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Low Temperature Measurement of the Electrical Conductivity in Amorphous InGaZnO Thin Films

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We examine the temperature-dependent electrical conductivity in amorphous InGaZnO thin films with various cation compositions. In-rich films are metallic, while Ga-rich films are semiconducting with logarithmic conductivities linear to $-T^{-1/4}$ above T = 60 K. The Zn-rich films are also semiconducting but have $>10^2$ times higher conductivity than the Ga-rich films. At T > 60 K, thermal electronic excitation dominantly contributes the conduction, while at T < 60 K, certain impurity scatterings or structural disorders have importance in the electrical properties in low carrier *a*-IGZO system.
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Amorphous indium gallium zinc oxide (*a*-IGZO) has drawn much attention since it has enormous potential as a functional material in modern electronic devices such as transparent amorphous oxide semiconductor (TAOS) transistor[1,2] and resistive switching (RS) memory.[3,4] The electrical properties of the *a*-IGZO system have been studied widely and it has been shown that the mobility and its temperature (T) dependence vary largely with the cation compositions.[5,6] So far, the electrical measurements have been performed mostly at or above the room temperature (RT) for the purpose of commercial applications. However, studies at low T are also in need in order to understand the nature of the electrical conductivity (σ) in the *a*-IGZO system.[7]

Generally, T dependence of σ is largely influenced by the electron-phonon scattering process, which becomes more important at high T such as RT. In the case of a crystalline system, the phonon distribution should be highly dependent on the crystal structure and thus, the atomic composition. Therefore, the atomic composition can be an important factor to determine the carrier mobility. On the other hand, in amorphous system, the contribution of the phonons to the σ becomes somewhat indeterminate due to lack of long range lattice modulations. This hinders an easy prediction on how the σ will evolve with the cation compositions as well as T in the case of amorphous system.

In most TAOS films, there exist certain impurities or defects. Their contribution to the σ's can be estimated by measuring σ(T) at a sufficiently low T, namely, far below Debye temperature (typically a few hundreds of kelvin) due to disappearance of phonon scattering. Therefore, we measured σ(T) of *a*-IGZO films in a wide T range of 5 K – 300 K. The *a*-IGZO films with various cation compositions were prepared by a sputtering method. It is well known that the sputtered films can be less ordered and defective due to the kinetic collision process during the growth. Although the sputtering method is widely used in industry to date, the significance of the defects and their consequence in the electrical performance are rarely known and could even vary systematically depending on the targeted atomic composition. This implies that it is hard to judge if certain compositional dependence is originated either from the true chemical effects or from the evolution of the defect density. Nevertheless, it is meaningful to examine the overall σ evolution in the films deposited under the same condition in regard of the film manufacture engineering.

a-IGZO films were deposited on a glass substrate using an rf magnetron co-sputtering method. Three polycrystalline ceramic targets of In_2O_3, Ga_2O_3, and ZnO were used to deposit the *a*-IGZO films with different cation compositions using Ar plasma (0.7 Pa) without any additional gas. The composition ratios of the co-sputtered films were tuned by changing the input rf powers for the respective targets in a range of 100–200 W.[8] The films were grown at RT with a thickness of 150 nm. We measured the cation concentration ratios in the films using X-ray fluorescence (XRF). The values of the cation concentrations in the films were calibrated with the values from the three powder targets. The XRF results for total 11 samples are summarized in Fig. 1 with their respective number indexes. Samples 1–4 have Ga-rich compositions while samples 7 and 8 (samples 9–11) have Zn (In)-rich compositions. Sample 6 has the ratio of In:Ga:Zn = 1:1:1, i.e. $InGaZnO_4$. Its conductance was found to be closer to that of the Zn-rich samples (see Figs. 2 and 3). X-ray diffraction (XRD) measurement showed all samples except for sample 8 (the most Zn-rich one) were indeed amorphous.

We measured the resistance of samples 5 to 11 using silver epoxy contacts in a 4-probe geometry at T = 5 K – 300 K. And the electrical conductivities of the films were deduced from the values of the resistances assuming a homogeneous current within the full film thickness and width of the electrodes. On the other hand, for samples 1–4 we used a 2-probe geometry instead to improve the signal-to-noise ratios

