Chapter 3

Characterisation of Zinc Tin Oxide Thin Films Prepared by Pulsed Laser Deposition

This chapter describes the preparation of zinc tin oxide (ZTO) thin films by pulsed laser deposition (PLD) technique and their optical and electrical characterisations.

3.1 Introduction

Demands for visibly transparent and electrically conductive materials are rapidly growing in technological applications in optoelectronic devices like solar cells, liquid crystal displays, energy efficient windows and 'invisible electronic circuits' etc. A few crystalline materials like tin doped indium oxide (ITO), aluminium doped zinc oxide (ZnO:Al) and antimony doped tin oxide (SnO₂:Sb) in thin film form are presently being used for such
applications. Zinc tin oxide films have the advantages of both ZnO (higher transparency and more stability in activated hydrogen environments than ITO and SnO₂) and SnO₂ (high stability in acidic and basic solutions and in oxidizing environments at higher temperatures) [165-170]. Zinc tin oxide films have been grown by radio frequency and direct current magnetron sputtering, filtered vacuum arc deposition etc [171-175]. Most of these works were devoted to understand the optical and electrical properties of polycrystalline films deposited either by substrate heating or by high temperature post deposition annealing.

Amorphous transparent conductors are much attractive because they need a low processing temperature and can be grown on plastic substrates to form high-quality films suitable for practical devices. Since the mobility of conduction electrons is proportional to the width of the conduction bands and a narrow band tends to localize carriers, a large overlap between relevant orbitals is required to achieve a large mobility degenerate conduction in amorphous semiconductors. In addition, the magnitude of the orbital overlap needs to be insensitive to the structural randomness, which is intrinsic to the amorphous state, to reduce the formation of shallow localized states (often referred to as tail states). Metal oxides composed of heavy metal cations (HMCs) with an electronic configuration (n - 1)d^{10}ns^{0} (with n ≥ 4) satisfy these requirements. A large band gap in oxides is attained by the low energy of oxygen 2p orbitals, which constitute the valence band maximum region. The bottom part of the conduction band in these oxides is primarily composed of ns orbitals of HMCs [59, 60].
3.2 Experimental conditions

Polycrystalline ceramic targets were prepared from a mixture of ZnO (99.999% pure) and SnO$_2$ (99.999% pure) powders (Zn:Sn = 1:1, 2:1, 4:1 and 8:1). The mixed powders were initially calcined at 1000°C for 4 hours and then hydrostatically pressed at a pressure of 1000 kg cm$^{-2}$ to form a pellet of 1 cm diameter. The pellets were then sintered at 1450 °C for 6 hours. As discussed later in this session, the target with composition Zn:Sn = 2:1 formed a single phase compound of Zn$_2$SnO$_4$, and the other composition target lead to a mixture of ZnO, SnO$_2$, and Zn$_2$SnO$_4$, which were confirmed by XRD measurements (Figure 3.2). Thin films were deposited at RT by PLD from ceramics targets of ZTO with a KrF excimer laser (248 nm wavelength, 10 Hz repetition frequency). Laser ablation was carried out at a laser energy density of 35 mJ cm$^{-2}$ pulse$^{-1}$. Films were deposited on glass substrates placed at a distance of 30 mm from the target. The depositions were carried out for 30 minutes by varying oxygen pressure ($P_{O_2}$) from 0 to 9 Pa. The resulting film thicknesses varied from 110 - 200 nm. To study the effects of post-deposition annealing on film properties, some films were annealed at temperatures up to 800°C in air.

3.3 Chemical composition

Chemical composition of the targets and thin films were determined from the XRF analysis. Figure 3.1 shows the compositional variation in the films with $P_{O_2}$ during deposition. It was confirmed that the Zn/Sn ratios of the sintered targets were the same as those of the corresponding starting compositions (Inset of figure 3.1). Film composition shows some variation
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Figure 3.1: Zn/Sn compositional variations with respect to oxygen partial pressure for the PLD films deposited using different targets with the Zn:Sn ratios of 1:1 and 2:1. Inset shows the Zn/Sn composition in the sintered target.

with $P_{O_2}$, but is more or less the same as that of the PLD target, indicating that the PLD process can reproduce the chemical composition of the target in the films if an appropriate deposition condition is chosen.

