Si-incorporated amorphous indium oxide thin-film transistors

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Amorphous oxide semiconductors, especially indium oxide-based (InOx) thin films, have been major candidates for high mobility with easy-to-use device processability. As for a dopant in an InOx semiconductor, we proposed Si as a strong oxygen binder to design a thin-film transistor (TFT) channel for the suppression of unstable oxygen vacancies in InOx. In this review, we focus on the overall properties observed in Si-incorporated amorphous InOx TFTs in terms of bond-dissociation energy, Gibbs free energy, Si-concentration dependence, carrier transport mechanism, and bias stress instability. In comparing low and high doping densities, we found that the activation energy and density of states decreased at a high Si concentration in InOx TFTs, implying that the trap density was reduced. Furthermore, the inverse Meyer-Neidel rule observed in the highly Si-doped InOx TFT indicated reasonable ohmic contact. With simple element components based on InOx, it is possible to systematically discuss vacancy engineering in terms of conduction properties.

1. Introduction

High-mobility thin-film transistors (TFTs) are in high demand for high-speed switching operations in next-generation large-area flat panel displays (FPDs). The typical field-effect mobility of hydrogenated amorphous silicon (a-Si:H), which is extensively used for TFT backplanes in liquid crystal displays, is limited to $<1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Electron transport is strongly perturbed in the conduction band of Si, where carrier transport paths consist of sp³ orbitals with strong directivity. The resulting bond angle fluctuation significantly alters the electronic levels, leading to high density trap states. On the other hand, although the fabrication process is compatible with conventional amorphous-Si TFTs, amorphous indium oxide (InOx) has far superior electrical properties compared with a-Si:H, owing to its unique carrier transport properties. The conduction bands in InOx-based materials are known to originate from the 5s orbital of In atoms, and the spherically spreading orbital suppresses the perturbing effect. It is widely believed that InOx-based thin-films have advantages in mobility over a-Si:H films. Furthermore, since metal oxides exhibit deformability of the amorphous phase and low temperature processability, flexible and transparent TFTs with reliable operation can be fabricated on plastic substrates if metal oxide materials are used for the active and dielectric layers and the electrodes. Thus, InOx-based TFTs are expected to be the most promising candidates for next-generation switching TFTs.

There have been many reports on InOx-based TFTs such as In–O, In–Al–O, In–Ga–O, In–Ge–O, In–Hf–O, In–Si–O (ISO), In–Sn–O (ITO), In–W–O (ITO), In–Zn–O (IZO), In–B–Zn–O, In–C–Si–O, In–C–W–O, In–C–Zn–O, In–Ga–Zn–O (IGZO), In–Hf–Zn–O, In–Sc–Zn–O, In–Si–W–O, In–Si–Zn–O, In–Sn–Zn–O, In–Ta–Zn–O, In–W–Zn–O, and In–Zr–Zn–O.

Recently, we proposed that W- and/or Si-doped InOx is suitable for high-mobility TFTs with preferable stable electrical behavior. The homogeneous bilayer TFT developed based on the results showed field effect mobility of 19.6 cm² V⁻¹ s⁻¹, and the shifts of turn-on voltages (V_ON) under positive and negative bias stress instability measurements were 0.2 and 0.8 V, respectively. The successful demonstration above the high mobility and stability is due to the control of the VO formation. An appropriate oxygen binding dopant is required to obtain such reliability. Here, we report our concept of dopant selection in InOx semiconductors from the viewpoint of bond-dissociation energy. Then, electrical properties and electron transport in the Si-incorporated amorphous InOx TFTs based on Si-concentration dependence and temperature dependent I–V characterization are discussed. Finally, the aforementioned bilayer TFT is introduced in high-performance operation.

2. Device fabrication and characterization

Our TFTs for electric characterization were fabricated by the following typical procedure. The InOx-based TFTs were fabricated on a heavily doped p-type Si substrate with a thermal SiO₂ layer. The substrate was first cleaned using a process of ultrasonication in acetone and isopropyl alcohol,

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2. Device fabrication and characterization

Our TFTs for electric characterization were fabricated by the following typical procedure. The InOx-based TFTs were fabricated on a heavily doped p-type Si substrate with a thermal SiO₂ layer. The substrate was first cleaned using a process of ultrasonication in acetone and isopropyl alcohol,
followed by UV-ozone exposure. An InOx-based semiconductor film with a thickness of 10 nm was then deposited by DC magnetron sputtering at room temperature with various O2/Ar + O2 ratios. The sputtering power and working pressure were optimized depending on the sputtering target compositions. We emphasize that all sputtering targets used in our study were completely Zn-free. The channel width (W = 1000 μm) was defined by using a stencil shadow mask. After deposition, the post annealing process was performed. Source and drain electrodes (40 nm) were formed by vacuum evaporation (thermal or electron beam) through a stencil shadow mask, which defined the channel lengths (L) from 50 to 350 μm with an interval of 50 μm. The devices had a simple bottom-gate top-contact TFT configuration without any passivation layer.

