FABRICATION OF NOVEL NANO-ARCHITECTURE FOR *epi*-IZO THIN FILMS ON ⟨100⟩ Si, GaAs AND InP SINGLE CRYSTAL WAFERS BY L-MBE

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It is believed that this is the first time that laser molecular beam epitaxy, i.e. pulsed laser deposition (PLD), deposited epitaxial indium zinc oxide (epi-IZO) thin films on float glass, ⟨100⟩ Si, GaAs and InP wafers have been applied to semiconductor – insulator – semiconductor type heterojunction solar cell structures as wide band gap transparent conducting oxides front electrode collector layers. In the present work, the effects of substrate temperatures, substrates and heavy indium oxide incorporation on epi-IZO thin film growth and novel surface morphological properties were analysed. Hitachi SEM and nanoscope atomic force microscopy revealed that the films were high quality nanostructures, which vary with different substrate temperatures and type of substrate. The morphological study is significant as reported so far. Increasing the substrate temperature causes the films to form a fine nanostructure. Better surface quality was observed on InP than Si and GaAs. Therefore, by the use of PLD with different substrate temperatures and substrates as control tools, a novel nano-architecture was developed for IZO thin films on glass, Si, GaAs and InP semiconductor single crystal wafers. Heavy indium oxide incorporation improves the surface quality of the thin films. The present work will be used, and these data may be helpful, as a scientific or technical basis in semiconductor processing and technology, such as nano-electronics (invisible security circuits) and nanomachining technology. SE/S280

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INTRODUCTION

Epitaxial indium zinc oxide (*epi*-IZO) thin film is a promising transparent conducting oxide (TCO) candidate suitable for opto-electronic applications. It exhibits transport and optical properties rivalling or exceeding those of many TCOs. High quality TCO films can be prepared by different techniques, such as metal organic chemical vapour deposition (MOCVD), atomic layer epitaxy (ALE) and molecular beam epitaxy (MBE).[1–14] Each technique has its own advantages and disadvantages. Laser molecular beam epitaxy (L-MBE) i.e. pulsed laser deposition (PLD), is a promising thin film growth technology which has been adopted in the present work to grow high surface quality IZO thin films on silicon (Si), gallium arsenide (GaAs) and indium phosphide (InP) substrates for semiconductor – insulator – semiconductor (SIS) heterojunction solar cell application. In the present work, the effects of substrate temperatures, substrates and heavy indium oxide incorporation on indium zinc oxide thin film growth and novel surface morphological properties were analysed. On the basis of the literature,[6] chemical and thin film strategies were framed for the development of high quality TCOs. In addition, the feasibility of developing high quality TCO thin films was studied.

EXPERIMENTAL DETAILS

In the present study, a single target PLD system was employed to deposit highly oriented, epitaxially lattice matched *epi*-IZO nanocrystalline thin films on float glass and semiconductor single crystal substrates (Si, GaAs and InP) held at room temperature (RT), 350 and 450°C. Si, GaAs and InP single crystals of different types (semi-insulating (SI), n, p) and ⟨100⟩ orientation were used as substrates for the preparation of *epi*-IZO thin films. These wafers were grown at Hebei Semiconductor Research Institute (HSRI), Ministry of Informatics, Hebei, China, then lapped and polished with $HBr – K_2Cr_2O_7 – H_2O$ solution. They were degreased, cleaned with trichloroethylene (3 min), acetone (4 min), methanol (3 min) and dried. The targets were made by mixing Johnson – Mathey specpure grade 10%ZnO and 90%In_2O_3 powders with polyvinyl alcohol binder and hot water. They were stirred, slurred, crushed into powder, dye palletised, kept in a furnace at 600°C for 3 h and sintered at 900°C for 3 h. The IZO target was ablated with the

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third harmonic of a Quantel, Yg 980, France, Nd:YAG laser (355 nm, 6 ns, 10 Hz) with an energy density of 5 J cm^{-2}. Throughout the experiment, the laser was set at pulse energy 250 mJ and repetition rate 10 Hz. The deposition chamber was initially evacuated up to 1×10^{-6} Torr (1 Torr = 133·322 Pa) pressure using a turbomolecular 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 was rotated to promote uniform deposition of the ablated material.

