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A novel nano-architecture for ZnO thin films on ⟨1 0 0⟩ Si, GaAs and InP single crystal wafers by L-MBE as value in nano-robotic (machining) device fabrication efforts

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Abstract

In this present work, the effects of various substrate temperatures and various substrates on Zinc Oxide (ZnO) thin film growth and on surface morphological properties were studied. To the best of our knowledge this is the first time that laser molecular beam epitaxy (L-MBE), i.e., pulsed laser deposited (PLD) zinc oxide (ZnO) 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 window layers, compatible with current semiconductor processing techniques. As well as our main aim, the feasibility of developing highly nano-tectured thin films was also studied simultaneously. The surface morphological and film growth characteristics of ZnO thin films laser deposited on to various substrates like glass, Silicon (Si), Gallium Arsenide (GaAs) and Indium Phosphide (InP) at various substrate temperatures like room temperature, 200 °C and 300 °C using ZnO pallets as targets are very novel, intelligent and significant from reported so for. The deposition process was optimized. The micro- and nano-scale photo-graphs of Scanning Electron Microscope (SEM) and Atomic Force Microscope (AFM) showed the improvements of crystalline and surface nature of ZnO thin films with respect to various substrate temperatures and substrates. Better surface architecture was observed for thin films deposited at 300 °C than RT, 200 °C and on InP than Si and GaAs. Increasing the substrate temperature leads the films to fine nano-structure world. The results were discussed in detail. Thus we have developed a novel nano-architecture to obtain high quality ZnO nano-crystalline semiconductor thin films of different nano-scale grain sizes on glass and Si, GaAs and InP semiconductor single crystal wafers by using different substrate temperatures and substrates as controlling tools as value in practical nano-robotic (machining) device fabrication efforts.

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

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1. Introduction

As a source of unique properties, Zinc Oxide (ZnO) has been widely studied as a novel matertial for its practical and potential applications such as micro, nano-electronics and micro, nano-robotic (machining) technology. Also, ZnO is a n-type II–VI, wide direct band-gap compound semiconductor material, alternative to Indium Tin Oxide (ITO) and analogous (isomorphic) to Gallium Nitride (GaN). Since its properties depend on the method of preparation, the preparation of ZnO thin films has been the subject of continuous research [1–8]. To the best of our knowledge this is the first time that pulsed laser deposited (PLD) deposited ZnO thin films on semiconductor wafers have been applied to Semiconductor–Insulator–Semiconductor (SIS) type multi-junction solar cell structures, as wide band-gap transparent conducting oxide (TCO) window layers, also suitable for III–V based high-speed opto-electronic devices compatible with current semiconductor processing techniques.

ZnO films can be prepared by different techniques such as metal organic chemical vapour deposition (MOCVD), Jet vapour deposition (JVD), Atomic layer epitaxy (ALE), molecular beam epitaxy (MBE) and PLD. Laser molecular beam epitaxy (L-MBE), i.e., PLD is a promising thin film growth technology, which has been adopted in the present work to grow high surface quality ZnO thin films on ⟨1 0 0⟩ Silicon (Si), Gallium Arsenide (GaAs) and Indium Phosphide (InP) substrates at room temperature (RT), 200 °C and 300 °C for SIS iso and hetero-junction solar cell application. Since bulk ZnO is quite expensive and unavailable in large wafers for the time being, ZnO thin films are relatively a good choice. PLD deposited ZnO films has good lattice matching with the III–V semiconductor crystal substrate, which has optimum energy gap values, high solar energy conversion efficiency and high radiation resistance.

PLD technique may also be a good technique to deposit both the buffer and functional layers in commercial grade electronics application. On the basis of referred literature [9], we framed the chemical and thin film strategies for the development of high quality TCOs. In this present work, the effects of substrate temperatures and substrates on ZnO thin film growth, surface morphological and on nano-structural properties were studied. As well as our main aim, the feasibility of developing highly nano-tectured thin films was also studied simultaneously.

2. Experimental

ZnO thin films were epitaxially grown on ⟨1 0 0⟩ Si, GaAs and InP substrates held at RT, 200 and 300 °C by PLD. PLD has been shown to be superior to sputtering and conventional MBE for growing highly transparent, low resistive, good nano-crystalline metal oxide epitaxial thin films for opto-electronic devices. Semi-insulating (SI), n and p type Si, GaAs and InP single crystal wafers having ⟨1 0 0⟩ orientation were used as substrates for the preparation of ZnO thin films. Single crystal wafers were obtained from Hebei Semiconductor Research Institute (HSRI), Ministry of Informatics, Hebei, P.R.China. A critical step to achieving high quality nano-tectured thin films was the treatment of the substrate surface. The substrates are lapped, polished with $HBr–K_2Cr_2O_7–H_2O$ solution. Also degreased, cleaned with trichloroethylene (3 min), acetone (4 min), methanol (3 min) 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 min. The pure (99.9%) ZnO powder is mixed with polyvinyl alcohol binder and hot water. Then stirred, slurred crushed into powder, dye palletized, kept in furnace at 600 °C for 3 h and sintered at 1200 °C for one 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 a 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 substrate holder is rotated for uniform deposition of the ablated material. Before 'metal oxide on semiconductor deposition', the deposition of ZnO was optimized with float glass substrates. The epi-n-ZnO thin film depositions were optimized using float glass plates, ⟨1 0 0⟩ SI-InP and ⟨1 0 0⟩ p-InP wafers as substrates. The optimum substrate temperature for epi-ZnO thin films was found to be 300 °C. The subsequent depositions on ⟨1 0 0⟩ oriented n-Si, p-Si, n-GaAs and n-InP wafers were carried out at $T_{sub} = 300$ °C.