The channel thickness was confirmed with an ellipsometer, and the film morphology was observed by atomic force microscopy (AFM) in tapping mode. The electrical characteristics of the fabricated TFTs were measured in the dark at room temperature using a precision semiconductor parameter analyzer (Agilent 4156C) connected to a probe station placed in a high vacuum chamber. After the characterization, a series of TFT parameters, i.e., field-effect mobility in the linear regime ($\mu_{FE}$), saturation field-effect mobility ($\mu_{sat}$), subthreshold swing (ss), and $V_{ON}$, on- and off-state current ratio ($I_{ON}/I_{OFF}$) were obtained. The $\mu_{FE}$, $\mu_{sat}$ and ss were extracted using the following equations:

$$\mu_{FE} = \frac{\partial I_D}{\partial V_{GS}} \frac{L}{W C_i V_{GS}},$$

$$\mu_{sat} = \left(\frac{\partial I_D}{\partial V_{GS}}\right)^2 \frac{L}{W C_i},$$

$$ss = \left(\frac{\partial \log_{10} I_D}{\partial V_{GS}}\right)^{-1},$$

where $L$ and $W$ are the channel length and width, respectively, and $C_i$ is the gate capacitance per unit area.

3. Strategies for choosing dopants in the InOx semiconductor

3.1. W-doping using acid insoluble WO3

We first focus on W-doped InOx (ITO), since the constituent WO3 is insoluble in acids except for hydrogen fluoride solutions. IWO is known as transparent conductive oxide films.61–64 Although there have been several studies on IWO electrodes for organic light-emitting diodes,65 organic solar cells,66 and flexible carbon-nanotube transistors,67 reports focusing on the significant semiconducting properties of this material are limited.68–71

Figure 1(a) shows a schematic TFT structure. The inset is a roughness profile of the IWO film observed by AFM after annealing three times at 100 °C for 5 min in N2, using rapid thermal anneal equipment. The use of N2 annealing is due to the improvement of TFT properties as has been reported for IGZO.72,73 In this case, the In2O3/WO3 ratio in the IWO target was 99/1 wt%. The root mean square (RMS) roughness measured was 0.27 nm, indicating that the surface was almost as flat as the Si substrate (0.24 nm). X-ray diffraction (XRD) and cross-sectional transmission electron microscopy (TEM) together with selected area electron diffraction indicate that the IWO film remained amorphous after the annealing treatment. The ionic radii of W6+ and In3+ are 0.06 and 0.08 nm, respectively, for the same coordination number.74 This difference is known to induce a distortion in InOx crystals; thus, the structural role of W atoms in InOx is of amorphization, leading to a very flat and smooth surface. Figures 1(b) and 1(c) show typical output ($I_D$ vs $V_{DS}$) and transfer ($I_D$ vs $V_{GS}$) characteristics. A clear pinch-off behavior, small hysteresis (∼0.7 V) and low $I_{OFF}$ ($I_{OFF}^{-1} \sim 10^{-14}$ A) can be seen. At $V_{DS} = 40$ V, the estimated $\mu_{sat}$, $I_{OFF}/I_{ON}$ and ss are 19.3 cm2 V−1 s−1, 8.9 × 109, and 0.47 V decade−1, respectively. The $\mu_{sat}$ value was calculated using Eq. (2). The $C_i$ in this case is estimated to be 1.73 × 10−8 F cm−2 based on a dielectric constant of 3.9 for SiO2.

3.2. Bond-dissociation energy with oxygen

A target of the IWO TFT development was to realize a stable TFT without a passivation layer by using acid resistant oxides. Fortunately, W–O binding has strong bond-dissociation energy (BDE) and is more rigid to acid. For further effective BDE elements, we use three elements, W, Ti, or Si, that have high BDE and compare InOx-based films doped with these elements. We demonstrate that considering the BDE is useful when selecting appropriate dopants for InOx-based semiconductors.

