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# Electronic transport properties of amorphous indium-gallium-zinc oxide semiconductor upon exposure to water

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The effect of water exposure on amorphous indium-gallium-zinc oxide (*a*-IGZO) semiconductors was reported. It was found that water can diffuse in and out of the *a*-IGZO film, reversibly affecting the transistor properties. Two competing mechanisms depending on the thickness of the active channel were clarified. The electron donation effect caused by water adsorption dominated for the thicker *a*-IGZO films ( $\geq 100$  nm), which was manifested in the large negative shift ( $>14$  V) of the threshold voltage. However, in the case of the thinner *a*-IGZO films ( $\leq 70$  nm), the dominance of the water-induced acceptorlike trap behavior was observed. The direct evidence for this behavior was that the subthreshold swing was greatly deteriorated from 0.18 V/decade (before water exposure) to 4.4 V/decade (after water exposure) for the thinnest *a*-IGZO films (30 nm). These results can be well explained by the screening effect of the intrinsic bulk traps of the *a*-IGZO semiconductor. © 2008 American Institute of Physics. [DOI: 10.1063/1.2838380]

Transparent oxide thin film transistors (TFTs) are of great interest for the applications in mobile electronics, optoelectronics, and future displays.<sup>1–4</sup> In particular, high performance amorphous indium-gallium-zinc oxide (*a*-IGZO) TFTs have been suggested for future electronics applications, which showed high mobility and a reasonable on/off ratio.<sup>1,4</sup> In particular, *a*-IGZO is expected to solve the native problems including the nonuniformity of low temperature polysilicon and poor mobility of amorphous silicon TFTs. However, before *a*-IGZO TFTs are integrated into commercial products, the materials' intrinsic capabilities and limiting factors, such as defects and environments, should be well understood. Especially the effect of the environmental humidity on oxide transistor is of importance because it might affect the transistor performance during and/or after the device fabrication.

Recently, a few research groups have reported that the adsorbed oxygen ( $O_2$ ) is strongly associated with the electrical performance of oxide transistors.<sup>5–8</sup> Gas molecules are known to play an important role in carrier transport even at room temperature. Moreover, severe degradation of the performance of organic transistors has frequently been reported under ambient environments.<sup>9–11</sup> Ambient conditions may cause the formation of hydrogen-related metastable hole traps in organic semiconductors.<sup>12</sup>

In this study, we investigated the effect of water ( $H_2O$ ) adsorption on the performance of *a*-IGZO transistors. It was found that  $H_2O$  adsorption on *a*-IGZO surfaces significantly influenced the important parameters of the TFTs, including the threshold voltage ( $V_{th}$ ), subthreshold swing (SS), and off current ( $I_{off}$ ), due to their charge transfer.

A schematic of the fabricated TFTs with the inverted and staggered structure is previously reported.<sup>13</sup> The MoW (150 nm) used as a gate layer was deposited and patterned by conventional photolithography on a glass substrate. A 200-nm-thick  $SiN_x$  layer was formed as a gate insulator by

plasma enhanced chemical vapor deposition. Then, the *a*-IGZO active layer (*a*-IGZO target;  $In_2O_3:Ga_2O_3:ZnO = 1:1:1$  mol %) was grown by rf sputtering on the  $SiN_x$ /glass. The deposition condition is as follows: a rf power of 200 W, a pressure of 5 mtorr, 10% of oxygen [ $O_2/(O_2 + Ar) = 0.1$ ], and room temperature. The active and source/drain (S/D) regions were patterned using photolithography and lift-off processes, respectively. The S/D electrodes were formed with rf sputtered Pt (100 nm)/Ti (10 nm). All of the fabricated TFT devices were heat treated in a furnace at 350 °C in a nitrogen atmosphere for an hour. The thickness of the *a*-IGZO layer was measured by spectroscopic ellipsometry. For the humidity experiments, all of the TFTs were dipped and kept in distilled water [100% relative humidity (RH)] overnight (12 h). Then, the electrical characteristics of the TFTs were measured in a vacuum chamber with a probe station and a heater chuck coupled with a semiconductor parameter analyzer (HP4156).

