Room temperature deposition of zinc oxide thin films by rf-magnetron sputtering for application in solar cells

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ABSTRACT

Recent reports indicate that thin films of oxides of zinc: ZnO, Zn(O,S), or Zn-Mg-O, could be a better buffer component than CdS to provide an adequate band alignment with orthorhombic tin sulphide in thin film solar cells. Thin films of ZnO were grown by rf-magnetron sputtering on different substrates at room temperature. Thin films of ZnO obtained by different deposition methods show hexagonal crystal structure, usually with a preferential orientation of (002) crystallographic planes parallel to the substrate surface. However, in the present study XRD patterns indicate that thicker ZnO films on glass substrates have preferential growth of (103) planes, while that on chemically deposited CdS or ZnS films preferential orientation of (002) planes persists. Bandgap of ZnO films increases from 3.2 eV to 3.4 eV when the chamber pressure used for deposition varies from 2.3 mTorr to 6 mTorr. ZnO films were incorporated in a solar cell structure stainless steel/SnS(cubic)/SnS(orthorhombic)/SnS(cubic)/CdS/ZnO/ZnO:Al. It showed open-circuit voltage of 0.318 V, short-circuit current density of 3.6 mA/cm^2 and conversion efficiency of 0.82%.

Keywords: ZnO, rf-magnetron sputtering, XRD, solar cell.

1. INTRODUCTION

ZnO is a wide band gap semiconductor that has numerous applications such as in solar cells, flat displays, heat mirrors, TFTs and chemical sensors.[1,2] ZnO thin films have been deposited using various techniques such as pulsed laser deposition, thermal evaporation, chemical vapor deposition, electron beam evaporation, spray pyrolysis, sol-gel method and magnetron sputtering on a variety of substrates.[3–14] The role of substrate is significant in the deposition of thin films owing to any lattice mismatch between it and the film, which generally leads to the development of stress in the deposited film. Nucleation and binding of growth species may vary due to the movement of substrate which can affect crystalline quality. In solar cell structure, ZnO has to be grown on substrate with different coating already present that can influence the properties of the ZnO thin films. In this work we deposited ZnO on different substrates, and their structural properties have been investigated. We have previously reported an open circuit voltage, V_{oc} of 0.470 V, short-circuit current density, J_{sc} of 6.2 mA cm^{-2} and conversion efficiency (η) of 1.28 % for a solar cell in a structure, stainless steel (SS)/SnS/CdS/ZnO/ZnO:Al.[15] In the present work we fabricated SnS based solar cells using ZnO layer in different structural configurations.

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2. EXPERIMENTAL

Thin films of ZnO were deposited on glass substrates by rf magnetron sputtering using commercial ZnO target (99.999% pure, 3 inch dia, Kurt J. Lesker). Depositions were carried out in a controlled atmosphere of argon to favor the formation of ZnO phase. Sputtering power to ZnO target was fixed at 200 W and substrates were rotated to get uniform depostion. XRD patterns of the films were recorded on a Rigaku D-Max 2200 diffractometer with C$K\alpha$ radiation both in standard and in grazing incidence modes. Optical transmittance (T) and reflectance (R) spectra of the films were recorded on a Shimadzu UV-Vis-NIR 3100 PC double beam spectrophotometer. ZnO films were Incorporated in solar cell structure as described below. Prior to the deposition SS substrates were immersed in HCl solution (diluted to 50% od as-supplied HCl). This changed the reflective mirror-like surface of SS to a relatively rough surface. These substrates were then immersed in a dilute solution of Na_2S (0.03 M) for 12 h at room temperature to activate the surface. A 0.1 M solution of Sn (II) was prepared by heating with stirring 2.26 g of $SnCl_2.2H_2O$ (Aldrich) in 30 mL of glacial acetic acid and 1 mL of concentrated HCl. De-ionized water was added to this mixture to take the final volume to 100 mL. To 10 mL of this solution taken in a beaker, 30 ml of 3.7 M triethanolamine, 16 ml of 30% NH_3 (aq.), and 10 ml of 0.1 M thioacetamide were added. The final volume was taken to 100 mL with de-ionized water. SS substrates were placed in the solution supported vertically on the beaker-wall. After 10 h inside this bath at 17 ^oC, the substrates were removed and rinsed in de-ionized water. The SnS film is of thickness 200 nm. The same procedure was repeated for three consecutive deposition of SnS thin film on SS. Thin films of CdS with 50 nm or 200 nm in thickness was deposited on SS/SnS (550 nm) at 80 ^oC in 30 min or 120 min, respectively.[15] A ZnO thin film of 180 nm thickness was deposited on these substrates by sputtering at rf power of 180 W, 6 mTorr argon pressure for 30 min duration. ZnO:Al Electrode was deposited on this at 280 W rf power, 2 mTorr argon pressure and 30 min duration which led to 450 nm of thickness. A shadow mask of 0.256 cm^2 area was used to define the cell area. Silver paste were used to take electrical connections. Keithley 690 multimeter and 230 programmable voltage source interfaced to a computer were used to record dark and photo-current levels. A tungsten halogen lamp of 1000 Wm^{-2} intensity was used to illuminate the solar cell.

