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Optical and electrical properties of Mg-doped zinc tin oxide films prepared by radio frequency magnetron sputtering

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ABSTRACT

In this study, magnesium (Mg)-doped zinc tin oxide (ZTO) films were deposited by radio frequency (RF) magnetron sputtering. The Mg was selected as an electron suppressor for the ZTO films. X-ray diffraction (XRD) was carried out to observe the crystallinity of the films. The Mg-doping effects on the elemental properties of the films were investigated by X-ray photoelectron spectroscopy (XPS). The optical properties, such as transmittance, optical band gap, Urbach energy, and refractive index, were compared as a function of Mg content. Bottom-gate transparent thin-film transistors (TTFTs) were fabricated on N^+ Si wafers. The turn-off voltage, threshold voltage, and mobility variation as a function of Mg content were studied.

1. Introduction

Amorphous Si and polycrystalline Si thin film transistors [1,2] have been widely used as switching devices for flat panel displays. Recently, however, transparent thin-film transistors (TTFTs) [3–5] are attracting increasing attention because of the intensifying competition between manufactures of flat panel displays to develop displays with better resolution. Accordingly, many researchers have tried to develop TTFTs with enough mobility for fast-switching circuits and have found a way to enhance the mobility using indium-containing transparent films. However, the main material for transparent conducting films, indium, is rare and expensive. Therefore, studies on indium-free materials for TTFTs are ongoing.

Amorphous oxide semiconductors containing post-transition metal cations are known to show high electron mobility due to the overlapping of *n*s orbitals (*n* is the principle quantum number) having a large radius and an isotopic shape [6]. Among them, amorphous zinc tin oxide (ZTO) films have been considered one of the most promising materials for the active layer of TTFTs [7,8]. The merit of ZTO films is in their high mobility and large optical band gap. Radio frequency (RF) magnetron sputtering, sol–gel, spray methods, etc. have usually been employed to deposit ZTO films. However, the resistivity of as-deposited ZTO films is too low to be adopted as the active layer of TTFTs [9,10]. Thus, an electron suppressor that reduces the electron concentration is required in order to use ZTO films as active layers.

In this study, we chose Mg as an electron suppressor for ZTO films. It was expected that the magnesium oxide (MgO) mixed into ZTO would increase the optical band gap and consequentially lower the electron concentration of ZTO films. Mg-doped ZTO films were deposited by RF magnetron sputtering, and the optical and elemental properties of the films were studied. Finally, we fabricated TTFTs using Mg-doped ZTO films as active layers, and obtained the mobility of 7.7 $cm^2/V\,s$.

2. Experimental

Three kinds of targets manufactured by mixing ZnO, SnO_2, and MgO powders were purchased from LTS Research Laboratory, Inc. The diameter of the targets was 3″. In the targets, the atomic ratio of Zn to Sn was fixed at 5:4 and the Mg content was varied at 0, 5.0, and 10.0 at.%, respectively. ZTO films were deposited on 7059 glass or SiO_2-coated Si wafers. RF magnetron sputtering was carried out in pure argon at 667 mPa and 90 W. Transmittances in the visible range were measured by a UV/vis spectrophotometer. The absorption coefficients were calculated from the transmittances, and the optical band gap, Urbach tail energy, and refractive index were obtained from the absorption coefficients. The crystallinity of the films was investigated by X-ray diffraction (XRD). X-ray from the Ni-filtered Cu K_α (λ = 1.5418 Å) radiation was scanned between $2\theta = 20^\circ$ and 60° with a step of 0.01°. X-ray photoelectron spectroscopy (XPS) was conducted to study the elemental properties using the monochromated Al K_α X-ray. In the XPS measurements,

