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Semiconducting properties of amorphous GaZnSnO thin film based on combinatorial electronic structures

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Semiconducting properties and electronic structures of amorphous GaZnSnO (GZTO) thin films are investigated with respect to metal cationic composition. An increase of the cationic Sn ratio resulted in an increase of the carrier concentration and a decrease of the mobility of the films. Combinatorial analysis revealed that the electrical characteristics of GZTO films are strongly correlated to changes in electronic structure. The increase in carrier concentration is related to the generation of vacancies by the changes of oxygen coordination around the cationic metal and the shallow band edge state below the conduction band. On the other hand, the decrease of mobility can be explained by the deep band edge state, and the difference between the experimental conduction band and simulated conduction band by the combinatorial electronic structure based on the chemical composition. © 2014 AIP Publishing LLC.

Amorphous oxide semiconductors (AOSs) are promising materials with potential applications in transparent electronic devices and flexible electronics due to their high electron mobility and high optical transparency. Recently, InGaZnO (IGZO) oxide semiconductor thin film transistors (TFTs) have been extensively studied for their applicability in high performance displays, including active matrix liquid crystal displays (AM-LCDs) and organic light emitting diode displays (OLEDs). AOS TFTs exhibit high field effect mobility relative to conventional a-Si:H TFTs (<1 cm² V⁻¹ s⁻¹) and can be fabricated at low process temperatures below 400°C. Several research groups have reported that Indium-based AOSs have good performance, but the material costs of Indium are high. GaZnSnO (ZTO) oxide semiconductors, fabricated using widely available ZnO have gained attention since they can be used as cost-effective, In-free AOSs.

GaZnSnO (GZTO) oxide semiconductors have also been investigated to control the electrical properties through the addition of the appropriate Ga carrier suppressor. A few papers have reported that GZTO TFTs present very good device characteristics. Even though previous studies have found these good performances, the semiconducting mechanism of GZTO has not yet been systematically studied.

In this study, we perform a combinatorial analysis of the electronic structure of GZTO films to understand their semiconducting properties with respect to metal cationic composition. The correlation of electrical properties is investigated in terms of the electronic structure, such as the chemical bonding states, conduction band features, and the band edge states below the conduction band.

GZTO thin films with a 30 nm thickness were RF co-sputtered on the plasma-nitrided SiN/Si substrates with a Ga doped ZnO (GZO, 5 wt. % Ga₂O₃) target and SnO₂ target, each with a 4-in. diameter. In order to study the electrical properties of the GZTO films as a function of metal cationic composition, the RF power applied for each target were changed within a range of 40–110 W, while the total sum of both was limited to 150 W.

The elemental composition of the films was obtained through energy dispersive x-ray spectroscopy (EDS) on a scanning electron microscope operating at 20 kV. The carrier concentration and mobility were measured via a Hall-effect measurement system using the van der Pauw method. The chemical bonding states were examined using x-ray photoelectron spectroscopy (XPS) with a monochromatic MgKα (1253.6 eV) source and a pass energy of 50 eV. Spectroscopic ellipsometry (SE) and x-ray absorption spectroscopy (XAS) were performed in order to analyze the electronic structure and the features of the conduction band. SE data were obtained with incident angles of 65°, 70°, and 75° at photon energies of 0.75–6.4 eV using a rotating analyzer system with an auto retarder. XAS measurements were carried out by a total electron yield mode using a coherent x-ray beam source at the Pohang accelerator laboratory (PAL) on beam line 10D.

The chemical composition of GZTO films resulting from the changes in the RF sputtering power of the GaZnO and SnO₂ targets, was studied using a cationic elemental analysis of the EDS and XPS measurements, as shown in Table I. The cationic Sn ratio varied from 34% to 85%, while the Ga and Zn ratios varied from 14% to 3% and from 52% to 12%, respectively. The relative ratio of [Zn]/([Ga] + [Zn]) was fixed at about 80%, regardless of the combination of RF plasma power, which indicates that the composition of the GaZnO target is maintained with a change in plasma power. As a result, we mainly considered the cationic Sn ratio of 34%, 63%, and 84% for the following discussion.

Figure 1 shows the GZTO films’ carrier concentration and Hall mobility as a function of the cationic Sn ratio. As the cationic Sn ratio increased beyond 63%, the carrier...
concentration significantly increased and became saturated at \( \sim 10^{19} \text{ cm}^{-3} \). On the other hand, with an increase in the Sn ratio, Hall mobility drastically decreased from 20.3 cm\(^2\) V\(^{-1}\) S\(^{-1}\) to 1.42 cm\(^2\) V\(^{-1}\) S\(^{-1}\). In order to interpret the detailed origin of the electrical properties in GZTO films, further discussion is provided below and considering the chemical bonding states and electronic structures, including the conduction band feature and the band edge states below the conduction band.