Initially, the deposition of IZO was optimised with float glass substrates before deposition on ⟨100⟩ wafers at different substrate temperatures (T_{sub}), i.e. RT, 350 and 450°C. The optimum substrate temperature for *epi*-n-IZO thin films was 450°C. Subsequent depositions on ⟨100⟩ n-Si, p-Si, n-GaAs and n-InP wafers were then carried out at T_{sub} = 450°C for high quality *epi*-n-IZO thin films. Surface analysis was carried out using SEM (Hitachi S-450). For a detailed surface study, atomic force microscopy (AFM, Nanoscope-III) was applied to characterise the microstructural properties of the as grown IZO thin films.

RESULTS AND DISCUSSION

Surface morphological and microstructural properties

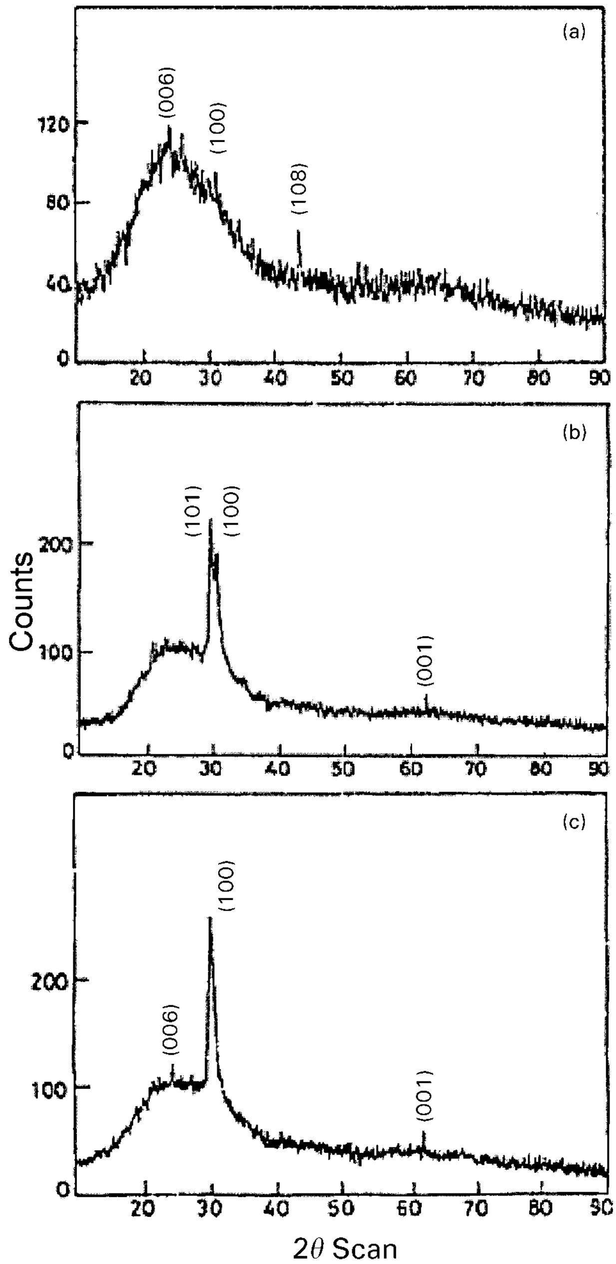
Determining film properties is an interesting area in surface physics. The IZO thin film depositions were optimised using float glass plates, then ⟨100⟩ SI InP and ⟨100⟩ p-InP wafers. The optimum substrate temperature for IZO thin films was 450°C by X-ray diffraction (Philips-Xpert-XRD) analysis (*see* Fig. 1). Subsequent depositions on ⟨100⟩ oriented n-Si, p-Si, n-GaAs and n-InP wafers were carried out at T_{sub} = 450°C.