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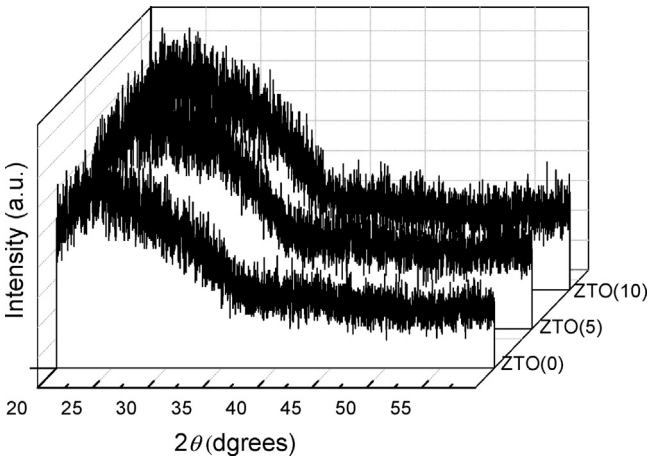

Fig. 1. XRD patterns of ZTO films. ZTO(0), ZTO(5), and ZTO(10) denote ZTO films sputtered with ZTO targets containing 0, 5.0, and 10.0 at.% Mg, respectively.

spectral shifts occur by surface charging. The measured XPS spectra were compensated using C1s (284.6 eV) and Ar2$p_{3/2}$ (241.6 eV) peaks as references.

TTFTs were fabricated on N^+ Si wafers that played the role of gate electrodes. SiO_2 was first grown on the Si wafers by dry oxidation to a thickness of ~120 nm. Then, ~50-nm-thick Al_2O_3 films were sequentially grown by atomic layer deposition. The Al_2O_3/SiO_2 films were used as gate dielectrics of the TTFTs. ZTO films employed as active layers were then deposited onto the Al_2O_3/SiO_2 films by RF magnetron sputtering and annealed at 400 °C for 20 min. The thickness of the ZTO films was ~50 nm. Part of the Al_2O_3/SiO_2 films was etched out to provide contact holes for the N^+ Si wafers used as gate electrodes, which was followed by In evaporation to form source, drain, and gate electrodes. The active layer and channel was defined by shadow masks. The channel width and length were 400 μm each. The TTFTs were characterized by a semiconductor parameter analyzer.

3. Results and discussions

3.1. Elemental properties

The films sputtered with the ZTO targets containing 0, 5.0, and 10.0 at.% Mg are denoted as ZTO(0), ZTO(5), and ZTO(10), respectively.

The ZTO films were found to be amorphous by XRD results, as shown in Fig. 1. The ZTO films used as the active layer of TTFTs were ~50 nm which is too thin to tell small grains by XRD. Therefore, we grew about 300-nm-thick ZTO films for XRD.

Fig. 2 shows the XPS depth profiles of the ZTO(5) and ZTO(10) films deposited on SiO_2-coated Si wafers. We averaged the atomic ratios of Zn, Sn, and Mg over all the measured values except those of the surfaces. The average ratio of Zn to Sn was approximately 3:2 in both the ZTO(5) and the ZTO(10) films. The Sn content in the films was smaller than that in the targets, which indicates that the sputtering yield of Sn or SnO_2 is lower than that of Zn or ZnO. The Mg content in the ZTO(5) and ZTO(10) films was 5.5 and 9.7 at.%, respectively, which was similar to the Mg content in the targets.

Fig. 3 shows the XPS spectra of Zn2$p_{3/2}$, Sn3$d_{5/2}$, and Mg1s obtained from the ZTO(5) and ZTO(10) films. Fig. 3 was the XPS results measured after etching the surface of each samples for 90 s. From the results of ZTO(5), the center values of the Zn2$p_{3/2}$, Sn3$d_{5/2}$, and Mg1s peaks corresponding to binding energies were estimated to be 1022.7, 486.5 and 1304.9 eV, respectively, which are considered to originate from the Zn^{+2}, Sn^{+4}, and Mg^{+2} ions bonding with oxygens [11]. The binding energies of the metal ions obtained in