3.4 Structural characterisation

ZnO-SnO$_2$ systems are reported to have two phases: $Zn_2SnO_4$ and $ZnSnO_3$ [176]. The $Zn_2SnO_4$ has a spinal type structure and has high thermal stability. The $ZnSnO_3$ exists in a stable crystalline form at temperatures $< 600 ^\circ C$ and shows an ilmenite like structure. XRD patterns of the sintered targets are shown in figure 3.2. The target with composition $Zn:Sn = 2:1$ forms
Figure 3.2: XRD pattern of PLD targets with the Zn:Sn ratios of 1:1 and 2:1. The Zn:Sn = 2:1 target forms a single phase compound of Zn$_2$SnO$_4$. In the lower figure, * denotes Zn$_2$SnO$_4$ and + denotes SnO$_2$.

a single phase compound of Zn$_2$SnO$_4$, and the other composition lead to a mixture of ZnO, SnO$_2$, and Zn$_2$SnO$_4$. It has been reported that crystalline ZnSnO$_3$ cannot be prepared under calcination temperature $> 700 \, ^\circ C$ [177]. The only stable phases at high temperature ($> 1000 \, ^\circ C$) in the ZnO-SnO$_2$ system are Zn$_2$SnO$_4$, ZnO and SnO$_2$ [176]. As the Zn content in the target is increased, the ZnO phase in the target becomes more and more prominent as observed from the increased intensity of diffraction peaks from ZnO planes. For films, glancing angle XRD analysis were performed at an incident angle of 0.5°. As evident from the GXRD pattern of films, all films were amorphous irrespective of the variations in oxygen partial pressure (Figure 3.3). Figure 3.4 show GXRD patterns of the films deposited using
Figure 3.3: GXRD pattern of ZTO thin films prepared from targets with Zn:Sn ratios of 1:1 and 2:1 at different oxygen partial pressures.
Figure 3.4: GXRD patterns of the films deposited using targets having Zn:Sn compositions 1:1 and 2:1 as a function of annealing temperature. Zn:Sn ratio and annealing temperature are shown above the corresponding GXRD pattern.
Figure 3.5: GXRD patterns of the films deposited from targets having Zn:Sn compositions 1:1 and 2:1 after annealing at 800 °C.

PLD targets with the Zn:Sn ratios of 1:1 and 2:1 as a function of post annealing temperature. It shows that the deposited films are amorphous, but 450 °C annealing crystallizes the films partially to give crystalline phases of the simple oxides, ZnO and SnO₂. The halos around $2\theta = 33^\circ$ indicate that some or large portion of the amorphous phases still remain. This result should be compared with the results on films grown by sputtering in references [110] and [173], in which the former reported no crystallization up to 600 °C while the latter reported the crystallization temperature as $\sim$600 °C. The low crystallisation temperature in the present PLD grown films would be attributed to the different growth kinetics of the films between PLD and sputtering, where in general, deposition precursors have larger ki-
netic energies for PLD owing to the excitation by high energy laser pulses and few collisions of the deposition precursors with gaseous molecules due to a lower $P_{O_2}$ deposition condition. That is, it is speculated that higher energy precursors in PLD deposition form a more relaxed amorphous structure that is more easily crystallized. Further higher temperature annealing at 600 - 800 °C (Figure 3.5) eliminates the remaining amorphous phases, producing a new crystalline phase ZnSnO$_3$ as a consequence of solid state reactions between the ZnO and SnO$_2$ phases segregated at 450 - 600 °C and the remained amorphous ZTO film [176, 178].

Figure 3.6 shows the AFM images and root-mean-squares (rms) surface roughness of the as-deposited films as a function of the chemical composition and $P_{O_2}$. It shows that the surface roughness depends on both the chemical composition and $P_{O_2}$ and ranges up to 11 nm. The films with the Zn:Sn composition 1:1 have larger roughness compared to the 2:1 composition films, and its roughness decreases with the increase of $P_{O_2}$. The films deposited from the Zn:Sn = 2:1 target have atomically flat surfaces with surface roughness less than 0.3 nm at low $P_{O_2} \leq 2Pa$. For TFT applications, an applied gate bias modulates the conductance of the semiconductor layer and form an accumulated channel of carriers in a narrow region confined at the semiconductor-insulator interface. Hence the surface flatness of an active layer is an important parameter because carrier transport in TFT channels is significantly affected by the carrier scattering due to roughness at the channel - gate insulator interface [179]. Smoother the interface, better will be the mobility of the carriers in the channel.

