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ABSTRACT
Transparent amorphous oxide semiconductors (TAOSs) based transparent thin-film transistors (TTFTs) with high field effect mobility (µFE) are essential for developing advanced flat panel displays. Among TAOSs, amorphous (a-) SnO₂ has several advantages against current a-InGaZnO₄ such as higher hFE and being indium-free. Although a-SnO₂ TTFT has been demonstrated several times, the operation mechanism has not been clarified thus far due to the strong gas sensing characteristics of SnO₂. Here we clarify the operation mechanism of a-SnO₂ TTFT by electric field thermopower modulation analyses. We prepared a bottom-gate top-contact type TTFT using 4.2-nm-thick a-SnO₂ as the channel without any surface passivation. The effective thickness of the conducting channel was ~1.7 ± 0.4 nm in air and in vacuum, but a large threshold gate voltage shift occurred in different atmospheres; this is attributed to carrier depletion near at the top surface (~2.5 nm) of the a-SnO₂ due to its interaction with the gas molecules and the resulting shift in the Fermi energy. The present results would provide a fundamental design concept to develop a-SnO₂ TTFT.

Transparent amorphous oxide semiconductors (TAOSs) based transparent thin-film transistors (TTFTs) with high field effect mobility (µFE) are essential components for advanced flat panel displays such as transparent organic light-emitting diode (OLED) displays and rollable OLED displays. Currently, amorphous (a-) InGaZnO₄ is widely applied as the TAOS of the TFT channel of commercially available OLED displays; the optical bandgap of a-InGaZnO₄ is ~3 eV, transparent in the visible light region, and the µFE of a-InGaZnO₄ (~10 cm² V⁻¹ s⁻¹) is two orders of magnitude higher than that of previously used a-Si. However, the use of a-InGaZnO₄ must be reduced because the consumption of rare element such as indium (Clarke number: 1%) is not desirable for maintaining sustainable usage of resources. Therefore, development of post-a-InGaZnO₄ TAOSs showing high µFE, which are composed of abundant elements, is crucial.

Among several indium-free TAOSs, a-SnO₂ is a promising candidate for overcoming the issues with a-InGaZnO₄. Sn is one of the abundant metal elements with the Clarke number of Sn which is 4 × 10⁻³%, 400 times larger than that of In. Moreover, SnO₂ TFT shows extremely high µFE > 100 cm² V⁻¹ s⁻¹,¹⁰–₁₂ which is one order of magnitude higher than that of a-InGaZnO₄. In 2007, Dattoli et al.¹⁰ reported that Ta-doped SnO₂ nanowire TFT exhibits uniform characteristics with average µFE exceeding 100 cm² V⁻¹ s⁻¹ at room temperature. In 2009, Sun et al.¹¹ fabricated SnO₂ nanocrystal TFTs at room temperature with µFE of 158 cm² V⁻¹ s⁻¹. In 2016, Shin et al.¹² reported that an extremely thin (<4.5 nm) undoped SnO₂ TFT exhibited µFE of 150 cm² V⁻¹ s⁻¹ at room temperature. In these reports, bottom-gate top-contact type TFTs were fabricated without any passivation showing high µFE. Thus, the top surface of SnO₂ channel was exposed to the atmosphere.

SnO₂ is a well-known gas sensing material.¹³,¹⁴ It is known that a-3–4-nm-thick depletion layer is formed at the SnO₂ surface. Oxygen molecules in the ambient atmosphere are adsorbed on the surface, seize free electrons near the surface, and form a depletion layer. In a reducing atmosphere, parts of the seized electrons are released back to the depletion layer. Thus, the transistor characteristics of the bottom-gate top-contact type SnO₂ TFTs would be strongly affected by the gases surrounding the exposed channel surface due to their gas sensing property. For this reason, the operation mechanism of the bottom-gate...
top-contact type SnO$_2$ TFTs including the conduction band bending and the effective channel thickness have not been clarified thus far.

Here we clarify the conduction band bending and the effective channel thickness of 4.2-nm-thick a-SnO$_2$ based bottom-gate top-contact type TFTs without any surface passivation. We analyzed the conduction band bending of the SnO$_2$ top surface by measuring the TFT characteristics in air and vacuum, and a large threshold gate voltage shift was observed; the Fermi energy in the carrier depletion region at the top surface (~2.5 nm) of the a-SnO$_2$ channel sensitively shifted with the changes in the gas atmosphere. The effective channel thickness ($t_{ch}$) was analyzed by the electric field thermopower ($S$) modulation method, and the $t_{ch}$ was $\sim$1.7 ± 0.4 nm in air and in vacuum. The present results would provide a fundamental design concept for developing a-SnO$_2$ TFTs.