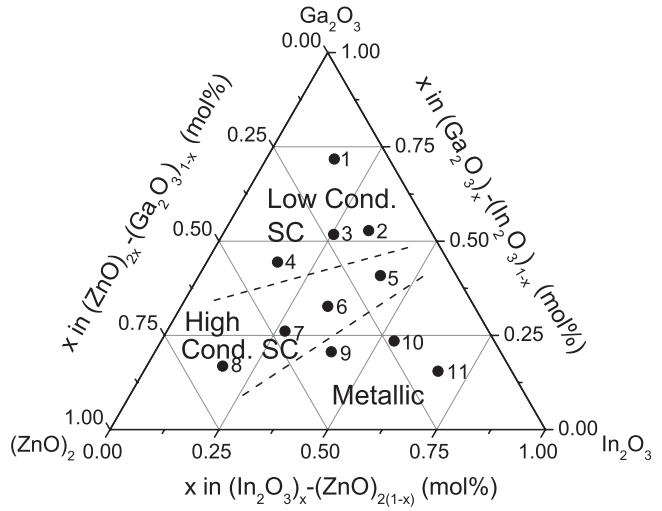

Figure 1. All 11 samples used for this work are shown with the respective indexes in the phase diagram of InO-GaO-ZnO. The cation compositions were measured by X-ray fluorescence. The electrical measurements (Figs. 2 and 3) reveal that the electrical conduction in the *a*-IGZO films vary significantly depending on the cation compositions from a metallic one to low-conductivity/high-conductivity semiconducting (SC) one.

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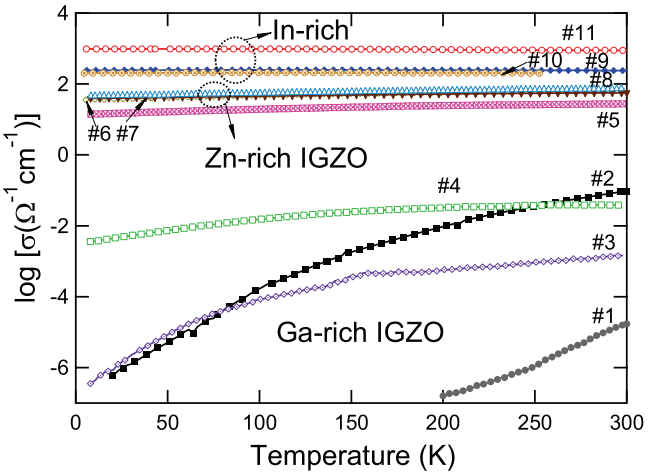

Figure 2. (Color online) log σ(T) is plotted as a function of T. The In-rich and Ga-poor samples show higher σ than the Ga-rich samples.

because of their very high resistance values (> MΩ). The resistance of the Cu leads and the silver epoxy contacts were found to remain below a few Ω's for all the T range. Since the resistance values of the samples are much higher than those of the leads as well as the contact resistances, we can obtain the resistance values of the samples approximately from the voltage and current values. To avoid a possible RS effect due to formation of local conducting channel in the film,[3,4] we limited the maximum current up to 0.1 mA by setting a compliance current level with monitoring an abrupt change in the output signal voltages. The samples were cooled down to 4 K using a He closed cycle refrigerator and the data points were collected while heating the samples to RT.