The changes in electrical properties of conducting and semiconducting films are generally associated with changes in their physical and chemical characteristics. GZTO films have amorphous physical structures, regardless of film composition. On the other hand, detailed chemical bonding states of Ga, Zn, Sn, and O change as a result of the variation in cationic Sn ratio, as shown in Figure 2. The O 1s spectra in Figures 2(a)–2(c) were carefully deconvoluted with three different Gaussian peaks, which were indexed as O1, O2, and O3 centered at 529.9 eV, 530.5 eV, and 531.5 eV, respectively.

The low binding energy peak (O1) is related to the O\(^2-\) ions of the metal oxide bondings, and the higher binding energy peak (O3) can be attributed to chemisorbed or dissociated oxygen or OH species on the surface of the GZTO films, such as -CO\(_3\), adsorbed H\(_2\)O, or adsorbed O\(_2\).\(^{10}\) The peak at the medium binding energy (O2) of the O 1s spectrum is associated with the OH bonding species and with O\(^2-\) ions that are in the oxygen-deficient Ga-Zn-Sn-O bonding matrix. O2 and O3 peaks slightly increased, while O1 peak decreased with an increase in the cationic Sn ratio. The increase of the oxygen deficient O2 peak is considered to generate extra free electrons along with the corresponding changes in the chemical coordination of metal the cation.\(^{1,11}\)

Figures 2(d) and 2(e) show the evolution of the chemical bonding states of the metal cation, relatively calculated by the area ratio of the ionic states using a Gaussian fitting of Ga 3d, Zn 2p, and Sn 3d spectra. As the cationic Sn ratio increased, the lower oxidation states of Ga\(^{1+}\), Ga\(^{2+}\), Zn\(^0\), and Sn\(^{2+}\) decreased, and the higher oxidation states of Ga\(^{3+}\), Zn\(^{2+}\), and Sn\(^{4+}\) increased. It is interesting that the oxidation states of Sn are dominantly changed rather than those of Ga and Zn, which are correlated to a change in the oxygen deficient states. The increase of higher oxidation states from lower oxidation states can be interpreted to generate free electron by the following relation; M\(^+\) \(\rightarrow\) M\(^{2+}\) + e\(^-\). From the changes in the chemical bonding states of oxygen and metal, carrier concentration can be seen to be strongly correlated to oxygen deficient states induced by the changes of coordination of the metal cation, especially as an effect of Sn due to the increase of the cationic Sn ratio.

In order to understand the electronic structure of the GZTO film, including the band gap, the optical absorption was measured via SE, as shown in Figure 3. These spectra were extracted from a simple four-phase model, which was comprised of a substrate, SiN layer, GZTO overlayer, and an ambient layer.\(^{12}\) The optical band gap of GZTO thin films has a value similar to \( \sim 3.3 \) eV as a function of the cationic Sn ratio. However, when the optical absorption of each oxide is considered (those are plotted in the bottom of the optical absorption spectra of GZTO film), the conduction band above the band gap converges to that of SnO\(_2\) above the cationic Sn ratio of 63%. These indicate that the cationic Sn

### Table I. Cationic metal compositions of Ga-doped ZnSnO thin films as the combination of RF plasma power for each target.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>GaZnO</th>
<th>SnO</th>
<th>Ga</th>
<th>Zn</th>
<th>Sn</th>
<th>Zn/(Ga + Zn) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>50</td>
<td>14</td>
<td>52</td>
<td>34</td>
<td>34</td>
<td>79</td>
</tr>
<tr>
<td>70</td>
<td>80</td>
<td>7</td>
<td>30</td>
<td>63</td>
<td>63</td>
<td>81</td>
</tr>
<tr>
<td>40</td>
<td>110</td>
<td>3</td>
<td>12</td>
<td>85</td>
<td>85</td>
<td>80</td>
</tr>
</tbody>
</table>
Ratio mainly influences the characteristic of the conduction band, similar to the carrier generation in the chemical bonding states.

Figure 4(a) shows the normalized O-K edge XAS spectra, which provide more information over wider conduction band than SE spectra and the unoccupied hybridized states between Ga 4sp, Zn 4sp, Sn 5sp, and O 2p by transition of the electron from the occupied O 1s. The normalization of the O-K edge spectra was performed by subtracting an x-ray background from the raw data and subsequently scaling the difference between the pre- and post-edge levels to an arbitrary, but uniform, value. The relative intensities of the peaks in these normalized O-K edge spectra reflect the molecular orbital bonding symmetries and crystal-field (C-F) splittings in the corresponding samples.