The surface analysis of the epi-ZnO thin films/Glass substrates and epi-ZnO thin films/⟨1 0 0⟩ semiconductor substrates prepared at RT, 200 and 300 °C was carried out by using SEM (Hitachi S-450 scanning electron microscope). For a detailed study, Atomic Force Microscopy (AFM) "Nanoscope-III" was applied to characterise the micro- and nano-structural properties of the as-grown ZnO thin films.

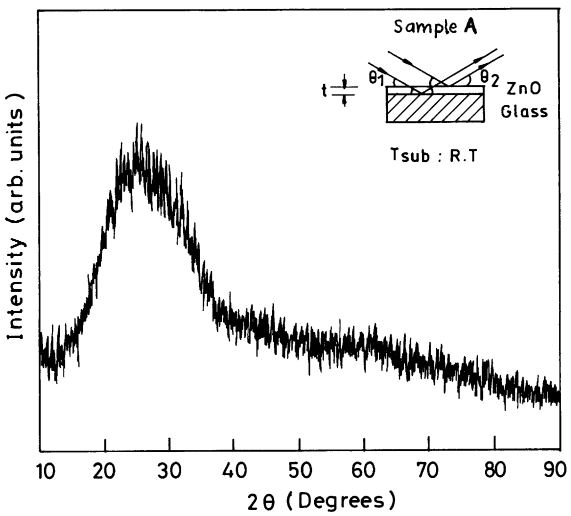
3. Results and discussion

3.1. Surface morphological and nano-structural properties

Dealing of film properties is one of the interesting area in surface physics. The effects of various substrates and substrate temperatures on film growth and nano-morphological properties of epitaxial ZnO thin films deposited on to glass, Si, GaAs and InP substrates were studied. The film growth characteristics are very novel, interesting and significant from reported so for [10–22]. The nano-tectured quality nature of epi-ZnO thin films also varies with various substrates and substrate or deposition temperatures. Generally, the films were uniform and film growth is insensitive to substrate surface irregularities. Deposition occurs equally well on to well-treated surfaces of substrates. The micro- and nano-scale photo-graphs of SEM and AFM showed the improvement of crystalline nature of zinc oxide thin films with respect to various substrates and substrate temperatures. The optimum substrate temperature for epi-n-ZnO thin films was found to be at 300 °C by X-ray diffraction analysis (refer Figs. 1–3).

AFM Figs. 4–6 illustrate the surface morphological analysis of the various epitaxial ZnO thin films deposited on float glass substrates at RT, 200 °C and 300 °C. These micrographs depict the rough films with too many channel irregularities at RT, but smooth and uniform films at 200 and 300 °C. At 300 °C, the film has well defined preferred growth.

Similarly, in the case of epitaxial zinc oxide thin films/ ⟨1 0 0⟩ oriented semi-insulating Indium Phosphide (⟨1 0 0⟩ SI-InP) substrates, rough and non-uniform films having nano-scale granular finish was observed at RT (SEM: Fig. 7 and AFM: Fig. 8) and 200 °C (Fig. 9). In particular film deposited at 200 °C has terrain like



Figs. 1–20. Phillips X-pert XRD graphs, Hitachi: SEM and Nano-scope III: AFM micro-nano scan (with different magnification) photos of epi-ZnO thin films deposited on various float glass, Si, GaAs and InP substrates prepared at RT, 200 and 300 °C.

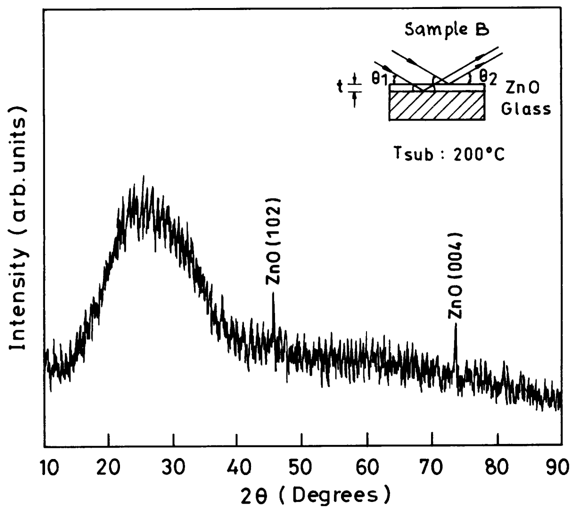


Fig. 2.