The Ti-, W-, and Si-doped InOx sputtering targets contained 1 wt% TiO2, WO3, and SiO2, respectively, hereafter denoted ITiO, IWO, and ISO, respectively. After the sputtering deposition of these channel layers at various oxygen partial pressures ($P_{O2}$), an Au source/drain electrode was formed.167 Figure 2 shows the electrical conductivity of the as-deposited films as a function of the $P_{O2}$ used during sputtering deposition. Each value was extracted from the linear region of the output characteristics when carriers are highly induced ($V_{GS} = 30$ V). Similar to other oxide semiconductors such as IGZO75,76 and ZnO,77 the electrical conductivity of the InOx-based films depends on the $P_{O2}$; this behavior is caused by the strong dependence of the carrier concentration during deposition.8,78 Although the dopant concentration is only 1 wt%, the choice of dopant species strongly affects the electrical conductivity. For the ITiO, the electrical conductivity changes significantly based on $P_{O2}$; however, this behavior does not occur in the ISO film. The effect of Si is greater than that of Ti because the atomic ratio of In:Si:O in ISO and In:Ti:O in ITiO are 38.9:9.0:9:60.2 and 39.2:0.7:60.1, thus, the percentages of dopant content in In (Si/In and Ti/In) are 2.3 and 1.8%, respectively. On the other hand, the percentage of W/In (In:W:O = 39.6:0.2:60.1) is 0.6%, and even though ratio is much smaller than that of Ti, the change in conductivity is rather small. The ISO exhibits the most stable electrical conductivity among the three films, indicating that the slope of the electrical conductivity as a function of the $P_{O2}$ could be related to the BDE of the dopant. The BDE is defined as the strength of the chemical bond determined when a diatomic species decomposes into individual atoms. If the energy of the metal-to-oxygen bond (X–O, where X is the dopant material) is low, then oxygen can be easily released, which increases the carrier density.8,42 In contrast, if a dopant with a high BDE is introduced to InOx, we expect the electrical properties of the
oxide film to be more stable over the range of $P_{O_2}$ used during deposition (the inset of Fig. 2). The conductivity slopes become flatter in the order of ITiO, IWO, and ISO, which corresponds to the order of their BDE: 666.5, 720, and 799.6 kJ mol$^{-1}$ for Ti–O, W–O, and Si–O respectively. These changes in the conductivity strongly support that the BDE can be used to determine the role of the dopant in InO$_x$-based semiconductors.

Figures 3(a)–3(f) show the typical electrical properties of the fabricated TFTs annealed at 150 °C in air. Figures 3(a), 3(c), and 3(e) show the output characteristics ($I_D$–$V_{DS}$) for the three TFTs, each with a different dopant. The transfer
characteristics ($I_D-V_{GS}$) in the saturation region ($V_{DS}=30$ V) for ITiO, IWO, and ISO have negligibly small hystereses and high $I_{ON}/I_{OFF}$. The transistor properties observed in three TFTs are summarized in Table I. The $\mu_{sat}$ are 32, 30, and 17 cm$^2$ V$^{-1}$ s$^{-1}$ for the TFTs fabricated using the ITiO, IWO, and ISO targets, respectively. The field-effect mobility for ISO is slightly suppressed, which may be due to the incorporation of the strong binder Si into InO$_x$. However, the comparison of precisely controlled W and Si dopant concentrations shows that the mobility of ISO is higher than

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**Fig. 3.** (Color online) Typical output and transfer characteristics of fabricated TFTs: (a), (b) ITiO, (c), (d) IWO, and (e), (f) ISO. The devices were annealed at 150 °C in air. The TFTs were measured at room temperature in the dark under ambient atmosphere. The TFT dimensions include a channel length $L$ of 350 $\mu$m, a channel width $W$ of 1000 $\mu$m, and a gate capacitance per unit area $C_G$ of $1.21 \times 10^{-8}$ F cm$^{-2}$ (based on a dielectric constant of 3.9 for SiO$_2$). Adapted with permission from Ref. 18. Copyright 2013. AIP Publishing LLC.
that of IWO\textsuperscript{57}) because Si has a smaller ionic radius than W regardless of coordination number or valence state,\textsuperscript{82}) suggesting that the scattering cross section of Si is smaller than that of W.\textsuperscript{31}) In addition, the most significant scattering in InO\textsubscript{x} systems is ionic scattering.\textsuperscript{83}) A charge carrier screening effect in which the Coulomb potential of the ion core hole creates localized trap states by pulling an orbital out of the conduction band\textsuperscript{84,85}) is reduced in an ionic scattering source.\textsuperscript{86}) Thus, the higher mobility of the ISO may have been obtained because a higher carrier density is induced in the ISO compared with the IWO at the same \( V_{\text{GS}} \)\textsuperscript{26}) Parthiban and Kwon reported that dopants with high Lewis acid strength effectively enhance charge carrier screening.\textsuperscript{26}) Such dopants polarize electronic charges away from the 2\textit{p} valence band, where the polarity is dependent on the Lewis acid strength. Because Si\textsuperscript{4+} has a higher Lewis acid strength (8.096) than W\textsuperscript{6+} (3.158), the higher mobility realized by the charge carrier screening is confirmed to be compatible with the discussion regarding the Lewis acid strength of the dopants.

By comparing the mobilities of IGZO and IZO, it is reasonable that the lower mobility of IGZO could be caused by the incorporation of Ga, as suggested by Kamiya et al.\textsuperscript{7}) In IGZO, Ga-incorporation effectively stabilizes the TFT electrical properties because the BDE of Ga–O is 374 kJ mol\textsuperscript{–1}, a value slightly higher than that of In–O.\textsuperscript{87}) Thus, a large amount of Ga is needed in IZO for stabilization of the electrical properties. On the other hand, we examined the improvement of electrical stability by using dopants with higher BDE. The ISO fabricated TFT had higher electrical stability after annealing, even though the dopant density was rather low (1 wt%).\textsuperscript{18}) According to first-principle calculations,\textsuperscript{88}) the electrical stability of amorphous oxide semiconductors can be effectively controlled by incorporating Si, because the formation of \( V_O \) can be suppressed by the strong binding of Si–O.