Figure 3.7 shows the AFM images of the film deposited from Zn:Sn = 2:1 target at an oxygen partial pressure of 0.5 Pa as a function of annealing temperature. The roughness of the film increases as the films are
Figure 3.6: AFM images of ZTO films prepared from target composition (a) Zn:Sn=1:1 and (b) Zn:Sn=2:1. Both films are deposited at room temperature at an oxygen pressure of 0.5 Pa. (c) Dependence of surface roughness on oxygen partial pressure for the films deposited from targets having Zn:Sn compositions 1:1 and 2:1.
Figure 3.7: AFM images of ZTO films deposited from Zn:Sn = 2:1 target at an oxygen partial pressure of 0.5 Pa and then annealed at different temperatures.
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annealed at higher temperatures. As the films are annealed at higher temperatures, it crystallizes into different phases (refer figure 3.4). The higher film surface roughness at higher annealing temperatures is due to the facet formation. The smoother surfaces of amorphous films change to granular rough structures on annealing.

3.5 Optical properties

Figure 3.8 shows transmittance and reflectance spectra of the ZTO films deposited at a $P_{O_2}$ of 0.5 Pa. It shows that the ZTO films have average transmittances > 85% in the visible region and significant difference is not observed for the films having different chemical compositions.

The optical data in figure 3.8 were used in the Tauc plot to obtain the bandgap value [Figures 3.9(a,b)], which derived $E_g$ values 2.37 - 2.86 eV varying with $P_{O_2}$ as summarised in figure 3.9(c) (Method of bandgap evaluation is given in section 2.2.5). There was some uncertainty in the estimation of $E_g$ at low $P_{O_2}$ due to the presence of subgap states. The value of $E_g$ is insensitive to $P_{O_2}$ at $P_{O_2} \geq 2 Pa$. It should be noticed that the fundamental band gap is an intrinsic property of a material: however, the exceptionally small values are obtained for films grown at low $P_{O_2}$, because strong subgap absorption bands appear beneath the fundamental bandgap and superimpose with the fundamental band absorption as observed in figure 3.10. These results should also be compared with previously reported results. As summarized in introduction of reference [110] and reported in reference [173], the Tauc gaps of ZTO films are 3.35 - 3.89 eV. But those films were crystallized, and therefore they should not be compared with the
Figure 3.8: Optical transmission and reflection spectra of the ZTO films prepared at $P_{O_2} = 0.5 \text{ Pa}$ from targets having Zn:Sn compositions 1:1 and 2:1. The films are highly transparent across the visible region.

Present data for amorphous ZTO. It indicates that the fundamental optical gaps of ZTO films are reduced to 2.8 - 2.86 eV on amorphization.

Figures in 3.10 are $\log(\alpha) - h\nu$ plots that show subgap absorption more clearly. It is observed that the as-deposited films $P_{O_2} \leq 2 \text{ Pa}$ have absorption larger by many orders of magnitude just below the fundamental bandgap ($\sim 2.8 \text{ eV}$) compared to films deposited at $P_{O_2} > 2 \text{ Pa}$ [Figures 3.10(a,b)]. This is the reason for the exceptionally small apparent $E_g$ values obtained for amorphous ZTO films. At higher $P_{O_2}$, even though some subgap absorptions remain, they are more distinguishable from the fundamental band absorptions and give larger Tauc gaps $> 2.8 \text{ eV}$. It is also found that thermal annealing at 150 $^\circ\text{C}$ reduces the strong subgap absorp-
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Figure 3.9: (a) Tauc plots for the films prepared from the Zn:Sn=1:1 target at different $P_{O_2}$. (b) Tauc plots for the films prepared from the Zn:Sn=2:1 target at different $P_{O_2}$. (c) Dependence of Tauc gap of the a-ZTO films on $P_{O_2}$ during the growth. Inset shows the effect of annealing in air on Tauc gap of the films prepared at $P_{O_2} = 0.5 \text{ Pa}$. 
Figure 3.10: \( \log\alpha - h\nu \) plots for ZTO films. (a) As-prepared films deposited from the target of Zn:Sn composition 1:1. (b) As-prepared films deposited from the target of Zn:Sn composition 2:1. (c) Annealed films (deposited at \( P_{O_2} = 0.5 \text{ Pa} \)) as a function of annealing temperatures.
tions observed in the films deposited at low $P_{O_2}$ [Figure 3.10(c)], and 300 °C annealing increases the Tauc gaps to $> 2.8 \text{ eV}$ as shown in the inset to figure 3.9c. The large increase in the subgap absorption for the 600 °C annealed films would be attributed to a strong reduction condition prevailing at high temperatures leading to high oxygen deficiency.