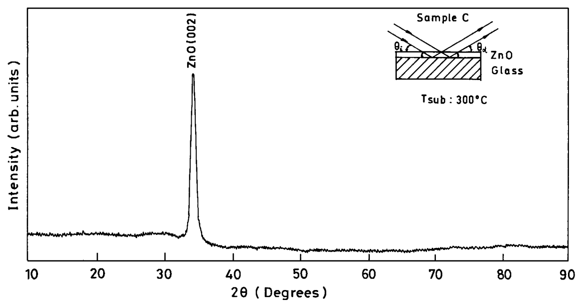


Fig. 3.

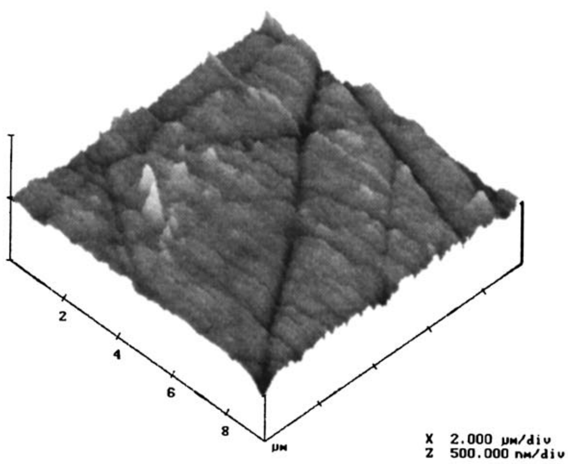
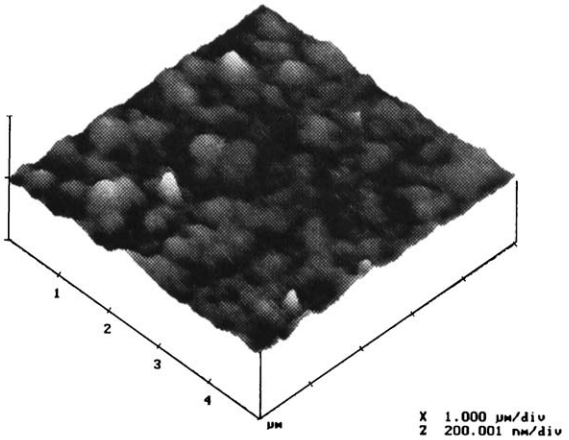


Fig. 4.

features with voids. At 300 °C (Fig. 10), the surface morphology was changed to preferrential growth but the film seems to be non-uniform.



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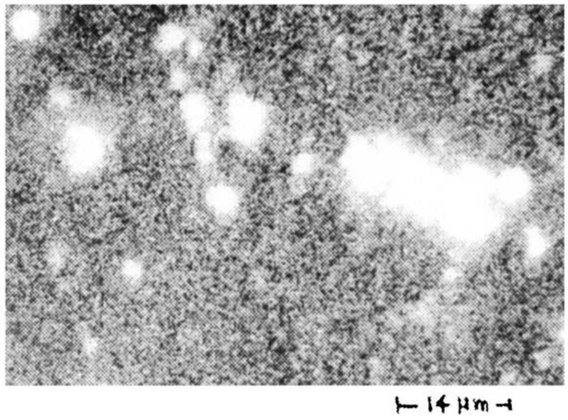

Fig. 7.

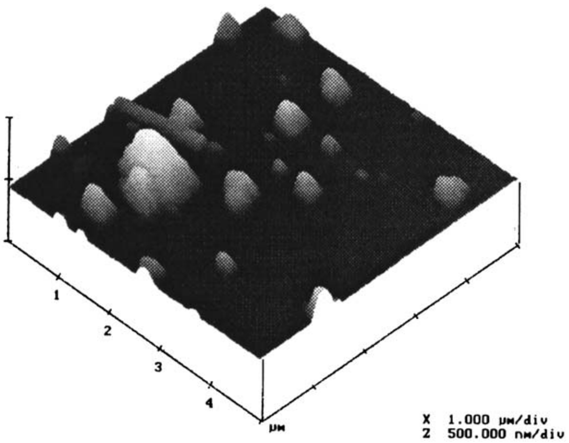

Fig. 6.

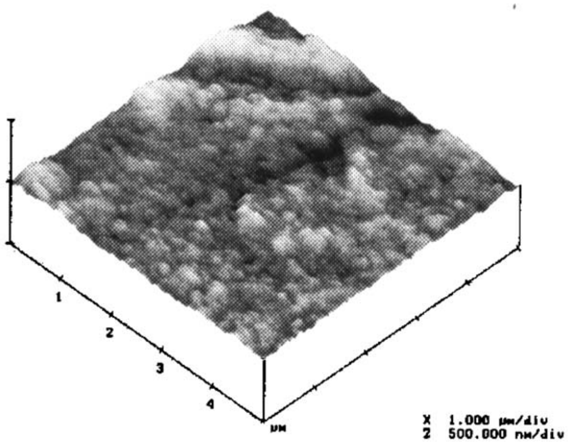

Fig. 8.

For zinc oxide thin films deposited on p-indium phosphide substrates (⟨1 0 0⟩ p-InP), on comparing the surface morphology of films at RT (Fig. 11: AFM), 200 °C (Fig. 12: AFM) and 300 °C (Fig. 13: AFM), the epitaxial growth evoluation is clearly understand. Also the film deposited at 300 °C has distinguished nano-scale array of ovel pearl stones like structure with hexagonal morphology (Fig. 14: AFM).