4. Si-concentration dependence in ISO TFTs

4.1. Series of TFT parameters

We consider the doping effect of Si in InO\textsubscript{x} films. For systematic understanding, we prepared three sputtering targets with different Si concentration; 3, 5, and 10 wt% SiO\textsubscript{2}, denoted ISO-3, –5, and –10, respectively. The films were fabricated at common conditions: DC sputtering was performed at a sputtering power of 200 W under an Ar/O\textsubscript{2} atmosphere at 0.25 Pa with various \( P_{\text{O2}} \). Then, the films were annealed at 250 °C for 30 min in air. After deposition of the Table I. Comparison of typical TFT properties estimated from the transfer characteristics presented in Fig. 3. \( I_{\text{ON}}/I_{\text{OFF}}\) is defined as the ratio of the maximum \( I_D \) to the minimum \( I_D \) in the graph (\(-20 \leq V_{\text{GS}} \leq 40 \) V). \( V_{\text{ON}} \) is defined as the \( V_{\text{GS}} \) at which \( I_D \) begins increasing. Adapted with permission from Ref. 18. Copyright 2013. AIP Publishing LLC.

| SiO\textsubscript{2} content (wt.%) | \( I_{\text{ON}}/I_{\text{OFF}} \) | \( V_{\text{ON}} \) (V) | \( \mu_{\text{sat}} \) (cm\textsuperscript{2} V\textsuperscript{–1} s\textsuperscript{–1}) |
|-------------------------------------|-----------------|-----------------|---------------------|
| ISO                                | 4.8 \times 10\textsuperscript{9} | 0.29            | 0.00                |
| IWO                                | 5.2 \times 10\textsuperscript{9} | 0.46            | –6.3               |
| ITIO                               | 9.4 \times 10\textsuperscript{9} | 0.30            | –4.0               |

Fig. 4. (Color online) Typical transfer characteristics of the ISO-3 (a) and ISO-10 (b) TFTs. Electrical properties of ISO TFTs over various SiO\textsubscript{2} contents and oxygen partial pressures during sputtering, showing changes in (c) \( \mu_{\text{FE}} \), (d) \( I_{\text{OFF}} \) and \( I_{\text{ON}} \) (blue) (e) \( \mu_{\text{sat}} \), and (f) \( V_{\text{ON}} \). The dotted lines are guides for the eyes. The electrical measurements were performed at room temperature in the dark under high vacuum (~10\textsuperscript{–4} Pa). Adapted with permission from Ref. 19. Copyright 2014. AIP Publishing LLC.
Mo source and drain electrode, the devices were again annealed at 150 °C for 30 min in air and then at the same temperature for 5 min in O2.

X-ray diffraction characterization showed that all the films were in the amorphous phase against thermal treatments up to 350 °C. The crystallization temperature of the films became higher as the SiO2 content ratio in ISO increased. The ISO-10 films were not crystallized even after thermal annealing at 600 °C. Because no Si clusters were observed, Si atoms were uniformly dispersed in an In2O3 matrix.89) Figures 4(a) and 4(b) are typical transfer characteristics of the ISO-3 and ISO-10 TFTs. As shown in Fig. 4(c), a series of TFT parameters (µFE, IOFF, ION, ss, and VON) can be obtained as a function of SiO2 content at various PO2 from the linear region in the transfer curve.

The energy levels of In atoms with dangling bonds, i.e., VO, are formed near the conduction band edge, which acts as a shallow donor state. The formation of VO is suppressed by the mixture ratio of Ar/O2 during sputtering.92,93) The suppression of VO in the ISO with high SiO2 content allows the small amount oxygen during sputtering to compensate the oxygen-deficient sites. We also clarify that the W has the same role as VO suppressor, but the thermotolerance is much different because of the different BDE of W.23)

4.2. Comparison of low and high Si concentrations

For a better understanding of the role of Si, two TFTs of ISO-3 and ISO-10 are compared. To adjust the VON to be 0 V, the PO2 was optimized; O2/(Ar + O2) = 50% for ISO-3, and O2/(Ar + O2) = 8.3% for ISO-10. The bias stress instabilities were measured against VGS = ±30 V for up to 3 h (Fig. 5). The lack of degradation in the ss values suggests that unstable defects were highly suppressed in the ISO film. Negative shifts in the VON, which are attributed to depopulation of donor-like traps, were observed in all the devices.95) Although a positive shift in VON originating from charge trapping in the gate insulator under continuous positive bias stress (PBS) has been commonly observed in oxide semiconductor systems,96,97) no positive shift was obtained for the ISO, indicating that the incorporation of SiO2 into In2O3 effectively reduces charge trapping.