3. RESULTS AND DISCUSSION

Figure 1 shows the Grazing Incidence XRD (GIXRD) patterns of ZnO thin films (180 nm) deposited for 30 minutes, which indicate hexagonal structure with (002) peak domination. Figure 2 shows the GIXRD patterns of ZnO thin films of different thickness obtained by deposited for different durations. These patterns show dominance of (103) peak for thicker films. Usually ZnO films grow in a c-axis orientation. Important factor governing the preferred orientation of thin films is the minimum surface free energy compared to volume energy. Since at lower thickness surface to volume ratio is large, the most densely packed plane have the lowest surface free energy. For ZnO film with hcp system, (002) plane has lowest surface free energy. Hence the intensity of x-ray beam reflected from (002) planes will be relatively more for thinner ZnO films. In the case of thicker films, the other possible factors such as velocity of growth in different directions and strain energy may lead to different preferential orientation of growth.

Figure 3 shows the XRD patterns of the ZnO thin films (600 nm) recorded with different grazing incidence angle and in standard mode. ZnO films shows (002) orientation in standard $\theta/2\theta$ scan and (103) orientation in GIXRD. In standard $\theta/2\theta$ geometry x-ray will be falling on small area and it will penetrate more, giving peaks from even substrates. Here all (002) planes of ZnO are parallel to substrates and so the relected intensity of x-ray from these planes in standard $\theta/2\theta$ geometry will

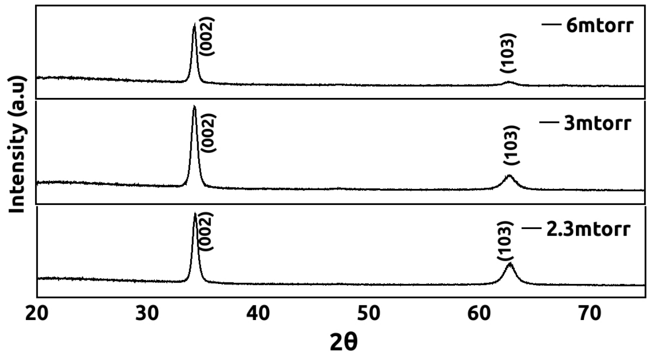

Figure 1. X-ray diffraction patterns of ZnO films deposited at different chamber pressure.