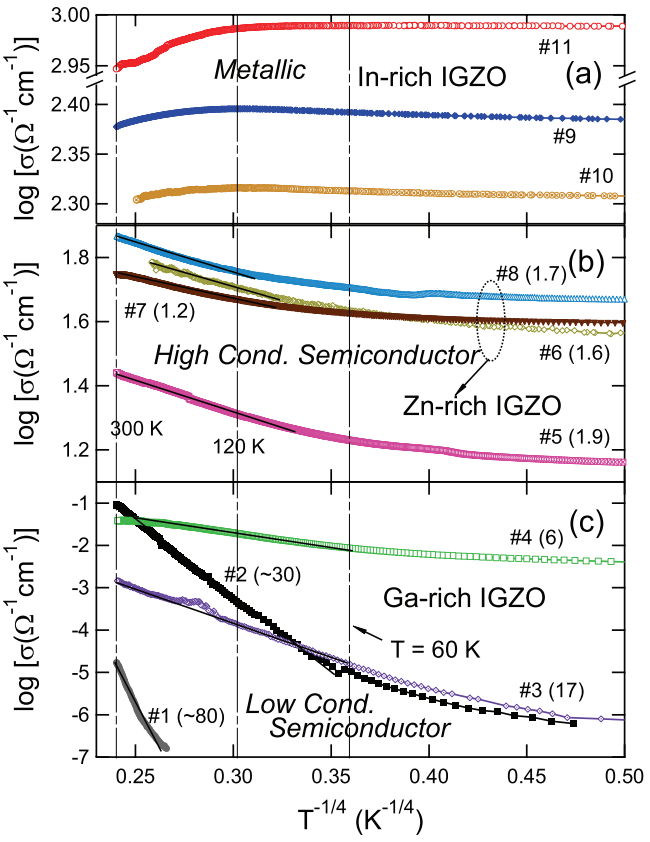

Figure 3. (Color online) log σ as a function of $T^{-1/4}$. (a) In-rich samples show (quasi-)metallic behaviors, (b) Ga-poor samples (Zn-rich samples and samples 5 and 6), a semiconducting behavior with high conductivity, and (c) Ga-rich samples, a semiconducting behavior with low conductivity. The numbers in parentheses are the values of the slopes (B's in Eq. 1) shown as solid lines. Overall, the linearity holds above T = 60 K.

Figure 2 shows the σ(T) of all the samples as a function of T. The values of the σ(T)'s in In-rich samples (samples 9–11), Zn-rich samples (samples 7 and 8), and $InGaZnO_4$ (sample 6) are high and show relatively weak T dependences, while those in Ga-rich samples (samples 1–4) are lower by more than 2 orders of magnitude and, at the same time, show strong T dependences. For the case of In-rich samples, the high conductivity can be understood easily by the small effective mass of In 5*s* electrons in the conduction band.[9] The weak T dependence reflects that the conductivity is dominated by band conduction in spite of the amorphousness of the films.[10] It can be further implied that the negative contribution of phonon scatterings to conduction is not significant within the experimental T range.

In contrast, the low σ in Ga-rich samples (samples 1–4) can be understood as to arise from insufficient density of states of such electrons seen in the In-rich samples. The decreasing σ with decreasing T reflects the insulating nature of the Ga-rich IGZO. Due to a smaller carrier density, the band conduction should be significantly limited so that the electron states can be highly localized.[10]

Interestingly, the values of the σ(T)'s in the Ga-poor samples (samples 5–8) appear to be as high as those of the In-rich samples (samples 9–11) but being more than 10^2 times higher than those of the Ga-rich samples (samples 1–4). The high conductivity in sample 5 could be rationalized by noting that the In concentration in sample 5 is comparable with that in sample 9, an In-rich sample (see Fig. 1). However, the In concentrations in the Zn-rich samples (samples 7 and 8) are low and even comparable to those in the Ga-rich samples. Therefore, their high σ(T)'s cannot be explained solely by the abundance of In 5*s* electrons as in the case of the In-rich samples.

Instead, we may assume that the abundance of Zn^{2+} ions can increase the conductivity. Regarding the conduction mechanism in IGZO, it has been proposed that the conductivity of amorphous IGZO is contributed by certain random formation of conduction channels.[10] A long-range electrical conduction is prohibited by energy barriers randomly distributed over the system but the conduction electrons are localized. However, if the electrons somehow become to overcome the energy barriers more easily, a percolative electrical conduction can be facilitated. In the IGZO system, the In^{3+} ions donate the conduction electrons and the randomly-mixed Ga^{3+}/Zn^{2+} ions possibly constitute the energy barriers. It is suggested that the electron hopping from In^{3+} ions to Zn^{2+} ions can be facilitated due to increased Zn concentration.[11]

Recent studies show that in some cases of zinc oxide-based TAOS such as *a*-IGZO or zinc tin oxide, the percolation conduction model[12] well explains the experimental results.[10,13,14] According to the percolation conduction model, logarithms of conductivity (σ) should be linear to $T^{-1/4}$ (Refs. 10 and 15), i.e.

$$\log \sigma = A - B\,T^{-1/4}, \qquad [1]$$

where 1/B is a measure of correlation radius of the conducting networks.[15]

Therefore, log σ(T) is plotted as a function of $T^{-1/4}$ in Fig. 3. In the case of In-rich samples [Fig. 3a], log σ(T) slightly decreases as T increases (or $T^{-1/4}$ decreases) at T > 120 K ($T^{-1/4}$ < 0.30). This confirms a metallic behavior, in which the phonon scattering effectively decreases the σ(T) as T increases. However, we can tell that the phonon scattering is not significant even at RT seeing that the drop of σ(T), namely, the values of |σ(120 K) - σ(300 K)|/ σ(120 K) are less than 10% for all the metallic IGZO films (samples 9–11). The slope [d(log σ(T))/d($T^{-1/4}$)] shows a weak transition across T ~ 120 K in Fig. 3a. It suggests that at T < 120 K, the phonon scattering has only marginal effect on σ(T). A tiny amount of decrease in conductivity with decreasing T at T < 60 K ($T^{-1/4}$ > 0.36) might be attributed to imperfect band conductions in the amorphous materials, so that we may consider their electrical properties "quasi"-metallic.

