Optical and electrical properties of amorphous zinc tin oxide thin films examined for thin film transistor application

Madambi K. Jayaraja
Optoelectronic Devices Laboratory, Department of Physics, Cochin University of Science and Technology, Kochi–682 022, India and Materials and Structures Laboratory, Mail Box R3-1, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

Kachiriyil J. Saji
Optoelectronic Devices Laboratory, Department of Physics, Cochin University of Science and Technology, Kochi–682 022, India

Kenji Nomura, Toshio Kamiya, and Hideo Hosono
Materials and Structures Laboratory, Mail Box R3-1, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503, Japan

(Received 15 November 2007; accepted 8 January 2008; published 27 March 2008)

Structural, electronic, and optical properties of amorphous and transparent zinc tin oxide films deposited on glass substrates by pulsed laser deposition (PLD) were examined for two chemical compositions of Zn:Sn=1:1 and 2:1 as a function of oxygen partial pressure ($P_{O_2}$) used for the film deposition and annealing temperature. Different from a previous report on sputter-deposited films [Chiang et al., Appl. Phys. Lett. 86, 013503 (2005)], the PLD-deposited films crystallized at a lower temperature <450 °C to give crystalline ZnO and SnO$_2$ phases. The optical band gaps (Tauc gaps) were 2.80–2.85 eV and almost independent of oxygen $P_{O_2}$, which are smaller than those of the corresponding crystals (3.35–3.89 eV). Films deposited at low $P_{O_2}$ showed significant subgap absorptions, which were reduced by postthermal annealing. Hall mobility showed steep increases when carrier concentration exceeded threshold values and the threshold value depended on the film chemical composition. The films deposited at low $P_{O_2}<2$ Pa had low carrier concentrations. It is thought that the low $P_{O_2}$ produced high-density oxygen deficiencies and generated electrons, but these electrons were trapped in localized states, which would be observed as the subgap absorptions. Similar effects were observed for 600 °C crystallized films and their resistivities were increased by formation of subgap states due to the reducing high-temperature condition. High carrier concentrations and large mobilities were obtained in an intermediate $P_{O_2}$ region for the as-deposited films. © 2008 American Vacuum Society. [DOI: 10.1116/1.2839860]

I. INTRODUCTION

Demands for visibly transparent and electrically conductive materials are rapidly growing in technological applications in optoelectronic devices such as solar cells, liquid crystal displays, energy efficient windows, and “invisible electronic circuits.” A few crystalline materials such as tin doped indium oxide (ITO), aluminum doped zinc oxide (ZnO:Al), and antimony doped tin oxide (SnO$_2$:Sb) 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 SnO$_2$) and SnO$_2$ (high stability in acidic and basic solutions and in oxidizing environments at higher temperatures).$^{1-6}$ Zinc tin oxide films have been grown by radio frequency and direct current magnetron sputtering, filtered vacuum arc deposition, etc., and most of these works have been devoted to understanding the optical and electrical properties of polycrystalline films fabricated by either substrate heating or high temperature postdeposition annealing.$^{7-11}$

Amorphous transparent conductors are very attractive because they need a low processing temperature and have an ability to grow on plastic substrates in order to form high-quality films applicable to 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 $n \geq 4$) 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.$^{12,13}$
Amorphous silicon (a-Si) channel thin film transistors (TFTs), which are widely used as switching devices in active matrix liquid crystal displays (AMLCDs), suffer from their low field effect mobility (~1.0 cm² V⁻¹ s⁻¹), photo/bias induced instability, and generation of photo-excited carriers because of the small band gap (~1.7 eV) (if no shadow mask is used in the devices). TFTs using transparent oxide semiconductors (TOs) as the channel layer have several merits compared with the conventional Si-TFTs when applied to flat panel displays. These include the insensitivity of device performance to visible light illumination and efficient use of backlight in LCDs or emitted light in organic light-emitting diodes (OLEDs). In addition, oxide TFTs have potential advantages over the covalent semiconductor-based TFTs in terms of their high voltage, temperature, and radiation tolerances.

Amorphous transparent semiconductor based TFTs have recently been investigated by several research groups. This includes the use of a-GaN, a-IGZO, a-ZTO, a-IZO, and a-Cd-In-Sb-O (Ref. 23) as active channel layers. Devices fabricated from them have relatively high mobilities despite their amorphous nature. In TFTs fabricated by Chiang et al., channel layers are sputter deposited from targets having the Zn:Sn ratios 1:1 and 2:1. Substrates were heated at 175 °C and devices were furnace annealed up to 600 °C. Görrn et al. have studied the stability of transparent zinc tin oxide (ZTO) TFTs where the channel layer was deposited by pulsed laser deposition (PLD) of ZTO with Zn:Sn atomic ratios varying from 1:1 to 2:1. Although TFT characteristics have recently been reported for amorphous ZTO, detailed study on their properties in relation to deposition condition, chemical composition, and postannealing has not been reported from the viewpoint of semiconductor materials. In this paper we focus on the preparation and characterization of room temperature (RT) deposited ZTO thin films prepared by PLD from the viewpoint of TFT channel materials.