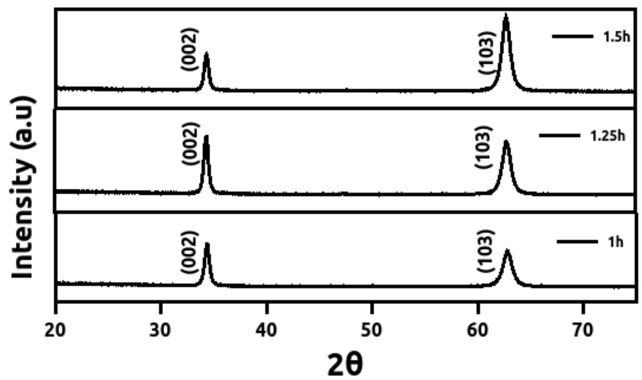

Figure 2. X-ray diffraction patterns of ZnO films deposited for different durations.

dominate the pattern. In GIXRD, x-ray beam illuminates more sample area and penetration depth will be small. Here the beam hitting those planes perpendicular to substrate satisfying Bragg condition will show diffraction. Since all (002) planes of ZnO are parallel to substrates, hence intensity of x-ray beam reflected from this plane in GIXRD will be less.

Figure 4 shows the GXRD pattern of ZnO thin films deposited for 2 h on different substrates

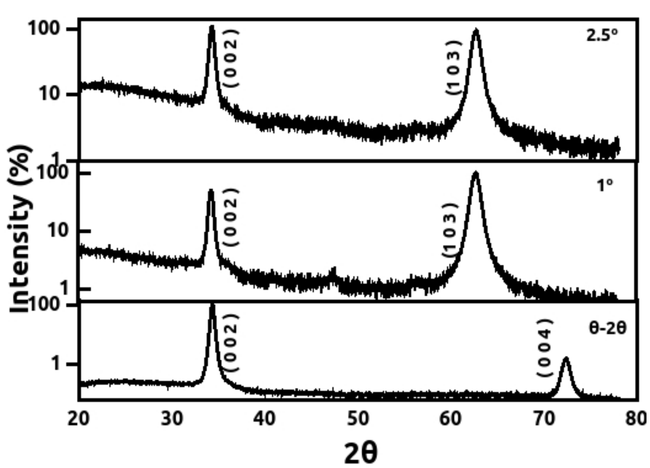

Figure 3. X-ray diffraction patterns of a ZnO thin film at different grazing angle

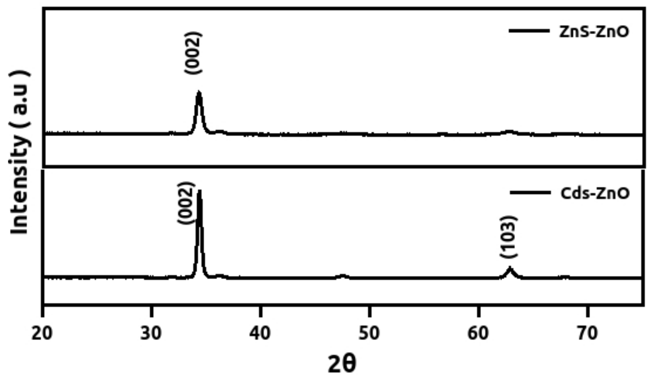

Figure 4. X-ray diffraction patterns of ZnO films deposited on different different substrates.

(chemical bath deposited CdS and ZnS on glass substrates). All the films are (002) oriented when it is deposited on such substrates. Hence it can be concluded that only thicker films of ZnO on glass substrates may have (103) orientation on its surface, indicating that incorporation of (103) orientated film of ZnO in solar cell structure is not feasible in substrate configuration.

Optical bandgap of ZnO thin films were evaluated using transmittance and reflectance spectra given in the Figure 5a. The transmittance spectra of the films deposited at different chamber pressure shows that the films are highly transparent in the visible region of the electromagnetic spectrum. The average transmittanWe acknowledge Maria Luisa RamÃşn GarcÃŋa for the XRD and JosÃľ Campos for electrical measurements, and Oscar GomezDaza for general assistance in laboratory. Financial support from projects CeMIE-sol 50 and IN116015 is also acknowledged. SKC and RRT wish to acknowledge DGAPA-UNAM for the post-doctoral fellowships.ce in the visible range was greater than 80%. Figure 5b shows the variation of optical bandgap of ZnO with chamber pressure. Bandgap of ZnO films increases from 3.2 eV to 3.4 eV when the chamber presure used for deposition varies from 2.3 mTorr to 6 mTorr.