The transistors with a 70-nm-thick active layer [ $W/L = 200/4$   $\mu m$ ] were firstly exposed to 100% RH conditions for 12 h. Upon the exposure of the *a*-IGZO TFTs to the above humidity conditions, the  $V_{th}$  was largely negatively shifted ( $>10$  V) compared to that of the pristine transistor (not shown). Then, the *a*-IGZO transistors were put in a vacuum chamber and pumped down to  $5 \times 10^{-6}$  Torr. The heater chuck in the chamber was also kept at 100 °C. Figure 1(a) shows the evolution of the transfer curves [drain current ( $I_{DS}$ ) versus gate voltage ( $V_{GS}$ )] as a function of the heating time in the vacuum chamber. The  $V_{th}$  of the *a*-IGZO TFTs was gradually shifted in the reverse direction with increasing heating time. As shown in Fig. 1(c), a previous study reported that the adsorbed  $O_2$  molecules on *a*-IGZO TFTs undergo partial charge transfer (forming depletion layers below the active surface) and that the  $V_{th}$  systematically moves in the positive direction.<sup>5</sup> In contrast, the adsorbed  $H_2O$  molecules showed the reverse behavior to the adsorbed  $O_2$  molecules, suggesting that the role of the adsorbed  $H_2O$  mol-

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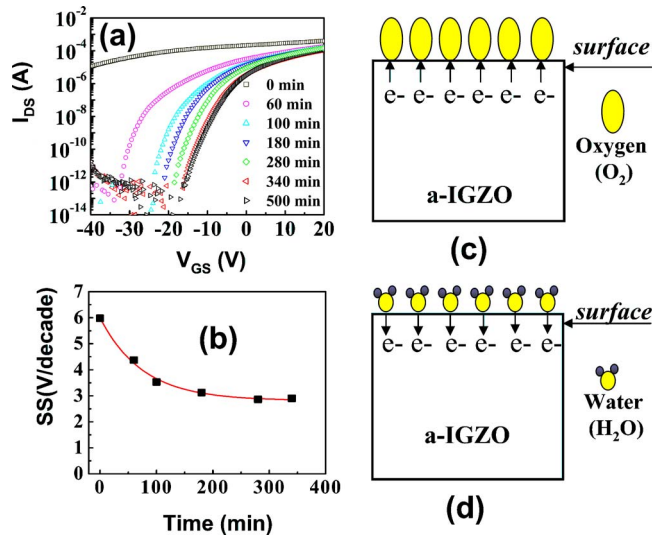


FIG. 1. (Color online) The evolution of (a) transfer curves and (b) SS value for *a*-IGZO TFT as a function of heating time in a vacuum chamber. The schematic diagram showing the role of (c) oxygen as an electron acceptor and (d) water molecules as an electron donor onto *a*-IGZO surface.

ecules seems to be to form an accumulation layer below the active surface [Fig. 1(d)].

Interestingly, the subthreshold gate swing also changed from 6.0 to 2.9 V/decade with increasing heating time, as shown in Fig. 1(b). This result indicates that the humidity process involves trap creation/removal in the active layer, which is in contrast to the result obtained for the O<sub>2</sub> molecules. Therefore, it is tentatively suggested that H<sub>2</sub>O molecules on or near the *a*-IGZO surface can act as electron trap centers, as will be discussed in detail below.

In order to obtain more information on the H<sub>2</sub>O-related behavior, the thickness effect of the active channel layer on the change of  $V_{th}$  and SS was investigated in detail, using various thicknesses, viz., 35, 70, 100, and 150 nm. Then, all of the TFTs were kept in 100% RH for 12 h. The transfer curves before and after the exposures to the above humidity conditions were compared. Figures 2(a) and 2(b) show transfer curves obtained with the 35-nm-thick and 150-nm-thick channels, respectively. The  $V_{th}$  for both devices shifted negatively after their exposure to humidity. Furthermore, the negative  $V_{th}$  shift was accompanied by the rapid increase of the leakage current from  $\sim 10^{-12}$  A to  $10^{-8}$ – $10^{-9}$  A. This suggests that H<sub>2</sub>O adsorption indeed donates a partial negative charge to the *a*-IGZO surface with either molecular or hy-

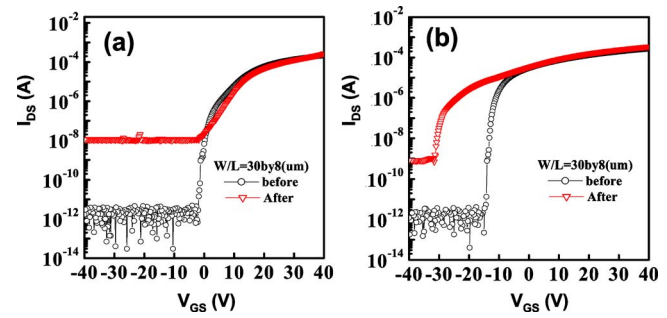


FIG. 2. (Color online) The comparison of the transfer curves before and after the water exposure for the device with (a) 35-nm-thick and (b) 150-nm-thick channels, respectively.