The negative shift observed in VON under PBS is considered to be triggered by Joule heating and the hot carrier effect.98,99) The application of higher VGS for a longer time resulted in a larger shift in the VON. The shift of VON is related to the trap densities at the semiconductor/insulator surface (N5) and the bulk of the film.95) The N5 can be approximated from the ss value using the following equation:100)

\[
N_5 = C \left( \frac{(ss) \times \log_{10}e}{k_B T} - \frac{1}{q} \right),
\]

where \(e, k_B, T\), and \(q\) are the Napier constant, Boltzmann constant, absolute temperature, and elementary charge, respectively. For the ISO-3 and ISO-10 at 20 °C, N5 of 2.50 × 1011 cm\(^{-2}\) and 1.08 × 1011 cm\(^{-2}\) are obtained, respectively. The observed VON shifts in ISO-3 were approximately 10 times larger than those in ISO-10. Then, the trend of the
shift in $V_{ON}$ observed could be proportional to the trap density at the semiconductor/insulator interface.

The activation energies of the charge carriers were investigated through temperature-dependent electron transport to clarify the origin of the bias stress instability. Transfer curve measurements were carried out at different temperatures, ranging from 35 to 55 °C, with a $V_{DS}$ of 1 V. Figures 6(a) and 6(b) are the Arrhenius plots of $I_D$ versus $1/k_B T$ of ISO-3 and ISO-10 under various $V_{GS}$. Thermal activation of $I_D$ was clearly observed in the subthreshold region. Negative shifts of 5.6 and 2.0 V in $V_{ON}$ were observed for ISO-3 and ISO-10, respectively. The smaller shift in $V_{ON}$ suggests that higher SiO$_2$ incorporation suppressed the charge carrier excitation under thermal stresses. The $I_D$ obeyed the Arrhenius relationship as follows:

$$I_D = I_{D0} \exp \left( \frac{E_a}{k_B T} \right),$$

where $I_{D0}$ is the prefactor and $E_a$ is the activation energy for charge carriers. $I_{D0}$ were almost constant irrespective of $V_{GS}$ above the threshold regions. In general, $I_{D0}$ and $E_a$ are correlated in disordered systems. The relationship is given by the Meyer-Neldel (MN) rule as follows:

$$I_{D0} = I_{D0} \exp \left( \frac{E_a}{E_{MN}} \right),$$

where $E_{MN}$ is the MN energy. $I_{D0}$ and $E_a$ can be extracted from the Arrhenius plots and their relation is shown in Fig. 6(c). $E_a$ as a function of $V_{GS}$ drastically increased in the subthreshold region. $E_a$ corresponds to the difference between the Fermi level $E_F$ and the conduction band edge $E_C$ at absolute zero. $E_F$ can be tuned in TFTs by changing $V_{GS}$. The ISO-10 showed a larger $E_F$ shift than ISO-3 by sweeping small $V_{GS}$. Because the dependency of the $E_a$ shift reflects the density of states (DOS), when the $E_a$ reaches the band tail state near $E_C$, the shift is suppressed due to the exponential increase in DOS at the band tail. The $E_{MN}$ values estimated from the inverse of the slopes at high $E_a$ (subthreshold region of $V_{GS}$) were 30.0 and 29.2 meV for ISO-3 and ISO-10, respectively. These MN energies are quite comparable to those observed in IGZO and $a$-Si:H. This universal $E_{MN}$ indicates that the electron transport at the conduction band tail could be expressed by the multiple trapping model.

$$E_{MN} = \frac{E_a}{T_e/T_l - 1},$$

where $T_e$ and $T_l$ are the electron temperature and lattice temperature (device temperature), respectively. Generally, under thermal equilibrium conditions where $T_e \approx T_l$, $E_{MN}$ and $E_a$ are strongly correlated for room temperature measurements. Comparing the ISO-3 with the ISO-10, smaller $E_a$ was observed for the ISO-10 in the regime above the threshold. This result is consistent with the difference between the $E_{MN}$ of ISO-3 and ISO-10. At above threshold voltages, the linear relationship between $I_{D0}$ and $E_a$ disappeared. As shown in Fig. 6(c), when $E_a$ was very small in ISO-10, the slope of $I_{D0}/E_a$ became negative, and $E_{MN}$ was also negative. Negative $E_{MN}$ were reported at low $E_a$ in IGZO TFTs and heavily doped microcrystalline-Si, where $E_F$ goes deeply into...