The bottom-gate top-contact TFTs (Fig. 1) were fabricated on 100-nm-thick ITO coated alkali-free glass (thickness: 0.7 mm, Corning 100-nm-thick ITO coated alkali-free glass (thickness: 0.7 mm, Corning EAGLE XG) substrates by pulsed laser deposition (PLD, KrF excimer laser, 10 Hz) technique. First, a 300-nm-thick polycrystalline Y$_2$O$_3$ gate dielectric film (the dielectric permittivity, $\varepsilon_r = 20$) was deposited at room temperature. The fluence of the KrF laser was $\sim$2 J cm$^{-2}$ pulse$^{-1}$, and the oxygen pressure was kept at 0.4 Pa during deposition. Then, a 4.2-nm-thick SnO$_2$ film was deposited on the Y$_2$O$_3$/ITO bilayer laminate through a stencil mask at 300 °C [see supplementary material Figs. S1(a) and S1(b)]. The fluence of the KrF laser was $\sim$0.3 J cm$^{-2}$ pulse$^{-1}$, and the oxygen pressure was kept at 1 Pa during the deposition. The optical bandgap ($E_g$) of the a-SnO$_2$ film was $\sim$4.3 eV [supplementary material Fig. S1(c)], which was larger than that of bulk SnO$_2$ ($E_g$ $\sim$ 3.6 eV). This is most likely due to the quantum size effect. Finally, 100-nm-thick ITO films, which were used as the source and drain electrodes (400 μm × 400 μm), were deposited at room temperature. The fluence of the KrF laser was $\sim$0.9 J cm$^{-2}$ pulse$^{-1}$ and the oxygen pressure was kept at 3 Pa during deposition. After these PLD processes, the device was annealed at 400 °C for 30 min in air. The channel length $L$ and the channel width $W$ of the resultant TFT were 200 and 400 μm, respectively. The resultant multiple layer was fully transparent in the visible light region (supplementary material Fig. S2).

The TFT characteristics such as transfer characteristics ($I_{ds}-V_{gs}$) and output characteristics ($I_{ds}-V_{ds}$) were measured using a semiconductor device analyzer (B1500A, Agilent Co.) at room temperature. As shown in Fig. 2(a), the resultant TFTs showed clear transfer ($I_{ds}-V_{gs}$) characteristics with the on-to-off current ratios of $\sim$10$^5$. All the TFTs show clear pinch-off in the output characteristics [supplementary material Fig. S3], indicating that the TFT operation obeys the standard field-effect theory. It should be noted that the threshold gate voltage ($V_{th}$), which was evaluated by plotting $I_{ds}$ vs. $V_{gs}$, was $-14$ V in air but shifted dramatically to $-23$ V in vacuum. The $\mu_{FE}$ calculated from $\mu_{FE} = \frac{S \cdot W}{V_{th}^2}$, where $S$ is the thermoelectric power, $W$ and $V_{th}$ are also shown. The threshold voltage ($V_{th}$) is $-14$ V in air and $-23$ V in vacuum. The gate leakage current ($I_{ds}$) is $< 100$ pA. (b) Electric field modulated thermopower ($S$) at various $V_{ds}$ ranging from $+4$ V to $-37$ V. The $S$ gradually decreases with $V_{ds}$.
Table I. On-off current ratio, threshold gate voltage ($V_{th}$), subthreshold swing factor (S.S.), and field effect mobility ($\mu_{FE}$) for SnO$_2$/TTFT.

|          | $V_{th}$ (V) | S.S. (V decade$^{-1}$) | $\mu_{FE_{\text{max}}}$ (cm$^2$V$^{-1}$s$^{-1}$) |
|----------|-------------|-------------------------|----------------------------------|
| Air      | $\sim 10^5$ | $-14$                  | $0.65 \pm 0.02$                  | 20                        |
| Vacuum   | $\sim 10^5$ | $-23$                  | $1.57 \pm 0.2$                   | 30                        |

Atmospheres (air, vacuum) to analyze the $\tau_{\text{eff}}$. Details of the electric field modulated $S$ measurement are described elsewhere.$^{17-20}$ Figure 2(b) shows the changes in $–S$ as a function of the effective gate voltage ($V_g – V_{th}$). The $S$ values were always negative, consistent with the fact that the SnO$_2$ film is n-type semiconductor. The absolute values of $S$ decrease gradually with increasing $V_g – V_{th}$ in both atmospheres due to an increase in the sheet carrier concentration ($n_s$), which was deduced from $n_s = C/(V_g – V_{th})e^{-1}$. Although a small variation in $S$ was observed due to the gate leakage current ($I_{GS}$), the observed $S$ could be used to analyze the $\tau_{\text{eff}}$ since the variation is less than 10%, and the difference in the air and vacuum atmospheres is noticeably clear.