droxyl forms. The similar formation of extra electron carriers has been attributed to the donation of electrons (called the “donor effect”) from the chemically adsorbed H<sub>2</sub>O molecules to the surface of oxides such as ZnO.<sup>14–16</sup> It is quite reasonable to suppose that extra electrons, induced by H<sub>2</sub>O molecules, can form a back channel layer with a high electron concentration, leading to a more negative voltage (i.e., lower  $V_{th}$ ) so as to deplete the channel layer.

The  $V_{th}$  shift and SS degradation were greatly dependent on the thickness of the active channel, as summarized in Table I. As the active thickness increased from 35 to 150 nm, the negative  $V_{th}$  shift also increased. The  $V_{th}$  shift for the 35-nm-thick device was  $-2.0$  V, while that for the 150-nm-thick device was  $-18.4$  V. The density of net created electron charge in the whole channel due to H<sub>2</sub>O adsorption on the *a*-IGZO surface can be estimated from the extent of the  $V_{th}$  shift ( $Q_{induced} = C_i \Delta V_{th} / q$ , where  $C_i$  is the gate capacitance per unit area). The  $Q_{induced}$  values for the 35-nm-thick and 150-nm-thick devices were  $\sim 3.6 \times 10^{11}/\text{cm}^2$  and  $\sim 3.3 \times 10^{12}/\text{cm}^2$ , respectively. However, this result is hard to understand, because it is reasonable to assume that the concentrations of adsorbed H<sub>2</sub>O molecules on the *a*-IGZO surfaces of the two devices are similar to each other. On the other hand, the change in the SS value decreased with increasing channel thickness. The SS change for the 35-nm-thick device was 4.22 V/decade, while that for the 150-nm-thick device was 0.31 V/decade. The created trap density was calculated by the following equation ( $\Delta N_t = C_i \Delta S / [\ln(10)kT]$ ).<sup>17</sup> The H<sub>2</sub>O-related trap density also decreased with increasing channel thickness, as shown in Table I. The created trap densities for the 35-nm-thick and 150-nm-thick devices were  $\sim 1.3 \times 10^{12}/\text{cm}^2$  and

TABLE I. A comparison of the various parameters including  $\mu_{FE}$ ,  $V_{th}$ , SS,  $I_{on/off}$  ratio and  $Q_{induced}$ , and  $N_{created}$  for the four transistors ( $W/L=30/8 \mu\text{m}$ ) before and after water exposure. The mobility was extracted from maximum transconductance and the  $V_{th}$  was defined by the gate voltage, which induces a drain current of 10 nA at  $V_{DS}$  of 5.1 V. The SS value was calculated from the maximum linear portion of  $\log I_{DS}$  vs  $V_{GS}$  plot.

Active thickness (nm)	Water exposure	$\mu_{FE}$ ( $\text{cm}^2/\text{Vs}$ )	$V_{th}$ (V)	SS (V/decade)	$I_{on/off}$ ratio	$Q_{induced}$ ( $10^{11}/\text{cm}^2$ )	$N_{created}$ ( $10^{11}/\text{cm}^2$ )
150	Before	14.9	$-12.1$	0.19	$1.4 \times 10^8$		
	After	18.7	$-30.5$	0.50	$5.0 \times 10^5$	33.2	0.95
100	Before	18.8	$-5.34$	0.16	$4.8 \times 10^8$		
	After	19.4	$-20.0$	0.42	$4.6 \times 10^5$	26.4	0.79
70	Before	17.9	0.17	0.15	$8.4 \times 10^7$		
	After	20.1	3.83	2.00	$3.7 \times 10^5$	6.58	5.57
35	Before	18.2	0.21	0.18	$1.4 \times 10^8$		
	After	15.2	$-1.80$	4.40	$1.1 \times 10^4$	3.62	12.7