Figs. 15–18 (AFM), 16 (AFM), 17 (SEM) and 18 (AFM) illustrate the surface morphology of the various epitaxial ZnO films deposited on ⟨1 0 0⟩ oriented n-Si, p-Si, n-GaAs and n-InP substrates at 300 °C, respectively. From these photo-graphs one can confirms the nano-scale granular nature, uniformity of the film, understand the preferred crystalline growth of ZnO film through-out the specimen, distinguished nano-scale 'cluster of flower buds' like 'hexagonal pyramidal morphology' with *c*-axis as preferred growth direction, specialized

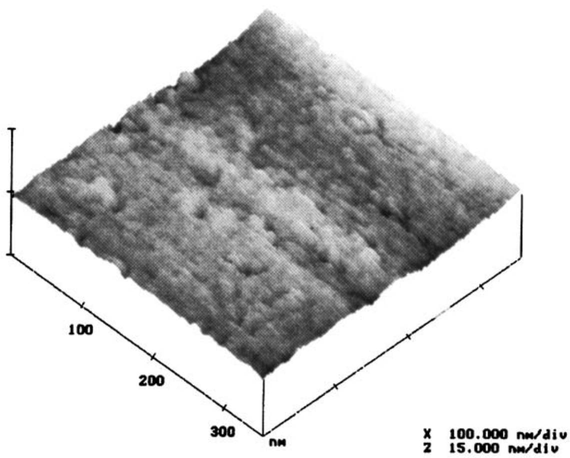

Fig. 9.

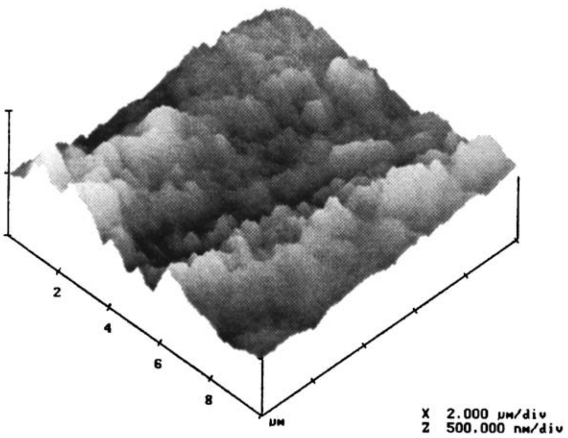

Fig. 10.

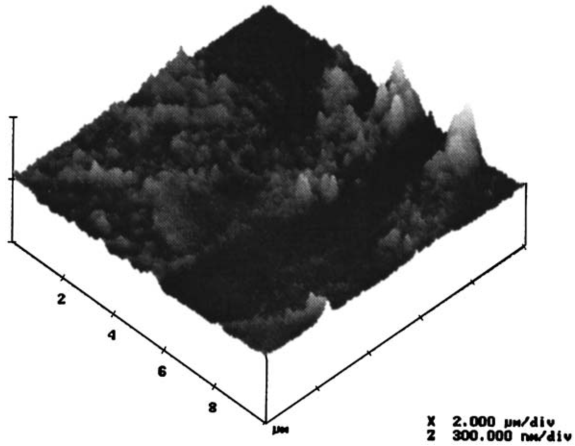

Fig. 13.

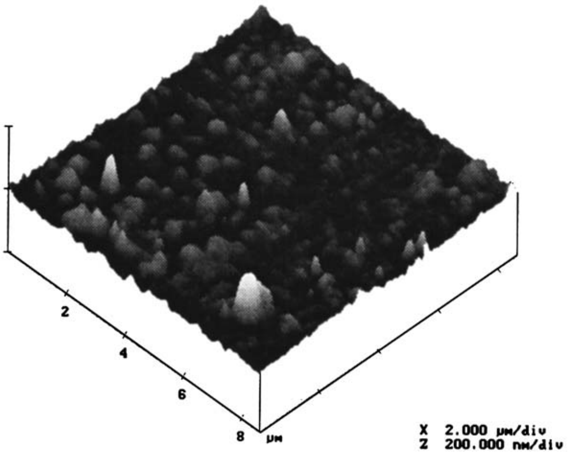

Fig. 11.

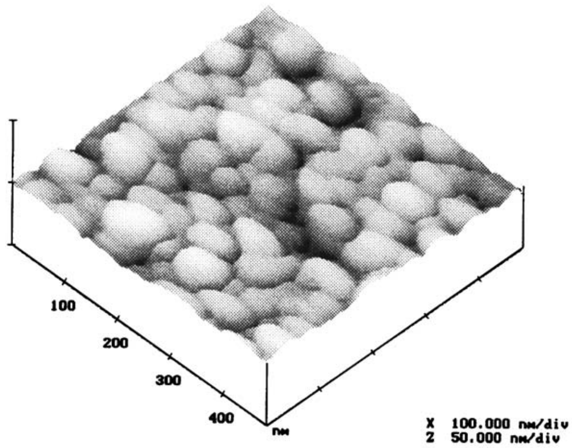

Fig. 14.