Fig. 6. (Color online) Temperature dependence of $I_D$ at various $V_{GS}$ for (a) ISO-3 and (b) ISO-10 at $V_{DS} = 1$ V. The closed circles denote measurements from the subthreshold region. The solid lines are least-squares fits to the experimental data using an Arrhenius relation. (c) Relationship between $I_{D0}$ and $E_a$ both for ISO-3 and ISO-10. Adapted with permission from Ref. 19. Copyright 2014. AIP Publishing LLC.
5. Desorption of excess oxygen in vacuum storage conditions

5.1. TFT properties in atmosphere and vacuum

Although the ISO-10 TFTs demonstrate stable operation, the TFT mobility slightly deteriorates (7.7 cm² V⁻¹ s⁻¹). To maintain both the high mobility of the ISO-3 TFTs (18.4 cm² V⁻¹ s⁻¹) and electrical stability of the ISO-10, it is necessary to clarify the electronic conduction instability. Here, we consider the excess oxygen generated during sputtering deposition of an amorphous oxide semiconductor film. The excess oxygen is an important part of the composition in an InOₓ-based film because excess oxygen can easily be incorporated into a film or easily diffuse out of the film, and the resulting TFT behaviors are drastically different.

We observed the effect of storage environment on the electrical stability to compare the excess oxygen contents in the ISO-3 and ISO-10 TFT. To adjust the V_{ON} to be 0 V, the ISO-3 and ISO-10 films were deposited at high P_{O₂} [O₂/(Ar + O₂) = 50%] and at low P_{O₂} [O₂/(Ar + O₂) = 8.3%], respectively. The V_{ON} is a key factor for TFT operation at low voltages. Due to the P_{O₂} optimization, the films with different O₂ incorporation are compared because a vast amount of oxygen molecules could be incorporated in the film under a high O₂ concentration. Figure 8 shows a flow of the fabrication of the TFT and I–V characterization for the excess oxygen characterization. The TFT fabrication process was the same as that of the TFTs in the previous section. The TFTs fabricated were sequentially measured in different three states: immediately after fabrication (as-fabricated), after storage in a vacuum desiccator (~10 Pa) for 3 months after the first measurement (stored in vacuum), and after exposure to ambient air for 2 weeks after the second measurement (exposure to air).

Figure 9 shows the transfer characteristics of the ISO-3 TFTs. For the as-fabricated TFTs, transfer characteristics at different channel lengths (L = 50–350 μm in steps of 50 μm) are presented in Fig. 9(a). The maximum I_{D} increased with decreasing L, while the V_{ON} was almost constant. After being stored in a vacuum desiccator, however, the V_{ON} significantly shifted to more negative voltages in the shorter channel TFTs. Even when V_{GS} = −100 V was applied, I_{D} was not fully turned off [Fig. 9(b)]. After being exposed to air for two weeks, the V_{ON} in each L tended to return to zero [Fig. 9(c)]. Figures 9(d)–9(f) are the transfer characteristics of ISO-10 TFTs with the same measurement conditions as those of the ISO-3 TFTs. In contrast to the large shift of V_{ON} in the ISO-3 TFTs, no V_{ON} shift was observed in the ISO-10 TFTs for any of the storage environments. For the TFTs stored in vacuum, the J–V characteristics for the ISO10 films were significantly different than those for the ISO3 films. To observe the possible changes in the TFT properties after vacuum storage, we extracted the contact resistance (R_c) and channel resistivity (ρ_{ch}) of the TFTs using the transfer line method (TLM) as shown in Fig. 10. Note that the V_{GS} is modified by the threshold voltage (V_{th}) in the ISO-3 TFTs because V_{th} for each L is different [Fig. 9(b)]. The width-normalized total resistance (R_{total}W) as a function of L is expressed by the following:

\[ R_{total}W = \frac{1}{L} \left( \frac{d \rho}{d \rho_S} \right)_{\phi_S = E} \]
where $W$ is the channel width, which was fixed at 1000 $\mu$m. $R_C$ is the contact resistance at the source and drain electrodes ($R_C = R_{source} + R_{drain}$) and is basically determined by the vertical axis of the intersection point ($L = 0 \mu$m). In the present case, the $R_C$ is extracted from the convergence point for each line. For oxide TFTs, ohmic contact is obtained due to oxygen diffusion from the channel toward the contact interface.\cite{115,116} Thus, effective channel lengths have to be shortened compared to the geometrical lengths. The extracted $R_C$ increased for the ISO-3 TFTs that were exposed to air. The increase in $R_C$ corresponds to an increase in the potential barrier height at the interface between the oxide semiconductors and contact electrodes due to the adsorbed oxygen molecules.\cite{117-119} Since the absorbed O$_2$ causes charge transfer from the ISO film, barriers are generated due to surface band bending.\cite{49} In contrast, as shown in Figs. 9(d)–9(f), the $R_C$ of the ISO-10 TFTs are almost constant for each state. In particular, an $R_C$ higher than that of ISO-10 was observed in the ISO-3 TFTs that were after exposed to air. The high $R_C$ observed confirmed that the contact resistance was dominated not only by the interfacial oxidation status\cite{56,120} but also by the density of states of the thin film channel, as shown in Fig. 7.\cite{121,122}
5.2. Change in the carrier transport mechanism

