Two Types of Correlation between Donor-level and Concentration in a-IGZO

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ABSTRACT

We propose the presence of oxygen-related acceptors in amorphous oxide semiconductors (AOS) based on a new finding of two types of correlation, positive and negative, between carrier concentration and activation energy, and HAXPES experiments. This finding was explained in terms of donor–donor and donor–acceptor interaction, leading to operation of TFTs.

1 Introduction

Amorphous oxide semiconductor (AOS), specifically Indium-Gallium-Zinc-Oxide (a-IGZO), have been widely used in the flat-panel display industry due to their well-balanced properties such as high mobility (10–30 cm²/Vs), excellent uniformity, and ultra-low off current at low processing temperatures (< 400°C) [1]. In recent years, TAOS-TFTs has attracted attention for capacitor-free next-generation memory applications owing to their ultra-low off-current. They require ultra-thin (several nanometers), threshold voltage stability, and strict requirements for precise control of carrier concentration; however, the carrier generation mechanism in AOS remains still elusive: In a-IGZO, there exist not only shallow level defects but also very deep level defects above the VBM [2], thus control of these defects are generally almost impossible in amorphous semiconductors. For example, performance of TFT largely depends on high-density impurity hydrogen [3], excessive oxygen [4] and carbon impurities [5] derived from its fabricating process. Our next challenge is to clarify the energy levels of extrinsic species, such as impurities and defects, and control their formation for the stable operation of high-mobility AOS-TFTs.

Here, we conducted Hall effects on a-IGZO under various conditions as a function of temperature to elucidate the concentration and energy levels of thermally active shallow donors. Understanding the relationship between donor density and activation energy is a key to understanding the carrier generation mechanism.

In general, the activation energy in n-type semiconductors is negatively correlated with the donor concentration as shown in the following equation

\[ E_a(N_D) = E_a(0) - \alpha (N_D)^{1/3} \]  

(1)

where \( E_a \) and \( \alpha \) and \( (N_D)^{1/3} \) indicate activation energy for band conduction at very low doping level, constant for geometrical factors, average distance between ionized donors [6]. Conventional semiconductors and oxide semiconductors have \( \alpha > 0 \), which indicate increase of activation energy is due to attraction between ionized donors. That is, the donor concentration increases, separation between donors decrease, leading to the overlap of the donor orbitals. As a result, the bonding and anti-bonding interaction occurs, and the energy level of the upper orbital become shallower. However, if there is positive correlation or both of positive and negative correlation occurs for film thickness and post-annealing process, it would lead to have novel picture in AOS for TFTs.

In this study, we measured temperature dependent Hall effect in various a-IGZO thin films and Hard X-ray Photoelectron Spectroscopy (HAXPES) to observe the electronic states of a-IGZO. Based on these experimental results, we propose the presence of oxygen-related acceptor in a-IGZO.

2 Experimental Methods

a-IGZO films were deposited using RF magnetron sputtering without intentional heating. The deposition conditions included an RF power of 150 W and a total pressure of 0.4 Pa. Partial oxygen pressure \( \text{O}_2 / (\text{Ar} + \text{O}_2) \) was employed at 0.25% to 25%. The electrical properties of a-IGZO were investigated using AC field temperature dependence Hall effect measurement (ResiTest8400, Toyo Corp.). In general, carrier density is expressed as

\[ n_c = N_D \exp \left( \frac{E_a}{kT} \right), \]  

(2)

where \( n_c \), \( N_D \), \( E_a \), \( k \) and \( T \) denote carrier density, donor density, activation energy, Boltzmann constant and temperature, respectively. The carrier concentration, activation energy, pre-exponential factor \( n_0 \) are obtained from Arrhenius plots. Depth-resolved electronic structures were measured using HAXPES and X-ray total reflection (TR) [7] for the 10 and 100 nm thick a-IGZO samples at room temperature at the BL09XU undulator in SPring-8. HAXPES is used as a bulk-sensitive probing method owing to its long inelastic mean-free-path (λ) of photoelectrons than conventional soft X-ray PES. However, since photoelectrons from the substrate are
detected for ultra-thin films, it is necessary to decrease the detection depth. Characters of TR-HAXPES are 1) high photoelectron intensity, 2) improved surface sensitivity, and 3) significantly reduced background, making it possible to perform highly sensitive measurements on ultra-thin films. In addition, to eliminate the influence of surface-adsorbed molecules, we also conducted regular non-TR-HAXPES and depth-resolved TR-HAXPES measurements. The total energy resolution was set to 150 meV, and the binding energy was referred to the Fermi level of an Au plate. The effective mean-free-path of photoelectron ($\lambda_{\text{eff}}$) is tuned with incident angle of hard x-ray, according to the following equation:

$$
\lambda_{\text{eff}} = \frac{(\lambda_e \lambda_p)}{(\lambda_e + \lambda_p)}
$$

(3)

where $\lambda_e$, $\lambda_p$ and $\lambda_{\text{eff}}$ indicate elastic mean-free-path, attenuation length, effective inelastic mean-free-path. $\lambda_p$ in solids is larger than the $\lambda_e$ for a larger incidence angle. The critical angle ($\theta_c$) for the a-IGZO surfaces was detected by the reflected X-ray intensity, and the calculated $\theta_c$ of 0.425° was used for the calibration of the incidence angle. $\lambda_{\text{eff}}$ of 7.16 and 1.67 nm were taken at incidence angles of 1.50° and 0.31°, respectively. Then, probing depth is about 5 nm for both samples.