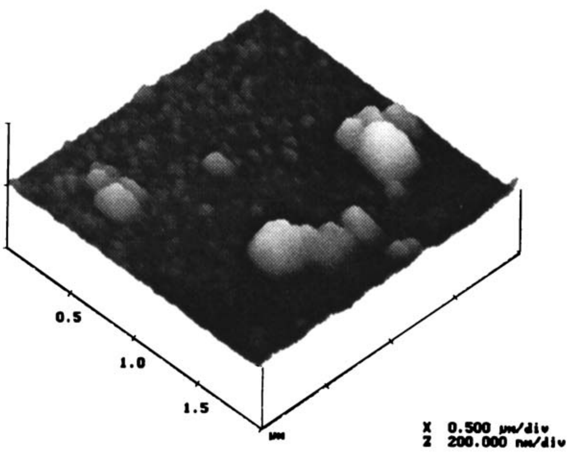

Fig. 12.

'micro-needle' like morphology. Also Figs. 19 and 20 (SEM) and 20 (AFM) depicted the surface nature of films deposited at 300 °C on n-InP substrates. Also, confirms that the films deposited at 300 °C have better film property than low temperature thin films. The 'dots' appeared block in the SEM and AFM images were due to low reflectivity regimes present in the thin films.

In reviewing the past literature of ZnO films prepared by various techniques like chemical vapour deposition (CVD), spray pyrolysis, we have found that 'triangle-faced stars' like morphology was obtained for optimized conditions.

Among ⟨1 0 0⟩ Si, GaAs and InP substrates, better surface nano-architecture was observed for thin films on indium phosphide than silicon and gallium arsenide. Both grain size and oriented crystalline quality no were affected by substrates. The average grain (r) sizes of zinc

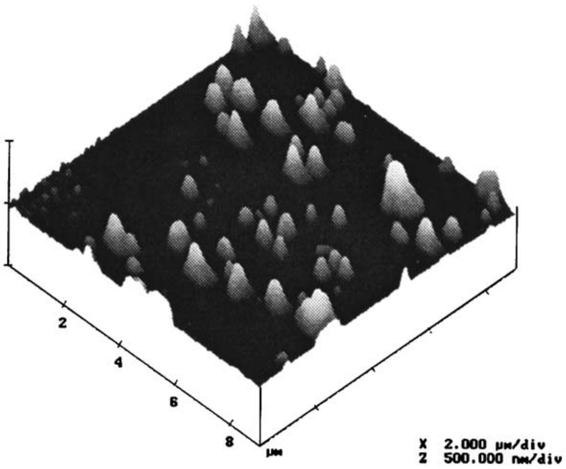

Fig. 15.

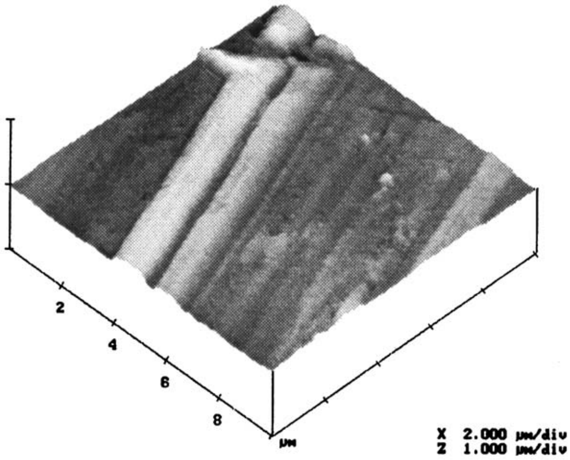

Fig. 18.

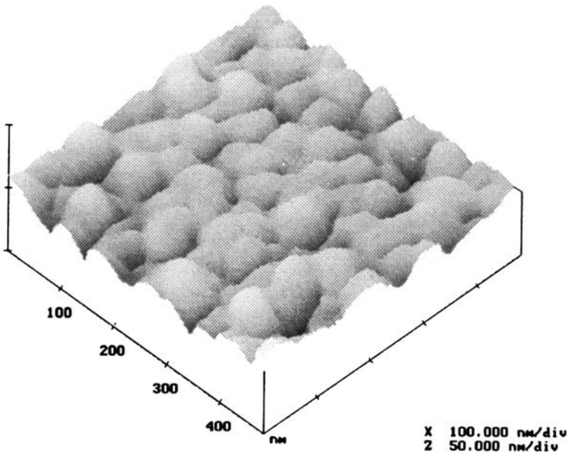

Fig. 16.

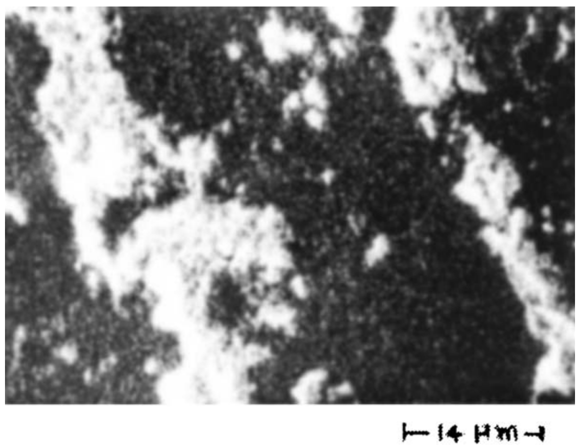

Fig. 19.