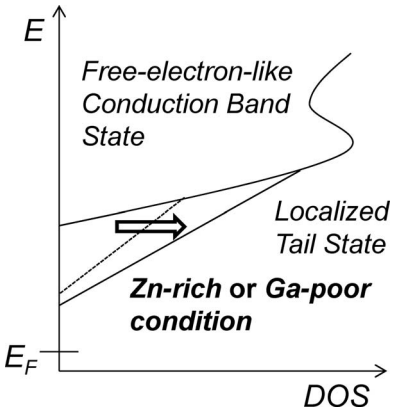

Figure 4. Schematic diagram of the conduction band DOS. A localized tail state is formed above the Fermi level (E_F) due to amorphousness. The feature of the tail state might be enhanced under the Ga-poor or Zn-rich condition (samples 5–8) to facilitate the hopping conduction.

In the cases of the samples other than metallic ones [Figs. 3b and 3c], it is shown by the fitting lines (solid) in the figures that the log σ increases almost linearly as $T^{-1/4}$ decreases at T > 120 K, roughly following the T dependence of the percolation conduction in semiconducting *a*-IGZO such as in $InGaZnO_4$ (Ref. 7). The σ(T)'s in samples 5–8 (Fig. 3b) increase significantly with the values of |σ(300 K) - σ(120 K)|/ σ(120 K) ∼ 25%, and those in samples 1–4 (Fig. 3c) increase even more (|σ(300 K) - σ(120 K)|/ σ(120 K) > 300%). The sharp increase of σ(T) with increasing T implies that the thermal excitation can drastically change the number of electrons. Therefore, the features near the bottom of the conduction bands (CB) must be quite spread in energy with a low density of states (DOS). This is very consistent with the scheme of long tail states near the CB minimum, which is usually employed for the localization picture of amorphous semiconductors.[10,15] The values of the slopes, B's in Eq. 1, are shown in the parentheses next to the sample indexes in Figs. 3b and 3c. The numbers alternatively represent the degree of localization of the conducting carriers.[15]

The relatively high conductivity in samples 5–8 (Fig. 3b) is consistent with the tendency of electron mobility increasing with Zn concentration in IGZO.[16] It should be noted that samples 5–8 have the T dependence of a semiconductor in spite of their high σ's. The negative slope with increasing $T^{-1/4}$ indicates that the number of carriers is not as large as that in a metallic system. Therefore, the high σ values in samples 5–8 might originate from increased mobility or enhanced electron hopping rather than the abundance in the carrier density itself. It is shown that the Ga-rich semiconducting samples (Fig. 3c) have larger B values (larger than 5) while samples 5–8 (Fig. 3b) have much smaller B values (less than 2). This clearly shows that samples 5–8 have higher CB DOS near the Fermi level than the Ga-rich samples being similar to the case of In-rich samples.

Figure 4 shows the schematic diagram of the CB DOS. The low energy part of the main CB is dominated by the In 5sp bands, which will contribute the free-electron-like conduction with electron energy of a few eV with respect to the Fermi level. A tail-like state is formed due to amorphousness of the IGZO system. The electrical conduction through this tail state is dominated by local hopping process rather than the band conduction due to limited electron mobility (Anderson localization). Our work demonstrates that in samples 5–8 (Ga-poor or Zn-rich) the electron hopping is enhanced considerably compared to the case of the Ga-rich samples. Therefore, it can be told that the DOS of the tail state should be increased under the Ga-poor/Zn-rich condition as depicted in Fig. 4.

At low temperature (below T = 60 K), the evolution in σ(T) of the semiconducting films becomes markedly weaker but lasts. The same tendency is also shown in metallic samples (Fig. 3a), suggesting that all the T dependences below T = 60 K might have similar origins such as impurities/defects or structural disorders in *a*-IGZO. This impurity scattering will be overcome more easily by the thermal energy resulting in an increase in σ(T) as T increases.

In conclusion, *a*-IGZO films show that various electrical characteristics are at work depending on the cation compositions in spite of their similar amorphous local structures; i) In-rich IGZOs – metal, ii) Ga-rich IGZOs- low conductivity semiconductor, and iii) Zn-rich IGZOs (including $InGaZnO_4$)- a different type of semiconductor with more than 10^2 times increased conductivity. The thermal electronic excitation to form percolative conducting networks contributes to the linearity of σ(T) to $T^{-1/4}$ above T = 60 K, while below the temperature, other scattering process such as certain impurity scattering might have importance at the low conductivity regime.

Acknowledgments

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