$\sim 9.5 \times 10^{11}/\text{cm}^2$ , respectively. It is worthwhile discussing the nature of the  $\text{H}_2\text{O}$ -related traps on the  $a$ -IGZO surface. The traps can be in either the tailing state (shallow) or deep-level state in the forbidden band gap of the  $a$ -IGZO semiconductor. The increase in the tailing state density is not the dominant mechanism causing the degradation of the SS value, because, if this were the case, the deterioration in the field-effect mobility would be observed (see Table I). Therefore, it is believed that the traps created due to  $\text{H}_2\text{O}$  adsorption are in the deep-level state. The deep-level state can be classified into acceptorlike and donorlike traps. We excluded the possibility of donorlike traps, since the creation of donorlike traps would cause a larger negative shift for a thinner device, which was not the case. Thus, the  $\text{H}_2\text{O}$ -related trap states are believed to show deep-level and acceptorlike behavior, although their chemical nature on or near the  $a$ -IGZO surface is not obvious at this time. Based on the above results, we speculated that the  $\text{H}_2\text{O}$  molecules can act either as electron donor or acceptorlike traps. In fact, the total densities of  $Q_{\text{induced}}$  and  $N_{\text{created}}$  were  $(1-4) \times 10^{12}/\text{cm}^2$  for all devices, as shown in Table I. The dominance of the donor density and acceptorlike trap density depends on the active channel thickness. As the active thickness of the  $a$ -IGZO transistor decreased, the acceptorlike traps overwhelmed the donor concentration. This can be understood by considering the concept of the screening length ( $\lambda$ ) over which the band bends to screen the applied gate field from the bulk of the semiconductor. The depth of band bending in an amorphous semiconductor with a high density of states is determined by the concentration of the intrinsic bulk trap density  $[\lambda(\epsilon_s/q^2N_t)^{1/2}]$ .<sup>18</sup> The bulk trap density of the  $a$ -IGZO channel was calculated from the SS values for the pristine transistors.<sup>18</sup> For the various devices, the screening length is estimated to be in the range of 78–81 nm. When the active thickness is larger than the screening length ( $t_{\text{active}} > \lambda$ ), the Fermi level near the back channel region is pinned when the gate voltage applied. Therefore, even though many acceptorlike traps are created, the created traps neither respond to the applied gate voltage as a trapping center, nor contribute to the gate swing change. This is why the thicker device (100, 150 nm) showed less degradation of the SS value. In the case of the thinner device ( $t_{\text{active}} < \lambda$ ), however, the change in the gate voltage causes band bending and the movement of the Fermi level simultaneously. Therefore, the acceptorlike traps strongly resulted in the deterioration of the SS value for the 35 and 70-nm-thick devices. Furthermore, the positive  $V_{\text{th}}$  shift, which was caused by the enhanced acceptorlike trap response, would be expected to compensate for the negative  $V_{\text{th}}$  shift due to the donor effect of some of the  $\text{H}_2\text{O}$  molecules. This hypothesis is verified by the fact that the  $V_{\text{th}}$  shifts for the device with the thinner channel (35, 70 nm) were much smaller ( $< 3.7$  V) than those for the device with the thicker channel (100, 150 nm).

It was observed that  $a$ -IGZO transistors are very sensitive to the surface adsorption of water and that their performance is easily deteriorated. The adoption of a passivation

layer on the  $a$ -IGZO channel prevented the degradation of the transistor characteristics under the severe humidity conditions (not shown).

In summary, we investigated the effect of water exposure on  $a$ -IGZO semiconductors with various active thicknesses. The water molecules reversibly diffused in and out of the  $a$ -IGZO thin film. While the adsorbed oxygen depleted the electron carriers on the  $a$ -IGZO film, the water molecules induced the formation of an accumulation layer of extra electron carriers. In addition, the adsorbed water can act as either electron donor or acceptorlike trap sites depending on the channel thickness. The  $V_{\text{th}}$  shift and SS change were greatly dependent on the thickness of the  $a$ -IGZO thin films: a large negative  $V_{\text{th}}$  shift ( $> 14$  V) and smaller SS changes ( $\leq 0.31$  V/decade) were observed for the thicker  $a$ -IGZO films ( $\geq 100$  nm), while for the thinner  $a$ -IGZO films ( $\leq 70$  nm), the  $V_{\text{th}}$  shift ( $< 3.7$  V) was strongly suppressed and the degradation of the gate swing ( $\geq 2.00$  V/decade) was enhanced. These results can be understood by considering the screening effect of the intrinsic bulk traps of the  $a$ -IGZO semiconductor. The knowledge of the details of the humidity effect on  $a$ -IGZO semiconductors can help to understand and improve the electrical properties of zinc-oxide-based transistors for future electronic applications.

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