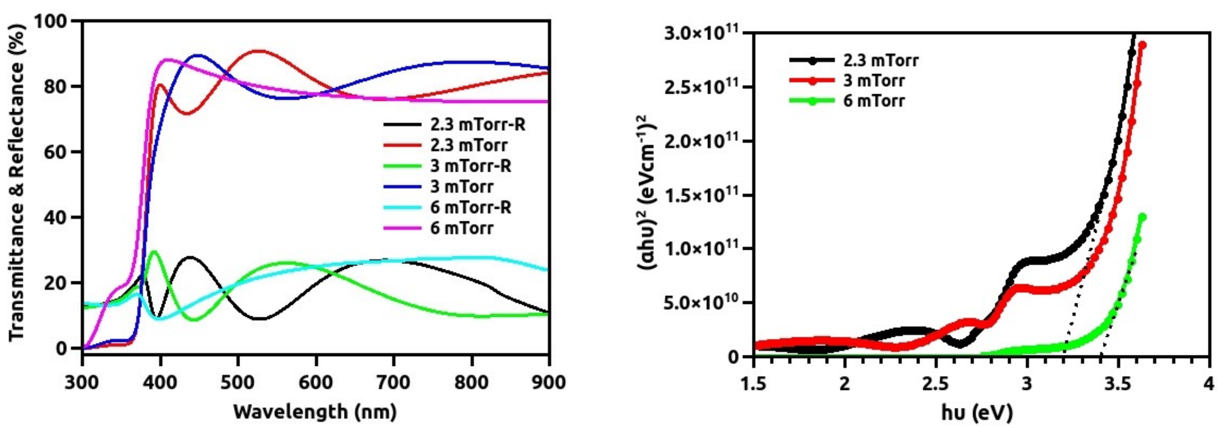

Figure 5. a) Transmitance and reflectance of ZnO thin films (left).(b) Variation of optical bandgap of ZnO thin films

Zinc oxide thin films were successfully incorporated in the fabrication of solar cell devices. First of all we tried to repeat the solar cell configuration already reported from the same lab. The different configuration of solar cell structures are shown in the Figure 6a.

Figure 6b shows the J-V characteristics of the cells measured under standard illumination of intensity 1000 Wm^{-2} in the photovoltaic testing system. Among the different configurations of solar cell structure, SS/SnS/CdS(200 nm)/ZnO:Al showed better cell performance with a V_{oc} of 0.370 V, s J_{sc} of 2.5 $mAcm^{-2}$ and η of 0.68 %. Solar cell parameters (V_{oc} and J_{sc}) are less as compared with the previously reported values. Solar cells with orthorhombic SnS film have shown efficiency of 3.6% to 4.36%.[16–19] Therefore we fabricated a solar cell with orthorhombic SnS in the structure SS/SnS(cubic)/SnS(orthorhombic)/SnS (cubic)/CdS/ZnO/ZnO:Al as shown in figure 7a. Fabrication process is already mentioned in the experimental section. Figure 7b shows the J-V characteristics of the cell which showed V_{oc} of 0.318 V, J_{sc} of 3.6 mA cm^{-2} and η of 0.82 %. Further investigations are required to improve the current results.