Therefore, the relative changes in combination with the electronic structure, comprised of GaOx, ZnOy, and SnOz, can be considered as a function of the cationic Sn ratio. The normalized O-K edge XAS spectra of each binary oxide are co-plotted for easy comparison to the changes in GZTO spectra. Similar to the SE spectra in Figure 3, SnO2 determines the evolution of XAS spectra as a function of the cationic Sn ratio. Another interesting finding is that there was a slight shift of the conduction band to a lower energy of ~0.4 eV, and there were also changes of the conduction band edge, which will be discussed along with Figure 5.

The shift of conduction band could be reflected to a schematic band alignment diagram with results of the optical band gap, as shown in Figure 4(b). The lower shift of the conduction band induces a relative narrowing between the conduction band minimum and Fermi level ($\Delta = E_C - E_F$) due to a similar band gap as a function of the cationic Sn ratio, which is related to an increase in the carrier density with a corresponding increase of cationic Sn ratio by $n = N_C e^{-(E_C - E_F)/kT}$.

In order to examine the conduction band edge in Figure 4(a) with more detail, Gaussian fits were performed by using the peak energy occurring in the second derivative spectrum analysis through 525 eV – 555 eV. Figures 5(a)–5(c) show a narrow energy region below the conduction band edge, which identifies two distinct band edge states located at about 0.1 eV (D1) and 1 eV (D2) from the conduction band edge. In a previous study, we used an analysis of SE data to interpret the presence of two distinct band edge states of the ZnO films annealed under various ambient atmosphere, and we found a correlation with the electrical properties of the ZnO film, such as carrier concentration and mobility, depending on the relative energy level and qualitative change within the band gap. Based on our previous study and the electrical data of GZTO film, the most plausible origin for the changes in electrical properties such as carrier concentration and mobility can be attributed to the evolution of the band edge states as a function of the cationic Sn ratio, which is related to oxygen vacancies. The qualitative changes calculated by the peak area of D1 and D2 are summarized in Figure 5(d). The increase of the carrier concentration as a function of the cationic Sn ratio, may be explained by the increase of the shallow band edge state (D1) because it means that the number of free electron which can conduct as a carrier is increasing with the generation of oxygen vacancies, and it is close to the conduction band edge. The mobility is associated with the deep band edge state (D2), which can have a higher effect on the degradation of the mobility by the unoccupied states because of charge trapping and an increase in charge scattering during carrier transport due to energy levels being far from the conduction band.

Figure 6 shows a comparison between the experimentally measured XAS spectra and the simulated XAS spectra.
using a combinatorial electronic structure. The simulation of the combinatorial electronic structure means there is a superposition with the experimental XAS spectrum of each binary oxide as shown in Figure 4(a). The ratio based on the composition of the GZTO film is multiplied by the XAS spectrum of each oxide before superposition. The interesting finding is that the difference between the experimental XAS spectra and the simulated XAS spectra is getting smaller as the cationic Sn ratio increases. These results are explained by the formation of a compound or mixture within the electronic structure of each oxide. If a compound is formed by the combination of each oxide, the difference between the experimental XAS spectrum and the simulated XAS spectrum is large for a GZTO film with 34% Sn ratio because the chemical bondings among metals and oxygen are generated. On the other hand, if there is the mixture of each oxide, its difference is smaller because the electronic structures of each binary oxide are maintained without a modification of combinatorial electronic structure, and therefore is equivalent to a simple superposition of the electronic structure with each binary oxide. The interpretation of the combinatorial electronic structure could be strongly correlated with the changes in mobility of the GZTO film. The grain boundary of the electronic structure is smaller in the mixture of each oxide due to the preservation of characteristics of each electronic structure. Therefore, the changes in the grain boundary of the electronic structure can induce a degradation of the electron transport in GZTO film as the cationic Sn ratio increases, and resulting in the decrease of Hall mobility.

Amorphous GZTO thin films were deposited by co-sputtering of GaZnO and SnO2 targets as a function of a variation in the applied RF power. The semiconducting properties of the GZTO film were investigated with respect to metal cationic composition. Carrier concentration increased and mobility decreased with the increase of the Sn ratio. The electrical characteristics of the GZTO films are strongly correlated to changes in the electronic structure, such as the chemical bonding coordination, conduction band feature, and the band edge states below conduction band. The increase of carrier concentration is related to the increase of oxygen vacancies and the increase of the shallow band edge states below the conduction band. The decrease in mobility is related to the increase of the deep band edge state. In addition, combinatorial analysis reveals that the decrease in mobility is attributed to the independent combination of electronic structure of each binary oxides in GZTO films with the increase of Sn ratio, which could cause the increase of grain boundary on the electronic structure. An interpretation of semiconducting properties through the combinatorial electronic structure is a promising metrology for evaluating the electrical properties of oxide semiconductor thin films and can provide fundamental results for the synthesis of new oxide semiconductor or transparent conducting oxides.

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