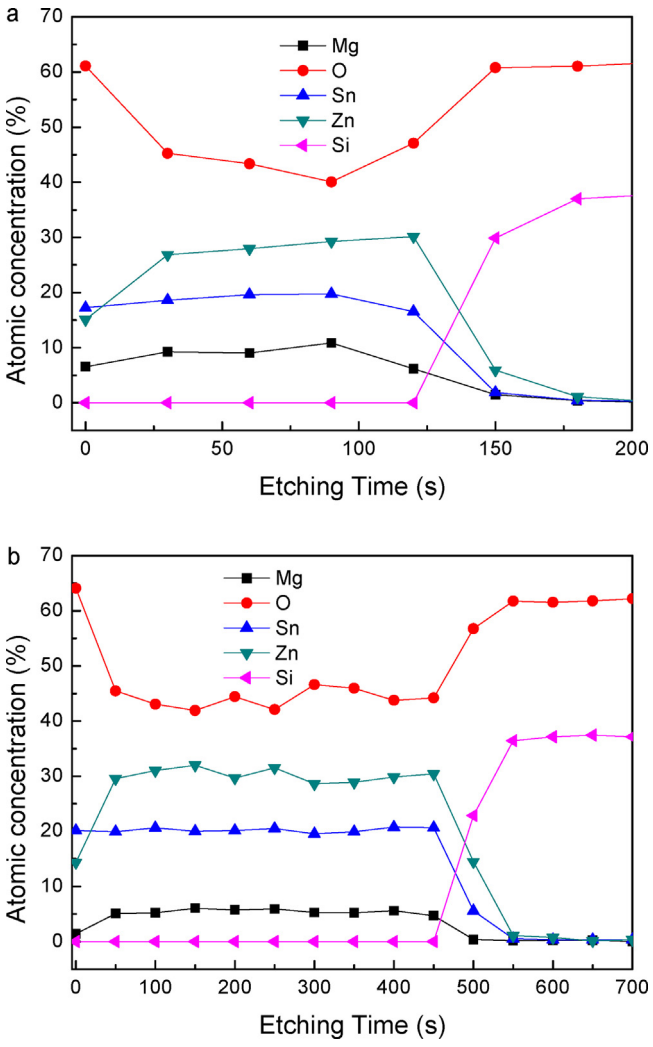

Fig. 2. XPS depth profiles of (a) ZTO(5) and (b) ZTO(10).

our study were larger than those in the previous reports [12–14], which is attributed to the different crystallinity. It was reported [15,16] that the In3$d_{5/2}$ peak in amorphous In_2O_3 shifts toward a higher value comparing with that in the polycrystalline In_2O_3. The shift was explained by a charge accumulation [16]. The positive charges generated by X-ray exposure are accumulated and establish a potential gradient across a film surface, which results in the binding energy shift to the higher value [17]. The charge accumulation is more sustainable in amorphous films than in polycrystalline films due to their higher resistivity. The Zn2$p_{3/2}$, Sn3$d_{5/2}$, and Mg1s peaks of ZTO(10) increased to 1023.1, 486.9 and 1305.4 eV, respectively. The electron suppression by Mg doping seems to be another cause to increase the binding energies [18]. The decreased free electrons by the electron suppression increase the effective positive charge in a nuclear, which leads to the binding energy increase of the metal ions.

Fig. 4(a) shows the O1s spectrum of ZTO(0) film measured after etching out the surface for 90 s. The peak was deconvoluted into two peaks: 530.4 and 531.9 eV. The peak at 530.4 eV is attributed to O^{2-} ions surrounded by metal atoms. The binding energies of O1s in ZnO [19], SnO_2 [20], and MgO [21] lattice are known to be almost same. The main peak at 530.4 eVwas deconvoluted no more. The peak at 531.9 eV is imputed to oxygen deficiencies [22]. Fig. 4(b) and (c) shows the O1s spectrum of ZTO(5) and ZTO(10) film, respectively, measured after etching out the surface for 90 s. The centers of the deconvoluted curves were 530.5 and 532.0 eV,