To investigate the intrinsic film conductivity, we discuss the intrinsic mobility ($\mu_i$) using the following basic equation:\textsuperscript{57)

$$\mu_i = \frac{1}{C_i W} \frac{\partial \sigma_{ch}}{\partial V_{GS}},$$

(12)

where $C_i$ is the gate insulator capacitance per unit area (13.8 nF cm$^{-2}$) and $\sigma_{ch}$ is the channel conductivity ($\sigma_{ch} = I_{ch}$). Figure 11 shows the reciprocal $r_{ch}$ as a function of $V_{GS} - V_{th}$ for the ISO-3 TFTs, and the reciprocal $r_{ch}$ as a function of $V_{GS}$ for the ISO-10 TFTs in each state. The $\mu_i$ obtained for the ISO-3 were 18.2, 21.9, and 18.5 cm$^2$ V$^{-1}$ s$^{-1}$ for the as-fabricated TFTs, TFTs stored in a vacuum, and TFTs exposed to air, respectively [Fig. 11(a)], whereas a constant $\mu_i$ of $\sim$7.0 cm$^2$ V$^{-1}$ s$^{-1}$ was obtained for ISO-10 in all cases [Fig. 11(b)].\textsuperscript{123) These results indicate that the TFTs become environmentally stable when using ISO-10 films sputtered with low $P_{O_2}$. Compared with the ISO-3 TFTs, the reliability of the ISO-10 TFTs was significantly improved, although the $\mu_i$ was reduced.
Exposure to air, the Fermi energy changed to the line plotted in blue. Above the TFT in a vacuum, the energy (plotted in red) was measured. Then, after plotting in black, was measured in the initial as-fabricated TFT. After storing TFTs: (a) stored in a vacuum and (b) exposed to air. The Fermi energy, nonbonded (or weakly bonded) to the Si atoms in the hold oxygen atoms around them, the excess oxygen is because of the charge transfer from the conduction paths of electrons, where the charge carrier transport is described by hopping mechanisms, i.e., so-called trap-limited conduction. Thus, we can infer that the molecules desorbed under vacuum could be excess oxygen, as illustrated in the inset of Fig. 12(a). If the desorbed molecules are H$_2$O, since they could be excess oxygen, as illustrated in the inset of Fig. 11(a), suggesting that desorption of excess oxygen is dominant on the electrical properties rather than H$_2$O effect. The oxygen removal from the film causes an increase in carrier density and leads to the shift of $E_F$ above $E_m$. Then, the electron transport changes from trap-limited to percolation conduction. In contrast, adsorbing oxygen from the ambient atmosphere reduces carrier concentration due to the charge transfer. Furthermore, in the percolation model, carrier transport strongly depends on the channel dimensions (L, W and t). The $V_{in}$ is also affected by these dimensions. For longer channel TFTs, a higher $V_{GS}$ is required to achieve a certain electrical conductivity compared with that in shorter channels. This phenomenon is consistent with the $I$–$V$ characteristics observed for the TFT stored in a vacuum [Fig. 9(b)].

### 6. Bilayer channel TFTs

Although $V_{dd}$ is necessary for electrical conduction in an InO$_x$-based semiconductor, the density of $V_{dd}$ can be easily changed by the adsorption/desorption of oxygen and/or hydrogen, which drastically degrades TFT properties. Furthermore, hydrogen contamination in oxide films may also cause instability in TFT operation. To avoid these gas sensitivities, we propose a homogeneous bilayer oxide semiconductor channel, where the top layer can prevent gas diffusion in and out of the film. The concept of the bilayer channel is schematically illustrated in Fig. 13(a). Bottom-gate top-contact TFTs were fabricated on a heavily doped p-type Si substrate with 250 nm of thermally grown.

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**Fig. 12.** (Color online) Fermi energy as a function of $V_{GS}$ for the ISO-3 TFTs: (a) stored in a vacuum and (b) exposed to air. The Fermi energy, plotted in black, was measured in the initial as-fabricated TFT. After storing the TFT in a vacuum, the energy (plotted in red) was measured. Then, after exposure to air, the Fermi energy changed to the line plotted in blue. Above and below $E_m$ correspond to percolation and trap-limited conduction, respectively. The inset shows a schematic illustration of the oxygen desorption/adsorption model. Adapted with permission from Ref. 119. Copyright 2015. AIP Publishing LLC.

