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Electrical, electronic and optical properties of amorphous indium zinc tin oxide thin films

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ABSTRACT

The electrical and optical properties of amorphous indium zinc tin oxide (a-IZTO) thin films were examined as a function of chemical composition. Effects of Sn/Zn composition ratio and In content on the electrical and optical properties of a-IZTO thin films are discussed. The electron mobility of thin film transistors with higher Sn/Zn composition ratio was dramatically improved due to a shorter zinc–zinc separation distance. The thin film transistor with the composition of In:Zn:Sn = 20:48:32 exhibits a high mobility of 30.6 $cm^2 V^{-1} s^{-1}$ and a high on–off current ratio of 10^9.

Introduction

Amorphous ZnO-based materials have been used as an active channel in thin film transistors (TFTs) for next-generation electronic devices due to carrier mobility ($\geq 10\,cm^2 V^{-1} s^{-1}$) higher than that of $\sim 1\,cm^2 V^{-1} s^{-1}$ for hydrogenated amorphous silicon TFTs (a-Si:H), which are commonly used in commercial applications [1,2]. Amorphous ZnO-based materials such as indium zinc oxide, zinc tin oxide, indium gallium zinc oxide (IGZO), and hafnium zinc oxide also have low gate sub-threshold swing and uniformity [3–6]. Indium zinc tin oxide (IZTO) films, particularly, can be one of the possible alternatives for transparent electrodes of various optoelectronic devices such as flat-panel displays, solar cells, and organic light-emitting diodes because of their good electrical conductivity, chemical stability, and low deposition temperature [7–9].

Amorphous oxide typically exhibits high mobility due to large overlapping of *ns* orbitals derived from spherically symmetric configurations in the conduction band [10]. IZTO is a heavy metal oxide with the $(n-1)d^{10}ns^0 (n \geq 4)$ electronic configuration. The overlap of *ns* orbitals can attribute to the creation of conduction paths for electron transport in amorphous thin films, which leads to better conductivity [11,12].

Nomura et al. [13] reported that the conduction paths resulted from the overlapped linkage between neighboring metallic ions are related to the local structure of amorphous transparent thin film semiconductors. This electron transport passage can create even a short range order in amorphous oxide films. Ohta et al. [12] found a condition needed to form conduction paths in amorphous IGZO (a-IGZO) by evaluating the overlap integral between *ns* orbital function of various metal ions. They reported that the overlap integral of the extended wave functions in the conduction band of metal *ns* orbitals can be formed when the $(n-1)d^{10}ns^0$ metal ions greater than the percolation threshold of 20% of the atoms. The overlap integral can be affected by the distance between the nearest neighbors of metal ions and the variation of the metal–oxygen–metal bond angles resulting from the change in the metal–metal distance on a-IGZO films [12]. This study demonstrated that the Zn^{2+} ions affected the electrical properties of a-IGZO to a great extent by creating the conduction paths in the films.

Several attempts have been made to enhance the electrical characteristics of IZTO TFTs by using an annealing process or varying the compositions of Zn and Sn. Ryu et al. [14] found that the change in Sn/Zn composition ratio can influence the electrical properties of IZTO TFTs. They reported that the field-effect mobility and the

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sub-threshold gate swing of IZTO TFTs were slightly decreased and improved, respectively, when the Sn/Zn composition ratio was increased from 0.35/0.45 to 0.45/0.35. Other studies reported the role of Zn and In contents in the carrier transport properties of an IZTO thin film and showed that the electron mobility increased with Zn contents and decreased with increasing In contents [15,16]. Both studies demonstrated that Zn and In contents would play a dominant role in altering the electrical properties of a-IZTO thin films. However, the detailed mechanism of this alteration has not been fully understood. Studies on the local structure related to the electrical properties give some insight into this point of view. In this study, we investigate the dependence of electrical and optical properties of a-IZTO thin films as well as the local structure in the films on different In/Zn/Sn compositions. We found that the electron mobility of a-IZTO thin films can be significantly improved by using a lower of Zn content in contrast to the electron mobility of the films with a different In content, which stayed relatively the same. The local structure was examined by extended X-ray fine structure spectra (EXAFS) and showed that the variation of the distance between Zn atoms can influence the electron mobility of a-IZTO thin films.

Experiment

IZTO thin films were deposited on glass substrates at room temperature in argon mixed with oxygen gas ($Ar:O_2 = 15:85$) by RF magnetron sputtering with the RF power of 200 W. The target composition ratios of In:Zn:Sn in IZTO thin films are 20:48:32 (denoted as IZTO-I), 20:56.7:23.3 (denoted as IZTO-II), and 13:60.2:26.8 (denoted as IZTO-III). All IZTO thin films were annealed at 350 °C for 1 h in air. Other experimental conditions for the TFTs preparation are described in detail elsewhere [17]. The electrical properties of IZTO thin films were measured using a Keithley 4200 semiconductor parameter analyzer. The voltages applied between the gate and the source (V_{GS}) and between the drain and the source were −20 V and 10 V, respectively. XPS measurements were performed using Mg *K*α source with the pass energy of 20 eV. The incident and the take-off angles of electrons from the surface normal were 55° and 0°, respectively. The binding energies were referenced to C 1s peak of hydrocarbon contamination at 284.5 eV [18]. The transmittance spectra of the IZTO thin films were measured by Genesys 6 model from Thermo Electron Corporation in the wavelength range of 300 to 1000 nm at *RT* at increments of 0.1 nm. The local structure and the local conduction of IZTO thin films were examined using X-ray absorption spectra (XAS) measurements at 8 C beam line in Pohang Light Source (PLS), South Korea, and with the electron storage performance of 2.5 GeV and 200 mA. The fluorescence mode with 7-element Germanium solid-state detector (SSD) system was used in the XAS measurements and the data was collected and analyzed at the Zn K-edge near 9659 eV using a suitable IFEFFIT program [19].