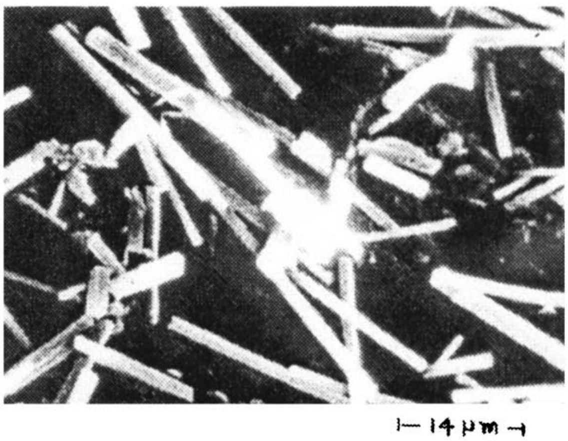

Fig. 17.

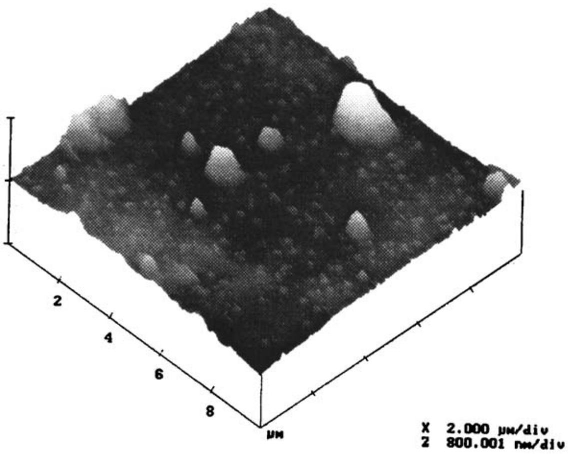

Fig. 20.

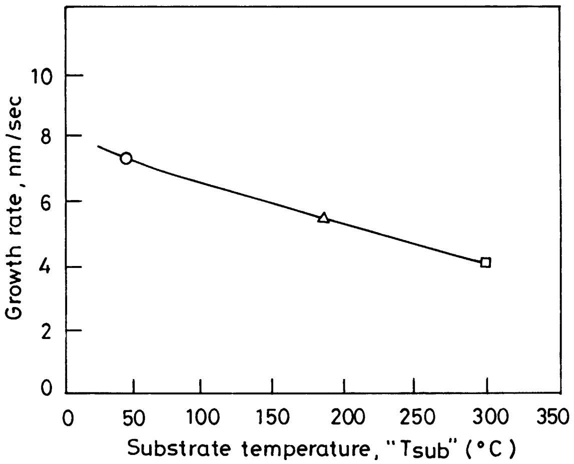

Fig. 21. Growth rate (nm/s) of epi-ZnO thin films vs. substrate temperature, T_{sub} (°C).

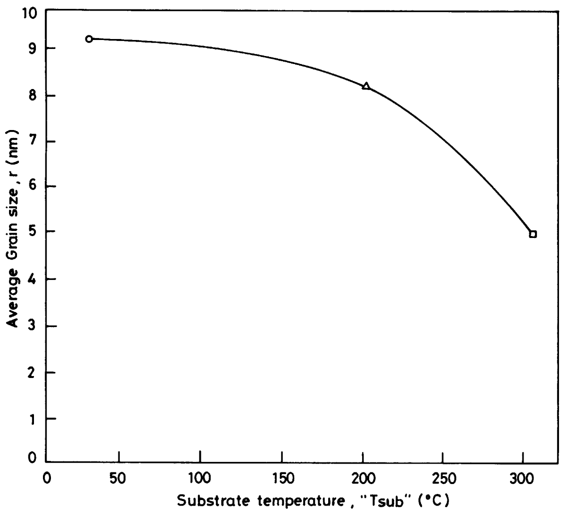

Fig. 22. Plot of average grain size, r (nm) of epi-ZnO thin films deposited on various glass and ⟨1 0 0⟩ Ssi, GaAs and InP substrates versus substrate temperature, T_{sub} (°C).

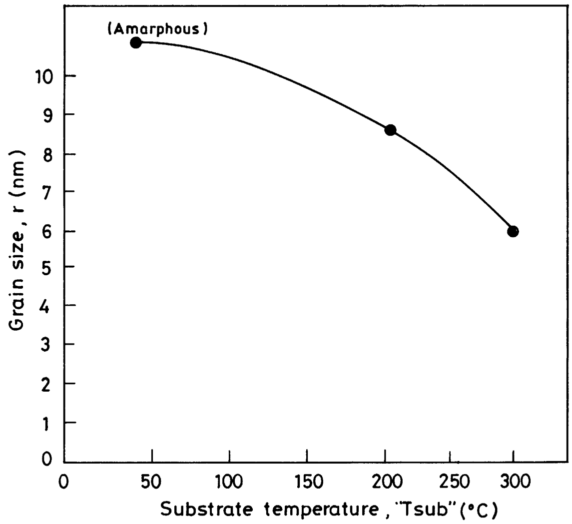

Fig. 23. Plot of grain size, r (nm) of epi-ZnO thin films deposited on float glass substrates alone vs. substrate temperature, T_{sub} (°C).