The surface nature of the IZO thin films deposited on float glass substrates at RT, 350 and 450°C was revealed by SEM and AFM analysis (Fig. 2). SEM micrographs also show that the RT deposited films were rough with too many irregularities, but smooth and uniform films were deposited at 350 and 450°C. AFM photos revealed that the films deposited at 350 and 450°C have well defined preferred growth with salient hexagonal morphology.

Rough and non-uniform films with a granular nature were observed for *epi*-IZO thin films deposited on ⟨100⟩ SI InP at RT (Fig. 3*a*) and homogeneous oriented growth at 350°C (Fig. 3*b*). At 450°C (Fig. 3*c*), the surface morphology was changed to preferential growth, but the film seems to be non-uniform.

From surface morphology of IZO films on ⟨100⟩ p-InP deposited at RT (Fig. 4*a*), 350°C (Fig. 4*b*) and 450°C (Fig. 4*c*), the epitaxial growth evolution can be clearly understood. AFM photos revealed that the films deposited at 450°C have homogeneous preferred growth with hexagonal morphology and jasmine cluster-like features.

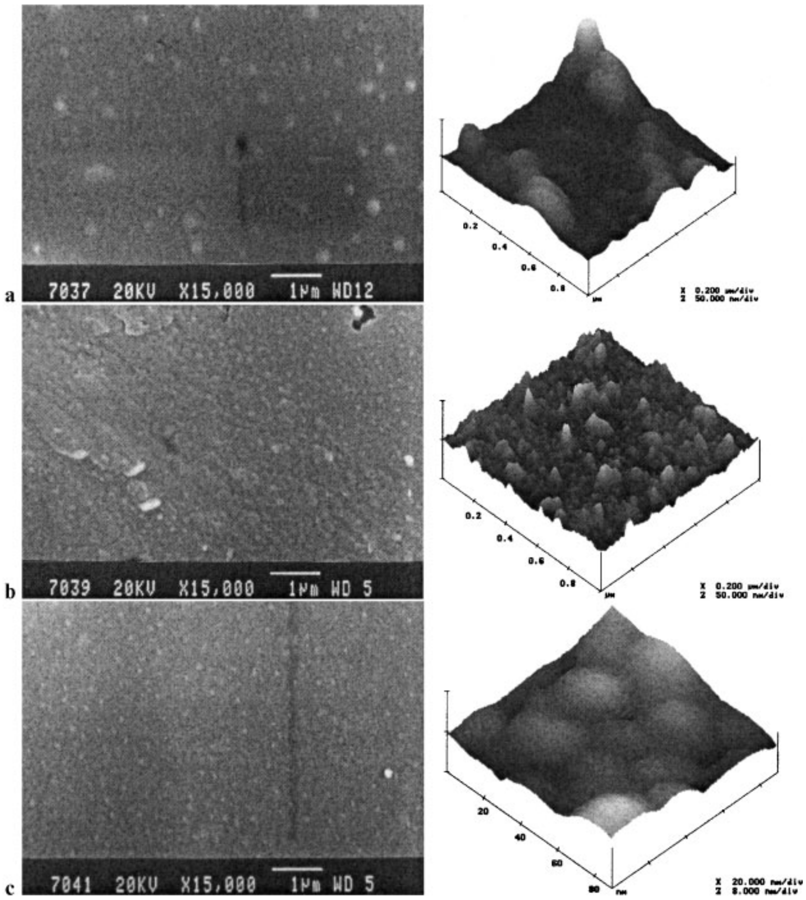
The results of the SEM and AFM analyses presented in Fig. 5 emphasise the surface morphological features of various *epi*-IZO films deposited on ⟨100⟩ n-Si, p-Si, n-GaAs and n-InP wafers at 450°C. From these SEM and AFM photographs, one can confirm the salient features of the films, e.g. homogeneous granular nature, hexagonal morphology, climbing