3 Results and Discussion

Fig. 1 shows the relationship between $N_D$ and $E_a$ calculated from the temperature dependence of the Hall effect. When the $P_{O2}$ during sputtering was reduced to increase the $V_D$, a decrease in $E_a$ was observed with an increase in $N_D$, as shown in the blue plot in Fig. 1. This is the behavior typically seen in common n-type semiconductors. The linear relationship between $N_D^{1/3}$ and $E_a$, indicating that this relationship is due to the interaction between $V_D$'s. As a-IGZO is fabricated with high $P_{O2}$ to reduce $V_D$, the deep donors appear below 0.12 eV from the conduction band minimum (CBM). By increasing $V_D$ by lowering $P_{O2}$, as shown in Fig. 2(a and b), average separation between donors is getting closer, causing the top of the occupied orbital become shallower due to orbital interaction. This $E_a$ shift continues until the donor levels become shallow near the CBM, eventually reaches degenerate state.

However, interestingly, when ultra-thin a-IGZO films, required for next generation memory applications, were fabricated, the $E_a$ showed a positive correlation with defect concentration, as shown in the red plot in Fig. 1. Increasing the film thickness from 20 to 200 nm results in a decrease in $N_D$ and $E_a$, from $1 \times 10^{19}$ to $2 \times 10^{17}$ cm$^{-3}$ and from 0.22 to 0.04 eV, respectively. Consequently, the carrier concentration increased from $2 \times 10^{15}$ to $7 \times 10^{16}$ cm$^{-3}$. Since the relationship between $N_D$ and $E_a$ is opposite to the donor–donor interaction, it is possible that an unoccupied acceptor level located just below the CBM, interact with a donor as shown in Fig. 2(c and d), results in a deepening of the occupied orbitals. This means the increase in $E_a$ with increasing $N_D$.

![Fig. 1. $E_a$ as a function of $N_D^{1/3}$. The points are evaluated by temperature dependence of Hall voltage. The dashed line shows experimental data from a-IGZO fitted by Eq. (1).](image)

![Fig. 2. Schematic illustrations of donor–donor interaction (a, b) and donor–acceptor interaction (c, d) models.](image)

The next question is, what is the origin of acceptor in a-IGZO? In order to induce defect-defect interactions, 1) the energy levels of donor and acceptor need to be close, and 2) the concentration of acceptors should be as high as that of the donor. Therefore, we conducted direct observation of electronic states of a-IGZO using surface-sensitive TR-HAXPES and bulk-sensitive non-TR-HAXPES. Fig. 3 shows the HAXPES spectra in the region of O 1s for two films [Fig. 3(a and b) for thickness of 100nm; Fig. 3(c) for 10nm]. As shown in Fig. 3 (a and b), there was no change in the oxygen peaks derived...
from surface adsorbed OH even when the probing depth was changed. Furthermore, since the surface area does not change in samples with different thicknesses, it can be seen that the change in electrical properties comes from the inside the thin film rather than the adsorbed molecules. Fig. 3 (b and c) show the thickness dependence of O1s core spectra with surface sensitive TR-HAXPES. The main peak is located around ~530 eV, while additional peaks appear at a larger binding energy around ~531 eV and ~532 eV range. The main peak observed corresponds to the 1s energy levels of the oxygen ions involved in the bonding between metals and oxygen (In − O, Ga − O, Zn − O). The sub-peaks around ~532 eV is attributed to film surface −OH bonds [8-10]. Note that a significant difference in the intensity of 531 eV between the 100 nm and 10 nm samples. These results suggest the existence of oxygen species which are more weakly bounded than lattice O2−.

The origin of O1s in oxide semiconductors is confusing, exemplified as large contribution of V O (if this assignment is correct, TFT should NOT work well!). Here, I like to emphasize that binding energy around ~531 eV has a possibility of oxygen-related acceptors as reported [11]. It is noted from the comparison between the 10 nm and 100 nm films higher signal intensity for oxygen-related acceptors in the thinner (10 nm) film. The presence of high concentration of oxygen-related species, which are detectable by HAXPES, can lead to interactions with donors. Possible candidates for oxygen-related acceptors include interstitial oxygen [4], O2− or O22−. According to our previous work [4], interstitial oxygen creates an unoccupied level just below the CBM. Also, the neutral charge level of O22− can create defect levels near the CBM. These results support the “positive slope” by donor-acceptor interaction.

Based on these results, we propose the formation of Frankel defects as shown in Fig. (4): As lattice oxygen displaces to interstitial sites, oxygen vacancies and interstitial oxygen pairs are formed, leading to the shift of donor levels. Note that, in case of amorphous oxide, interstitial sites are not only due to oxygen hopping, but also due to the metastable bond angles of point shared polyhedra frozen by non-equilibrium processes, unlike crystals. Frankel defect formation in amorphous SiO2 was identified [12] and the formation of Si-Si bonds associated with the Frankel defects has been observed. In the case of AOS, if Frankel defects are formed through this mechanism, In-In bonds may form between neighboring In atoms, potentially creating occupied defect levels within the bandgap. In TFT operation, these defects act as traps and deteriorate the ON characteristics of the transistor. In other words, even with the same carrier concentration, the stability of TFT operation should be significantly affected by the film thickness.

4 Conclusions

In this report, we found two types of correlation between N D and E g in a-IGZO and explained the shift in E g in terms of interactions between defects. Particularly in the ultra-thin film, the interaction of high-concentration donor-acceptor pairs leads to an increase in Nd and Eg, resulting in a suppression of ne. The presence of
oxygen-related acceptors is suggested from HAXPES O 1s. We propose the high concentrations of VO as donor and interstitial oxygen as acceptor are formed in thinner a-IGZO. Since, even the same concentration of \( N_d \), the dominant defect interaction is not the same. We need to notice this fact when the fabrication condition is tuned for the TFTs.

References