Results and discussion

Fig. 1 shows the XPS results of In 3d, Zn 2p, and Sn 3d states of thin films deposited with various chemical compositions. The spin–orbital splitting at 7.6 eV, 23.1 eV, and 8.5 eV was found for In 3d, Zn 2p, and Sn 3d peaks, respectively. The binding energy of all IZTO thin films was not changed with different In/Zn/Sn compositions. Fig. 1(a)–(c) shows that the binding energies for In $3d_{5/2}$, Zn $2p_{3/2}$ and Sn $3d_{5/2}$ peaks with oxygen were located at 444.3 eV, 1021.7 eV, and 486.3 eV in all IZTO thin films [20,21]. Thus, the XPS results show that IZTO thin films have mixed phases of metal and oxide. Fig. 1(d) shows asymmetric XPS spectra from O 1s of IZTO thin films. O 1s spectra of IZTO samples were deconvoluted by Gaussian–Lorentzian (with 20% Lorentzian) features at about 529.4 and 531.3 eV. The lower binding energy component (529.4 eV) of O 1s spectra is attributed to the bonding between oxygen and metal atoms [7]. The higher binding energy component (531.3 eV) corresponds to oxygen-deficient region [21]. The change in intensity at higher binding energy is related to a change in the oxygen vacancies in the IZTO thin films. These results indicate that the oxygen vacancies in IZTO thin films are more affected by the In content than by the Sn/Zn ratio. Moreover, according to the Kröger–Vink formula, an oxygen vacancy can generate electrons simultaneously as described in Ref. [22]. Therefore, the electron density of IZTO-III film is expected to be much lower than that of IZTO-I and IZTO-II films, respectively. In addition, the composition ratio of In:Zn:Sn estimated using the XPS spectra is shown in Table 1. The composition ratios of all IZTO thin films are almost the same as those provided by the target composition ratios. The Sn/Zn composition ratios for IZTO-I, IZTO-II, and IZTO-III films are approximately 0.6, 0.40, and 0.43, respectively. Hence, the Sn/Zn composition ratios for IZTO-II and IZTO-III films are closed to each other and those values are much higher than that of IZTO-I film.

We made use of REELS to investigate the dependence of the band gap energy E_g on the compositions in IZTO thin films and to examine the electronic structure near the band gap. As shown in Fig. 2(a), the plasmon loss peaks of the IZTO-I and IZTO-II films were located at around 19.2 eV, but the peak for IZTO-III was observed at a higher energy loss of 21.0 eV. The REELS spectra were used to estimate the energy band gaps of the IZTO thin films by the method described in our previous work [23]. The results show that the measured band gaps of the IZTO-I, IZTO-II, and IZTO-III thin films are 3.54, 3.42, and 3.31 eV, respectively, within an uncertainty of ±0.1 eV. For comparison, the band gap was also measured by utilizing a UV-spectrometer. The optical band gaps of the a-IZTO thin films were obtained from the Tauc relation [24] (which is valid only for amorphous thin films) by plotting $(\alpha h\upsilon)^2$ versus $h\upsilon$ where α, h, and υ are the absorption coefficient, Planck's constant, and the frequency of incident photons, respectively. As shown in Fig. 2(b), the optical band gaps of the IZTO-I, IZTO-II and IZTO-III thin films were 3.57, 3.41, and 3.37 eV, respectively. The measured optical band gaps are consistent with the band gap values determined by the REELS spectra. By comparing the band gaps of IZTO thin films with differing Sn/Zn composition ratios (IZTO-I and IZTO-II films), we found that the band gaps varied with differing Zn contents. The band gap of ZnO (3.37 eV) is smaller than those of SnO_2 (3.6 eV) and In_2O_3 (3.7 eV) [25–27]. The results show that the band gap in the amorphous films becomes smaller with increasing Zn contents. In addition, we measured the optical transmittance as a function of wavelength of a-IZTO thin films with differing In/Zn/Sn compositions. As shown in the inset of Fig. 2(b), in the visible light region, the transmittance coefficients are approximately 87% for all IZTO thin films without changing Sn/Zn ratios and the In contents. Hence, the transmittance coefficient of IZTO films is not greatly affected by the In/Zn/Sn compositions.

In our study, the extended X-ray absorption fine structure (EXAFS) spectra and the X-ray absorption near edge structure (XANES) spectra at the Zn K-edge were used to address the local structure of IZTO thin films. The absorption coefficient μ and its fine structure were extracted from the fluorescence mode of X-ray absorption measurement. Previous studies reported that the XANES spectra of ZnO_4 tetrahedral exhibited weaker intensity at the rising absorption edge (referred as the "white line") and showed a broader decay compared to ZnO_6 octahedral [28–30]. The inset 1 of Fig. 3 presents the XANES spectra for a-IZTO thin films. It was found that for all IZTO thin films, the Zn–O formed a tetrahedral structure based on the white line peak. Fig. 3 provides the k^3-weighted Fourier transformed spectra of Zn K-edge EXAFS from a-IZTO thin films. These spectra indicate the radial distribution of

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