a RT; *b* 350°C; *c* 450°C

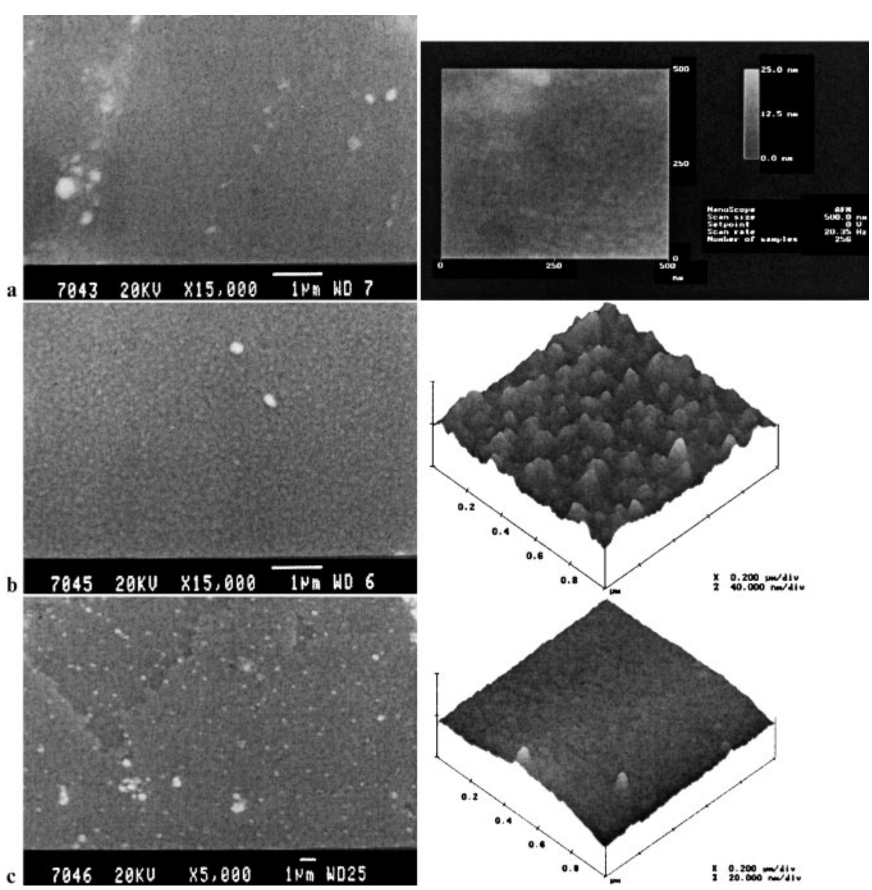
1 *X-ray diffractograms of epitaxial IZO thin films deposited on float glass substrates*

plant morphology, crystalline growth, single crystalline approachment and uniformity of the film. The presence of white smoke cloudiness and milky dots in the SEM and AFM images may be due to the segregation of Zn atoms at the grain boundaries in the IZO matrix and low reflectivity regimes present in the thin films. The milkiness and smog-like features observed in the SEM and AFM micrographs and nanographs are believed to be due to ambient oxygen gas phase reactions at higher substrate temperature, which may have introduced interfacial insulator oxide layer growth. The better defined grain boundaries in the SEM and AFM images were due to the involvement of the respective interfacial insulator oxide layer between functional thin films/base substrate structure, e.g. SiO_2 layer in the *epi*-n-IZO/⟨100⟩ p-Si structure. These layers provide a better surface for nucleation and adsorption of the functional thin film growth. It has also been observed by many workers[7–14] that the



