound hetero-structures.

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