**Fig. 13.** (Color online) (a) Concept of a bilayer channel. The top layer prevents desorption of excess oxygen in the bottom film. (b) Schematic diagram of the device structure. (c) Cross-sectional TEM image of the bilayer films with vertically stacked ISO-20 and ISO-3 on a SiO$_2$/Si substrate. (d) Electron-beam selected area diffraction image. Adapted with permission from Ref. 132. Copyright 2016. AIP Publishing LLC.
SiO₂. The bilayer ISO films were sequentially deposited using DC magnetron sputtering without exposure to atmosphere. The sputtering targets for the ISO contained 3 and 20.6 wt% SiO₂ and are denoted ISO-3 and ISO-20, respectively. The active channel was 5-nm-thick stacked ISO-3 and ISO-20. Because the Ti electrodes were directly evaporated on the bilayer, the Ti electrodes were located on the ISO-20 insulator without forming a hole [Fig. 13(b)]. The fabricated TFTs were finally annealed at 250 °C for 30 min in air. After annealing the stacked TFTs, we confirmed that the bilayer channel (ISO-3/20) was amorphous by using cross-section TEM [Fig. 13(c)] and selected area diffraction, which indicates a series of concentric diffuse rings [Fig. 13(d)]. Using X-ray diffraction (BL04B2 beamline at the SPring-8 synchrotron radiation facility) and X-ray absorption fine structure measurements (BL01B1 beamline at the SPring-8 synchrotron radiation facility), we confirmed that all of the films prepared in the same manner remained amorphous. The bilayer TFT with a channel length of 350 μm and channel width of 1000 μm showed no pronounced hysteresis in its transfer [Fig. 14(a)] and output [Fig. 14(b)] characteristics. Though the contact was formed on the insulating ISO-20 layer, no current crowding effect was observed in the I–V characteristics in the low-bias regime, indicating the formation of ohmic contact. A cross-sectional TEM image of the Ti contact reveals that the Ti at the ISO-20 interface is clearly oxidized. This result implies that the Ti contact takes oxygen molecules from the ISO-20 film, forming VO in the ISO-20. Through this process, the thin ISO-20 becomes conductive underneath the Ti contact, even though an insulating top layer was used. Carrier injection without any holes is fascinating due to process simplification, and the bilayer structure is unlike a TFT with an etched-stop layer. The excess oxygen in the ISO-20 causes oxidation of the Ti interface because of the low Gibbs free energy of Ti (∼848 kJ mol⁻¹ at 250 °C). The results are consistent from the viewpoint of oxygen bindings.

The TFT parameters of V₉₉, μₑₑₑₑ, Iₙₙₙₙ, and ss obtained are −0.4 V, 19.6 cm² V⁻¹ s⁻¹, 1.0 × 10⁻⁶, and 0.1 V dec⁻¹, respectively. We emphasize that a TFT was successfully achieved with both high mobility (>10 cm² V⁻¹ s⁻¹) and normally off operation even though the metallic contacts were formed on the insulating ISO-20 layer covering the semiconducting ISO-3. The single-layer ISO-3 TFT shows a large negative shift in V₀₉₉, and as a result, an unintentionally high carrier density is produced. Thus, the normally off characteristics indicate the effective suppression of oxygen desorption from the bottom layer of the ISO-3/20 channel. Similar effects have been reported for other insulator oxide films, in which the insulating film covering the oxide semiconducting channel suppresses the V₀₉₉ shift. In the bilayer TFT structure, the insulating ISO-20 can act as a protection layer for the adsorption/desorption of oxygen atoms to/from the semiconducting bottom layer without intentionally forming contact holes.

Finally, we mention the bias stress instability of the ISO-3/20 TFT. Figures 15(a) and 15(b) show the negative (V₉₉ = −20 V, 5000 s) and positive (V₉₉ = +20 V, 5000 s) bias stress instability measurements, respectively. Although the V₉₉ applied were different from those of the single-layer ISO-10 TFTs (Fig. 5), the V₀₉₉ shifts of 0.2 and 0.8 V for NBS and PBS, respectively, are very small, similar to crystalline IGZO TFT. Significant improvement of the stability, while maintaining high mobility and normally off operation, can be achieved in the homogeneous ISO stacked structure. This result implies that V₀₉₉ formation, which is the primary origin of the bias stress instability, is suppressed because the top layer prevents adsorption/desorption of O₂ molecules on/from the bottom layer. In addition, the thin insulating ISO-20 does not behave as a barrier for ohmic contact at the Ti electrode interface. Here, we emphasize that the unique and reliable bilayer ISO TFTs will allow these structures to be used in practical applications.

7. Conclusions

We have discussed the bond-dissociation energies of dopants in InOₓ-based semiconductors for controlling V₀₉₉ formation. We compared three dopants (Ti, W, and Si) in InOₓ films. These species have different BDE; thus, the choice of dopant modulated the electrical properties of the TFTs. The Si dopant in InOₓ can realize higher carrier density and field effect mobility than W and Ti dopants. Furthermore, the electrical properties could then stabilize when Si concentration increases. In particular, ISO-10 showed stable TFT operation even in the single-layer TFT structures due to the V₀₉₉ suppression and reduction in the DOS beneath the conduction band. We clarified that the instability of the ISO-3 is due to the desorption of excess oxygen in the film; however, the TFT with low Si concentration exhibited high mobility. We demonstrated bilayer ISO TFTs that realize...
high mobility (19.6 cm$^2$ V$^{-1}$ s$^{-1}$), high stability under bias stress instability measurements, and normally off operation. ISO TFTs are expected to lead to next-generation applications as representatives of the post-amorphous Si industries.

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