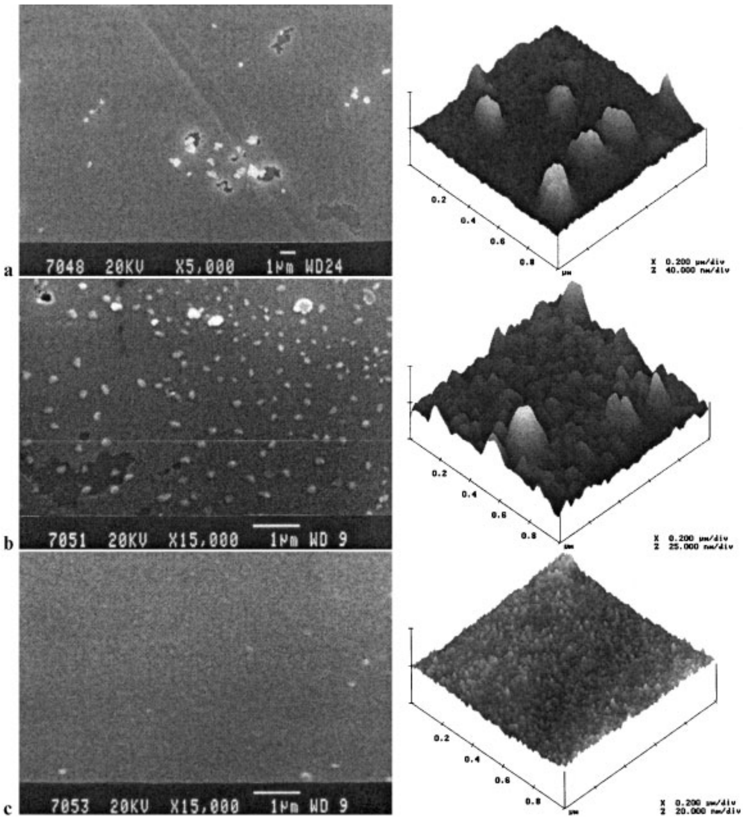
a RT; *b* 350°C; *c* 450°C

2 *SEM and AFM analyses of surface nature of IZO thin films deposited on float glass substrates*



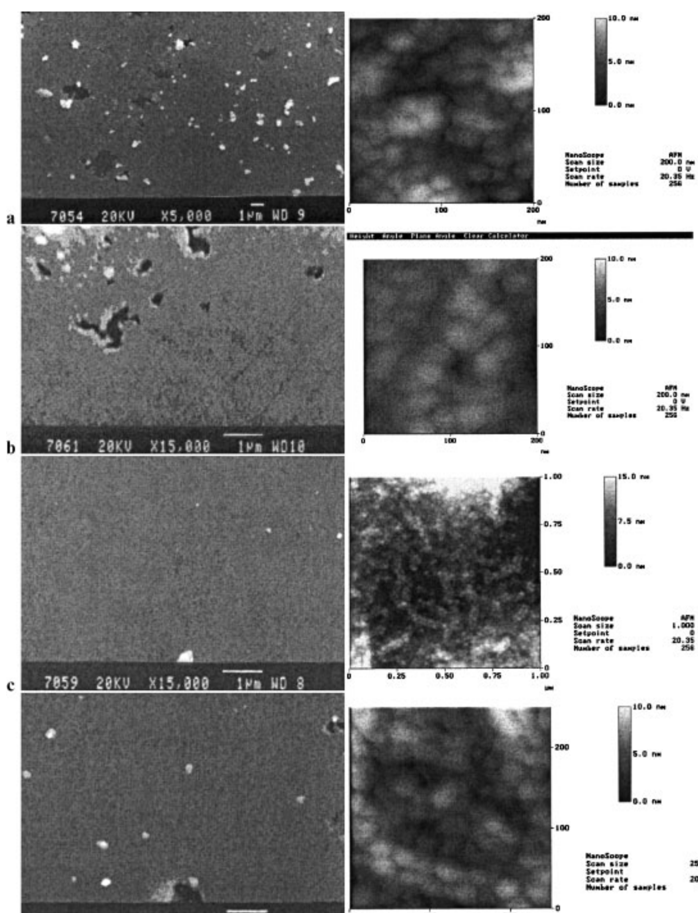
a RT; *b* 350°C; *c* 450°C

3 *SEM and AFM analyses of surface nature of epi-IZO thin films deposited on* ⟨100⟩ *SI InP*