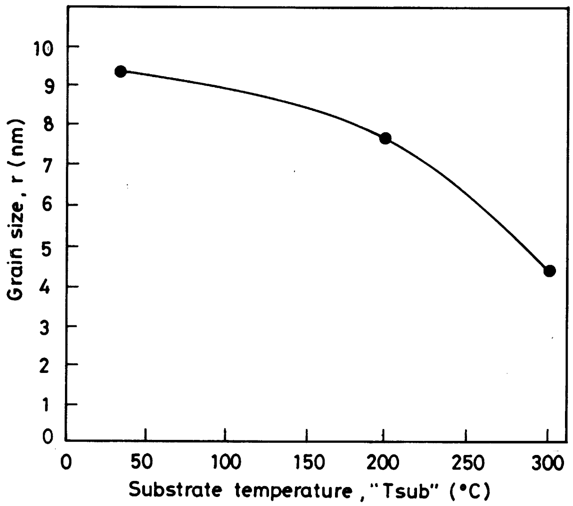

Fig. 24. Plot of grain size, r (nm) of epi-ZnO thin films deposited on ⟨1 0 0⟩ SI-InP substrates alone vs. substrate temperature, T_{sub} (°C).

oxide thin films deposited on float glass, ⟨1 0 0⟩ oriented Si, GaAs and InP substrates at RT, 200 °C and 300 °C were calculated by the Scherrer method (using respective X-ray diffracto-grams), graphically enumerated (refer. Figs. 21–26) and tabulated (refer. Table 1). The nano-grain size of deposited thin films decreases for higher substrate temperatures. From this, we knew that, we get good confined nano-architectured material beyond 300 °C. Increasing the deposition temperature leads the films to fine nano-structure world. Nano-scale science and technology is now emerging as vibrant, relevant and fundamentally exiting area of research. It has a potential application in creating a new generation of advanced materials with engineered properties. Recently, PLD has emerged as a promising technique for growing nano-particles of various materials. Now a days there has been much interest in developing nano-machining (robotic) devices and ramification of band-gap engineering by growing nano-particles of particular material of interest. AFM analysis carried out in this complete, detailed study further confirmed the homogeneous nano-structure nature of ZnO thin films composed of hexagonal, nanometer sized grains and crystallites, at the order of

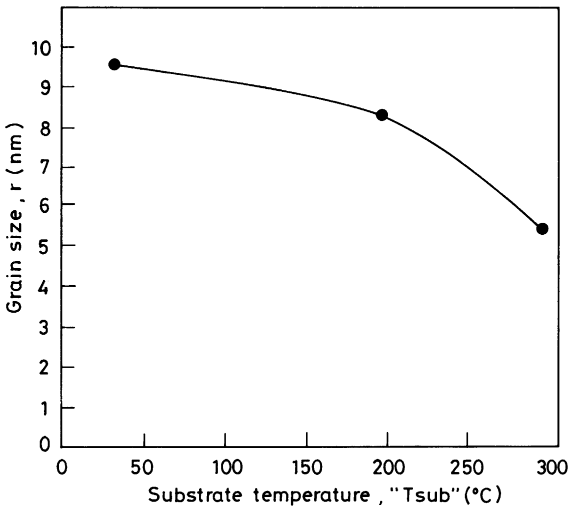

Fig. 25. Plot of grain size, r (nm) of epi-ZnO thin films deposited on ⟨1 0 0⟩ p-InP substrates alone vs. substrate temperature, T_{sub} (°C).

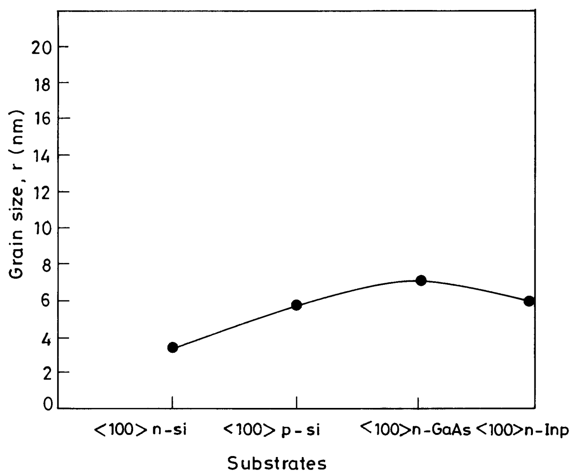

Fig. 26. Plot of grain size, r (nm) of epi-ZnO thin films deposited on ⟨1 0 0⟩ n-Si, p-Si, n-GaAs and n-InP substrates at optimized substrate temperature, T_{sub} (°C) = 300 °C.

~9, ~7 and ~5 nm, respectively, for RT, 200 °C and 300 °C. The difference in grain size can be attributed to the difference in growth nature of thin films. We emphasized the fact that the difference in size (of the order of 'nm') of the particulates or grains observed is due to their formation by the mechanism of clustering during the transit through ambient (oxygen) gas as a unique channel. The changing of the surface morphology with substrate temperature is probably due to the difference of the surface energy of the crystallite structure. Thus from the above we found that the critical parameter determining the surface quality of ZnO thin films 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 approachment, orientation, surface homogeneity and nano-structure growth of thin films. Generally, the best surface quality and nano-tectured film was obtained at a substrate temperature of 300 °C. With a host of exotic optical, structural and self-organizational properties, nano-crystalline semiconductors are promising constituents of nano-scale integrated devices.