II. EXPERIMENTAL DETAILS

Films were deposited at RT by PLD from ceramic targets of ZTO with a KrF excimer laser (248 nm wavelength, 10 Hz repetition frequency). Polycrystalline ceramics targets of ZnO:SnO₂ (Zn:Sn=1:1 and 2:1) were prepared from a mixture of ZnO (99.999% pure) and SnO₂ (99.999% pure) powders. The mixed powders were initially calcinated at 1000 °C for 4 h 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 h. The Zn:Sn = 2:1 target forms a single phase compound of Zn₂SnO₄, and the other composition target leads to a mixture of ZnO, SnO₂, and Zn₂SnO₄, which were confirmed by x-ray diffraction (XRD) measurements. 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 min by varying oxygen pressure (P₀₂) from 0 to 9 Pa. The resulting film thicknesses varied from 110 to 200 nm. To study the effects of postdeposition annealing on film properties, some films were annealed at temperatures up to 800 °C in air.

Structural characterization of the films was carried out by glancing incident x-ray diffraction analyses (GXRD, using RIGAKU RINT-2000 with Cu Kα radiation) at the incident angle of 0.5°. Surface roughnesses of the films were evaluated by atomic force microscopy (AFM). Energy dispersive x-ray spectroscopy (EDX) was used for compositional analyses, and a UV-VIS-NIR spectrophotometer (Hitachi U-4000) was used for optical characterization. Resistivity, carrier concentration, and Hall mobility were obtained by Hall effect measurements using the van der Pauw configuration.

III. RESULTS AND DISCUSSION

A. Film chemical composition

Figure 1 shows the compositional variation in the films with P₀₂. It was confirmed that the Zn:Sn ratios of the sintered targets were the same as those of the corresponding starting compositions. Film composition shows some variation with P₀₂, 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.

B. Film structure

Figure 2 shows GXRD patterns of the films deposited using PLD targets with the Zn:Sn ratios of 1:1 and 2:1 as a function of postannealing 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 2θ=33° indicate that some or a large portion of the amorphous phases still remain. This result should be compared with the results by sputtering in Refs. 18 and 9 in which the former reports no crystallization up to 600 °C and the latter reports the crystallization temperature is ~600 °C. This discrepancy would be attributed to the different growth kinetics of the
films between PLD and sputtering, where in general deposition precursors have larger kinetic 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 $\text{PO}_2$ 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 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 remaining amorphous ZTO film.$^{28,29}$

Figure 3 shows the root-mean-squares (rms) surface roughness of the as-deposited films measured by AFM as a function of the chemical composition and $\text{PO}_2$. It shows that the surface roughness depends on both the chemical composition and $\text{PO}_2$ 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 $\text{PO}_2$. The films deposited from the Zn:Sn = 2:1 target have atomically flat surfaces with surface roughness less than 0.3 nm at low $\text{PO}_2$ ≤ 2 Pa. 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.$^{30}$

C. Optical properties

Figure 4 shows transmittance/reflectance spectra of the ZTO films deposited at a $\text{PO}_2$ 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 absorption coefficient $\alpha$ of semiconductors generally follows a relationship of the form

$$ahv = (\text{cont}) (h\nu - E_{\text{opt}})^r,$$

where $h\nu$ denotes the photon energy, $E_{\text{opt}}$ is the optical band gap, and $r$ is a constant depending on the model. The $E_{\text{opt}}$ value is then obtained by linearly extrapolating the plot of $(ahv)^{1/r}$ vs $h\nu$ and finding the intersection with the abscissa. Tauc et al. showed that $r = 2$ holds in amorphous semiconductors assuming a parabolic band and a constant transition moments;$^{31}$ this behavior is indeed found for many amorphous semiconductors.$^{32}$ The optical data in Fig. 4 were analyzed with $r = 2$ (Tauc plot) [Figs. 5(a) and 5(b)], which derived $E_{\text{opt}}$ values 2.37−2.86 eV varying with $\text{PO}_2$ as summarized in Fig. 5(c). There is some uncertainty in the estimation of $E_{\text{opt}}$ at low $\text{PO}_2$ due to the presence of subgap states. The $E_{\text{opt}}$ value is insensitive to $\text{PO}_2$ at $\text{PO}_2 \geq 2$ Pa. It should be noticed that the fundamental band gap is an intrinsic property of a material: however, the exceptionally small
$E_{\text{g}}^{\text{opt}}$ values are obtained for the low $P_{O_2}$ films, because strong subgap absorption bands appear beneath the fundamental band gap and superimpose with the fundamental band absorption as will be observed in Fig. 6. These results should also be compared with previously reported results. As summarized in the Introduction of Ref. 18 and reported in Ref. 9, the Tauc gaps of ZTO films are 3.35−3.89 eV. But these films are crystallized, and therefore they should not be compared with the present data for amorphous ZTO. It indicates that the fundamental optical gaps of ZTO films are reduced to 2.8−2.86 eV by amorphization.