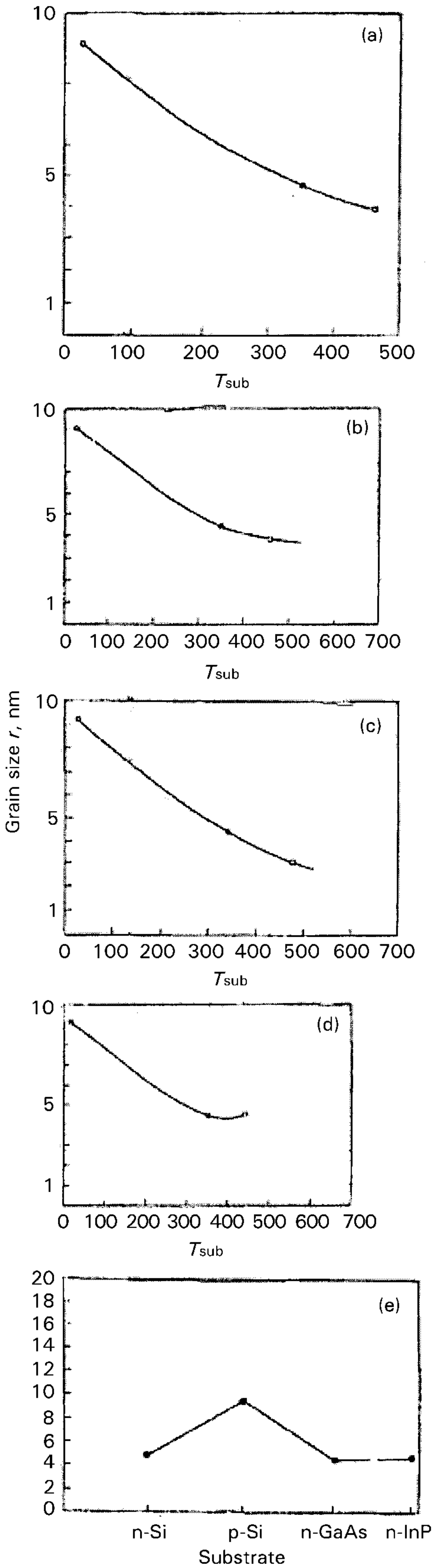
a RT; *b* 350°C; *c* 450°C

4 *SEM and AFM analyses of surface nature of IZO thin films deposited on ⟨100⟩ p-InP*



a ⟨100⟩ n-Si; *b* p-Si; *c* n-GaAs; *d* n-InP wafers at 450°C

5 *SEM and AFM surface morphological features of epi-IZO films deposited on various substrates*



a various glass and ⟨100⟩ semiconductor; *b* float glass; *c* ⟨100⟩ SI InP; *d* ⟨100⟩ p-InP; *e* ⟨100⟩ n-Si, p-Si, n-GaAs and n-InP

6 *Substrate temperature v. average grain size r, nm, of epi-IZO thin films deposited on various substrates; a–d deposited at 350°C and 450°C, e deposited at 450°C*

presence of interfacial insulator oxide layers between functional thin films and substrates may improve the structure and thereby enhance the properties of the deposited functional thin films.