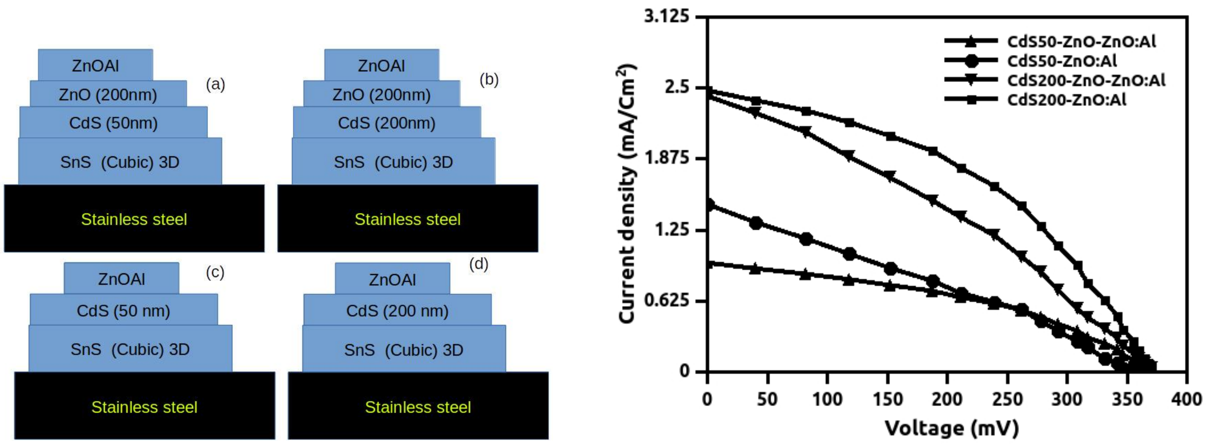

Figure 6. a) solar cell structures with different configurations.(left).(b) J-V characteristics

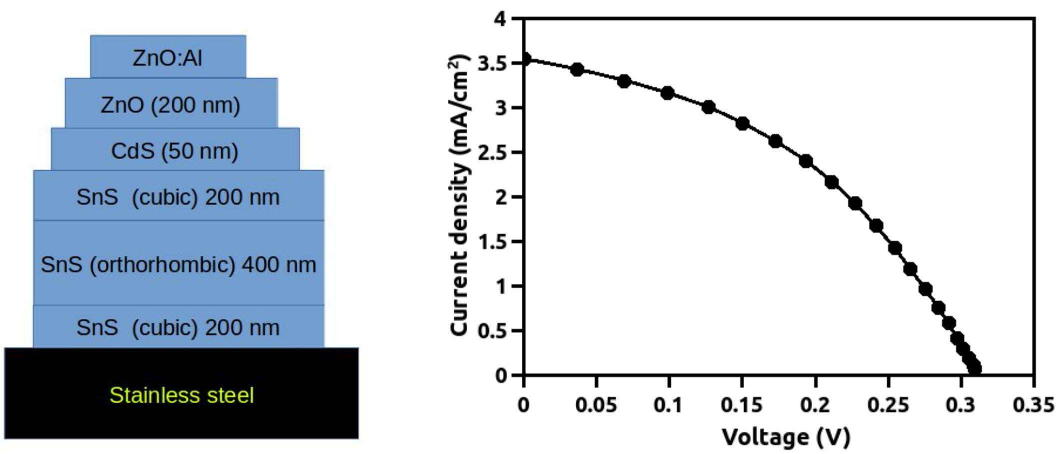

Figure 7. a) solar cell structures with SnS cubic and SnS orthorhombic films.(left).(b) J-V characteristics

4. CONCLUSION

We deposited ZnO thin films by rf-magnetron sputtering on different substrates at room temperature. ZnO films deposited on glass substrates with thickness 180 nm showed hexagonal crystal structure, usually with a preferential orientation of the (002) plane. GIXRD of ZnO films with more than 500 nm in thickness showed (103) orientation while that on chemically deposited CdS and ZnS films were

(002) oriented. Therefore, it can be concluded that (103) orientation only exist in the surface layer of thicker film of ZnO on glass substrates. Solar cell structure: SS/SnS(cubic)/SnS(orthorhombic)SnS (cubic)/CdS /ZnO/ZnO:Al showed V_{oc} of 0.318 V, J_{sc} of 3.6 mA/cm^2 and η of 0.82 %.

5. ACKNOWLEDGEMENTS

We acknowledge Maria Luisa RamÃşn GarcÃŋa for the XRD and JosÃľ Campos for electrical measurements, and Oscar GomezDaza for general assistance in laboratory. Financial support from projects CeMIE-sol 50 and IN116015 is also acknowledged. KCS and RRT wish to acknowledge DGAPA-UNAM for the post-doctoral fellowships.

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