Figure 6 is log $a$−$hv$ plots that show subgap absorption more clearly. It is observed that the as-deposited films have orders of magnitude larger absorption below the fundamental band gap of ~2.8 eV when deposited at low $P_{O_2}$ ≈ 2 Pa [Figs. 6(a) and 6(b)], which causes the exceptionally small apparent $E_{\text{g}}^{\text{opt}}$ values obtained above. 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 eV. It is also found that thermal annealing at ≈ 150 °C reduces the strong subgap absorptions observed in the low $P_{O_2}$ films [Fig. 6(c)], and 300 °C annealing increases the Tauc gaps to > 2.8 eV as summarized in the inset to Fig. 5. The large increase in the subgap absorption for the 600 °C annealed films would be attributed to
a strong reduction condition of the high temperature and formation of many oxygen deficiencies.

D. Electrical properties

Electrical properties of the as-deposited $\alpha$-ZTO films are summarized in Fig. 7. Previous papers on a disordered crystalline oxide semiconductor\textsuperscript{16,30,34} and amorphous oxide semiconductors\textsuperscript{16,30,34} indicate that carrier concentration should exceed a threshold value to obtain a large mobility needed for semiconductor devices using active layers with structural randomness. Similar to them, Hall mobilities comparable to or greater than 10 cm$^2$ V$^{-1}$ s$^{-1}$ are obtained in the $\alpha$-ZTO films when the carrier concentrations exceed $\sim 10^{16}$ cm$^{-3}$ for the Zn:Sn=2:1 films and $\sim 10^{18}$ cm$^{-3}$ for the Zn:Sn=1:1 films.

Figure 8(a) shows the controllability of the carrier concentration for the as-deposited ZTO films. Carrier concentra-
tion can be controlled from $\sim 10^{12}$ to $10^{19}$ cm$^{-3}$ by varying $P_{O_2}$ from 0 to 5 Pa. The large carrier concentrations and mobilities are obtained for the $P_{O_2}$ range of 2–7 Pa. The decrease of carrier concentration at higher $P_{O_2}$ is due to the suppression of the formation of oxygen deficiencies that may contribute to form donor states. However, the low carrier concentrations at low $P_{O_2}$ are not common in PLD deposited transparent conducting oxides. It would be explained for the ZTO films by the large subgap states below 3 eV observed in Fig. 6. Effects of postthermal annealing on the electrical properties of the films prepared at 0.5 Pa are shown in Fig. 8(b). Figure 6(c) showed that the postthermal annealing decreases the total subgap states. Up to 450 °C, there is a reduction of total subgap states that enhances the carrier concentration and hence the mobility. In the case of the 600 °C annealing, it again produces a large number of subgap states, although almost all the films become polycrystalline phases as observed in Fig. 2. It suggests that the contribution of reducing atmosphere at the high temperature increases defects (e.g., oxygen deficiencies) and localized states, which increases the film resistivity.

IV. 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 postdeposition annealing on the optical and electrical properties of ZTO films were also examined. It was found that optical absorption spectra showed strong subgap absorptions if the films were deposited at low $P_{O_2}$ $\leq$ 2 Pa. Tauc gaps of the ZTO films were increased to 2.80–2.85 eV by high $P_{O_2}$ deposition or postthermal 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 low $P_{O_2}$ films and by the reduction of the oxygen deficiencies for the high $P_{O_2}$ films. The high electron concentration films showed large Hall mobilities greater than 10 cm$^2$/Vs.

ACKNOWLEDGMENTS

MKJ wishes to thank Tokyo Institute of Technology for the award of visiting professorship and Y. Ogo and Y. Shimura for the help on lithography. TK is supported by Industrial Technology Research Grant Program (Project ID: 06A12203d) in fiscal year 2006–2007 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

Jayaraj et al.: Optical and electrical properties of amorphous zinc tin oxide thin films