Pulsed laser deposition has emerged as a promising technique for growing nanoparticles of various materials. AFM analysis carried out in this complete, detailed study further confirms the homogeneous nanostructure nature of IZO thin films composed of hexagonal, nanometre sized grains and crystallites. By means of the Scherrer grain size calculation method, it can be concluded that the particle/grain size of *epi*-IZO thin films decreased with increasing substrate temperature (*see* Table 1 and Fig. 6). Increasing the substrate temperature leads to a fine nanostructure in the films. Nanoscale science and technology is emerging as a vibrant area of research. It might create a new generation of materials with advanced engineered properties, nanoelectronics and nanomachining technology. There has been much interest in developing nanodevices in band gap engineering by growing nanoparticles of a particular material. Similarly, the band gap ε_g of the IZO thin films decreased with decreasing grain size and increasing substrate temperature. It is already known that the band gap ε_g of a semiconductor depends upon the size of the component crystallites in the nanometre regime. The reduction in sheet resistance of the IZO films observed may be due to the increased packing density of grains/crystallites. Therefore, the optical and electrical properties of a semiconductor thin film can be tuned by grain size using various substrate temperatures and substrates as control tools. It is emphasised that the difference in grain size of the particulates or grains observed is due to their formation by the mechanism of clustering during transit through the ambient gas as a unique channel. Changes in surface morphology with substrate temperature are probably due to the difference in surface energy of the crystallite structure. From the above, it was found that the critical parameter for surface quality of IZO thin films is the substrate temperature. The substrate temperature is critical in that a low substrate temperature results in low surface migration of adatoms, while too high a substrate temperature causes the adatoms to re-evaporate from the film surface. With a host of exotic optical, structural and self-organisational properties, nanocrystalline

Table 1 Variation in grain size with various semiconductor multijunctions

Semiconductor multijunction structures	Grain size r, nm	Preferential orientation
epi-n-IZO/glass/RT	9·03	⟨006⟩
epi-n-IZO/glass/350°C	4·57	⟨101⟩
epi-n-IZO/glass/450°C	4·16	⟨100⟩
epi-n-IZO/⟨100⟩SI InP/RT	9·17	⟨100⟩
epi-n-IZO/⟨100⟩SI InP/350°C	4·58	⟨100⟩
epi-n-IZO/⟨100⟩SI InP/450°C	3·059	⟨100⟩
epi-n-IZO/⟨100⟩ p-InP/RT	9·15	⟨100⟩
epi-n-IZO/⟨100⟩ p-InP/350°C	4·58	⟨100⟩
epi-n-IZO/⟨100⟩ p-InP/450°C	4·59	⟨100⟩
epi-n-IZO/⟨100⟩ n-Si/450°C	4·58	⟨100⟩
epi-n-IZO/⟨100⟩ p-Si/450°C	9·15	⟨100⟩
epi-n-IZO/⟨100⟩ n-GaAs/450°C	4·58	⟨100⟩
epi-n-IZO/⟨100⟩ n-InP/450°C	4·58	⟨100⟩

semiconductors are promising constituents of nanoscale integrated semiconductor devices.

The effects of substrate temperatures, substrates and heavy indium oxide incorporation on indium zinc oxide thin film growth and novel surface morphological properties were analysed. Higher T_{sub} enhanced the single crystalline quality, orientation, surface homogeneity and nanostructure growth of thin films. As a result of the surface study, it was observed that films deposited at 450°C have better film properties with ultrafine grain structures than low temperature thin films. Among ⟨100⟩ Si, GaAs and InP substrates, better surface architecture was observed for thin films on InP than for those on Si and GaAs. Neither grain size nor oriented crystalline quality was affected by substrates. Similarly, it was observed that, owing to heavy indium oxide doping, the surface quality of intrinsic zinc oxide thin films was increased.

CONCLUSION

In the present work, the effects of various substrate temperatures, substrates and heavy indium oxide incorporation on indium zinc oxide thin film growth and surface morphological properties were analysed. The morphological study is significant as reported so far. Using different substrate temperatures and substrates as control tools, a novel nano architecture was developed to obtain high quality IZO nanocrystalline semiconductor thin films of different grain sizes on glass and Si, GaAs and InP semiconductor single crystal wafers by L-MBE. This work will be used, and these data may be helpful, as a scientific or technical basis in semiconductor processing and technology, such as nanoelectronics (invisible security circuits) and nanomachining technology.

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