Table 1
Variation of grain size with various semiconductor heterostructures

Semiconductor hetero structures	Grain Size (r) (nm) with ⟨Preferential orientations⟩
epi-ZnO/Glass/RT	Amorphous nature
epi-ZnO/Glass/200 °C	8.96 ⟨1 0 2⟩
epi-ZnO/Glass/300 °C	6.02 ⟨0 0 2⟩
epi-n-ZnO/ ⟨1 0 0⟩ n-Si/300 °C	3.71 ⟨0 0 2⟩
epi-n-ZnO/ ⟨1 0 0⟩ p-Si/300 °C	4.69 ⟨0 0 2⟩
epi-n-ZnO/ ⟨1 0 0⟩n-GaAs/300 °C	6.0 ⟨0 0 2⟩
epi-n-ZnO/ ⟨1 0 0⟩ n-InP/RT	9.76⟨1 0 0⟩
epi-n-ZnO/ ⟨1 0 0⟩ n-InP/300 °C	5.70 ⟨0 0 2⟩
epi-n-ZnO/ ⟨1 0 0⟩ p-InP/RT	9.15 ⟨1 0 0⟩
epi-n-ZnO/ ⟨1 0 0⟩ p-InP/200 °C	8.18⟨1 0 0⟩
epi-n-ZnO/ ⟨1 0 0⟩ p-InP/300 °C	5.04 ⟨0 0 2⟩
epi-n-ZnO/ ⟨1 0 0⟩ SI-InP/RT	9.19 ⟨1 0 0⟩
epi–n-ZnO/ ⟨1 0 0⟩ SI-InP/200 °C	7.60 ⟨1 0 0⟩
epi-n-ZnO/ ⟨1 0 0⟩ SI-InP/300 °C	4.60 ⟨0 0 2⟩

Generally in this study, when we increase the substrate temperature the film lose their rough surface, which affect the physical properties of thin films and gained smooth continuous surface with a reduced grain size. That is, at higher substrate temperature, the films were influenced by thermal gradient, low stress and shocks resulted in the formation of a ordered moving and settlement of crystallites in their preferred sites inside the thin film structure to form a continuous film. This implies the approachment of single crystalline nature for high temperature thin films.

The 'milkiness smog' like feature observed, we believe it is due to ambient oxygen gas phase reactions at higher substrate temperature, which may have introduced insulator oxide layer growth. The better defined grain boundaries were due to the involvement of the respective interfacial insulator oxide layer between functional thin films/base substrate structure, for example, SiO_2 layer between epi-n-ZnO/⟨1 0 0⟩ p-Si structure. These layers providing a better surface for the nucleation and adsorption of the functional thin film growth. It was also observed by many workers that the presence of an interfacial insulator oxide layers between functional thin films and substrate may be improves the structure and there by enhance the properties of the deposited functional thin films. Thus we have developed a novel nano-architecture to obtain high-quality ZnO nano-crystalline semiconductor thin films of different nano-scale grain sizes on glass and Si, GaAs and InP semiconductor single crystal wafers by using different substrate temperatures and substrates as controlling tools as value in practical nano-robotic (machining) device fabrication efforts.

4. Conclusion

Surface and nano-structural morphological studies were carried out on the PLD epitaxial ZnO thin films on float glass, Si, GaAs and InP wafers. In this present work, the effects of substrate temperatures and substrates on ZnO thin film growth and on surface morphological properties were studied. As well as our main aim, the feasibility of developing highly tectured TCO thin films was also studied simultaneously.The surface morphological, nano-structural and film growth characteristics are very novel, interesting and significant from reported so for. To the best of our knowledge this is the first time that PLD deposited ZnO thin films on semiconductor wafers have been applied to SIS type multi-junction solar cell structures, as wide band-gap TCO window layers, also suitable for III–V based high-speed opto-electronic devices compatible with current semiconductor processing techniques. Higher substrate temperature enhances oriented nano-crystalline growth of thin films. Similarly, the surface homogeneity of thin films was increased when we approached higher T_{sub}. Also, better surface morphological and nano-architecture was observed for thin films on indium phosphide than silicon and gallium arsenide. The morphological nature of epi-ZnO films also varied with various substrates and substrate temperatures. The optimum deposition temperature was found to be about 300 °C and the deposition process was optimized. The micro- and nano-scale graphs of SEM and AFM shows the improvement of crystalline nature of ZnO thin films with respect to various substrates and subtrate temperatures. Increasing the substrate temperature leads the films to confined nano-structure world. Thus we have developed a novel nano-architecture to obtain high-quality ZnO nano-crystalline semiconductor thin films of different grain sizes on glass and Si, GaAs and InP semiconductor single crystal wafers by using different substrate temperatures and substrates as controlling tools as value in practical nano-robotic (machining) device fabrication efforts.

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