3.6 Electrical properties

Electrical properties of the as-deposited a-ZTO films are summarized in figures 3.11-3.13. Previous works on a disordered crystalline oxide semiconductor [180] and amorphous oxide semiconductors [126, 179, 181] indicate that carrier concentration should exceed a threshold value to obtain a large mobility needed for semiconductor devices with active layers having structural randomness. Similar to them, Hall mobilities comparable to or greater than $10 \text{ cm}^2/\text{V} \cdot \text{s}$ were obtained in the a-ZTO films when the carrier concentrations exceeded $10^{16} \text{ cm}^{-3}$ for the Zn:Sn = 2:1 films and $10^{18} \text{ cm}^{-3}$ for the Zn:Sn = 1:1 films.

Figure 3.12 shows the controllability of the carrier concentration for as-deposited ZTO films. Carrier concentration can be controlled from $10^{12}$ to $10^{19} \text{ cm}^{-3}$ by varying $P_{O_2}$ from 0 to 5 Pa. The large carrier concentrations and mobilities are obtained for the films grown at $P_{O_2}$ in the range of 2 - 7 Pa. The decrease of carrier concentration at higher $P_{O_2}$ is due to the suppression of the oxygen vacancies that may contribute to the formation of donor states. However, the low carrier concentrations at low $P_{O_2}$ are not common in PLD deposited transparent conducting oxides. It could be explained for the ZTO films by the large subgap states below 3 eV observed
in figure 3.10. These subgap states act as electron traps which limit number of electrons available to the conduction band. Effects of post thermal annealing on the electrical properties of the films prepared at 0.5 Pa are shown in figure 3.13. Figure 3.10(c) has shown that the post thermal annealing decreases the total subgap states. Up to the annealing temperature of 450 °C, there is a reduction of total subgap states which enhances the carrier concentration and hence the mobility. In the case of the 600 °C annealed films, it again produces a large number of subgap states although the films become polycrystalline as observed in the GXRD (Figure 3.4). This high subgap absorption at high annealing temperature suggests some reducing effect on the film properties. It suggests that the contribution of reducing atmosphere at the high temperature increases defects (e.g. oxy-
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Figure 3.12: Dependence of carrier transport properties of ZTO films on oxygen partial pressure for the as-deposited films.

...gen deficiencies) and localized states, which increases the film resistivity. This leads to a reduction in carrier concentration and hence the mobility (subsequently a higher resistivity) in the case of films annealed at 600 °C.

3.7 Conclusion

The structural, electrical and optical properties of amorphous zinc tin oxide films deposited by pulsed laser deposition were investigated for two Zn/Sn compositions as a function of oxygen partial pressure ($P_{O_2}$) and annealing temperature. The effects of post deposition annealing on the optical and electrical properties of ZTO films were also examined. It was found that
Figure 3.13: Dependence of carrier transport properties of ZTO films on post annealing temperature for the films deposited at $P_{O_2} = 0.5 \, Pa$. 

Conclusion

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optical absorption spectra showed strong subgap absorptions for the films deposited at $P_{O_2} < 2$ Pa. Tauc gaps of the ZTO films were increased to 2.85 eV on deposition at high $P_{O_2}$ or post thermal annealing, which resulted from the reduction of the subgap states. The carrier concentration - $P_{O_2}$ relations showed broad peaks, which is explained by the existence of the electron traps in the subgap states for the films grown at low $P_{O_2}$ and by the reduction of the oxygen vacancies on deposition of films at high $P_{O_2}$. The high electron concentration films were shown large Hall mobilities greater than 10 $cm^2/Vs$. 