In order to extract the $\tau_{\text{eff}}$, we plotted $–S$ as a function of $n_s$ [Fig. 3(a)]. An almost linear relationship with a slope of $–120 \mu$V K$^{-1}$ decade$^{-1}$ was observed in the $–S$ vs $\log n_s$ plot when $n_s$ exceeded $2.5 \times 10^{12}$ cm$^{-2}$ in air, and a slope of $–84 \mu$V K$^{-1}$ decade$^{-1}$ was observed in the same plot when $n_s$ exceeded $2.9 \times 10^{12}$ cm$^{-2}$ in vacuum. We also plotted the three-dimensional carrier concentration ($n_{3D}$) dependence of $–S$ measured from separately prepared SnO$_2$ thin films [Fig. 3(b), Table S1]. From the $–S$ vs $\log n_{3D}$ relationship, the carrier effective mass ($m^*$) of the SnO$_2$ films was extracted to be 0.47 $m_0$ using the following equations:

$$s = \frac{k_B}{\pi} \left( \frac{r + \frac{5}{2}}{r + \frac{3}{2}} \right) F_{r+1}(\eta) - \eta,$$

$$n_H = \frac{1}{eR_H} = \frac{8\pi(2m^*_0k_BT)^{3}}{3h^3} \left( \frac{r + \frac{3}{2}}{2r + \frac{3}{2}} \right) F_{r+2}(\eta) - \eta,$$

$$F_{n}(\eta) = \int_{0}^{\infty} \frac{x^n}{1 + e^{x-\eta}} dx,$$

and the thickness of the SnO$_2$ films was extracted to be $4.7 \pm 0.4$ nm, insensitive to the gas atmosphere.

Below the original conduction band bottom.$^{18,22,25}$ The $S$ and $n_s$ were modulated from ($–150 \mu$V K$^{-1}$, $2 \times 10^{12}$ cm$^{-2}$) to ($–80 \mu$V K$^{-1}$, $1 \times 10^{13}$ cm$^{-2}$) in air and from ($–110 \mu$V K$^{-1}$, $2.9 \times 10^{12}$ cm$^{-2}$) to ($–60 \mu$V K$^{-1}$, $1.3 \times 10^{13}$ cm$^{-2}$) in vacuum with increasing positive electric field in the a-SnO$_2$ channel. The difference between the measurements in air and in vacuum is attributed to the gas sensing property of SnO$_2$, where O$_2$ molecules are adsorbed in air and released in vacuum. The $\tau_{\text{eff}}$ $\equiv n_s/n_{3D}$ of the conducting a-SnO$_2$ channel were always $\sim 1.7 \pm 0.4$ nm, insensitive to the gas atmosphere [Fig. 3(c)].

FIG. 3. Electric field thermopower modulation analyses of the bottom-gate top-contact a-SnO$_2$ TTFT. (a) Change in $–S$ as a function of the sheet carrier concentration ($n_s$). The slope of the $–S$ vs log $n_s$ relationship is $–120 \mu$V K$^{-1}$ decade$^{-1}$ in air and $–84 \mu$V K$^{-1}$ decade$^{-1}$ in vacuum (dotted line). (b) Three-dimensional carrier concentration ($n_{3D}$) dependence $S$ of the SnO$_2$ films. We calculated the carrier effective mass ($m^*$) of the SnO$_2$ film around 0.47 $m_0$. (c) The effective thickness ($\tau_{\text{eff}}$), which is defined as $n_s/n_{3D}$, as a function of $V_g$. The $\tau_{\text{eff}}$ is always $\sim 1.7 \pm 0.4$ nm, insensitive to the gas atmosphere.
Here, we would like to discuss the operation mechanism of a-SnO2 TFT [Fig. 4]. Without any $V_g$ application [Fig. 4(a)], the conduction band minimum (CBM) at the surface is lifted due to the adsorption of oxygen when the TFT is exposed to air (higher oxygen atmosphere, black line). When the TFT is exposed to vacuum, the CBM at the surface is lowered (lower oxygen atmosphere, red line). The 2.5-nm-thick 2D electron gas (2DEG) layer is formed at the Y2O3/SnO2 interface. The $n_i$ increases up to $\sim 1 \times 10^{13}$ cm$^{-2}$ (thickness of 4.2 nm). Under positive $V_g$ application [Fig. 4(b)], the carriers accumulate at the Y2O3/a-SnO2 interface, and the $E_F$ locates above the CBM. As a result, the 1.7-nm-thick 2D electron gas (2DEG) is formed at the Y2O3/a-SnO2 interface. The $n_i$ increases up to $\sim 1 \times 10^{16}$ cm$^{-2}$ ($n_{3D} \sim 4 \times 10^{14}$ cm$^{-2}$). The surface region does not change. (c) Under negative $V_g$ application, the interface electrons are completely depleted, resulting in off states.

See the supplementary material for additional crystallographic analyses of the SnO2 thin film, optical transmission of the bottom-gate top-contact a-SnO2 TFT, transistor characteristics of the bottom-gate top-contact a-SnO2 TFT, and optical absorption spectrum of the polycrystalline Y2O3 thin film deposited on the SiO2 glass substrate.

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