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Remarkably high mobility ultra-thin-film metal-oxide transistor with strongly overlapped orbitals

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High mobility channel thin-film-transistor (TFT) is crucial for both display and future generation integrated circuit. We report a new metal-oxide TFT that has an ultra-thin 4.5 nm SnO₂ thickness for both active channel and source-drain regions, very high 147 cm²/Vs field-effect mobility, high I_{ON}/I_{OFF} of 2.3×10^7 , small 110 mV/dec sub-threshold slope, and a low V_D of 2.5 V for low power operation. This mobility is already better than chemical-vapor-deposition grown multi-layers MoS₂ TFT. From first principle quantum-mechanical calculation, the high mobility TFT is due to strongly overlapped orbitals.

The metal-oxide thin-film transistor (TFT)^{1–20} is a revolutionary technology for displays due to its high mobility and simple process. The high mobility of zinc-oxide (ZnO)-based materials was attributed to the spatially spread metal ns orbitals with isotropic shape, which is possible to overlap the neighboring metal ns orbitals⁷. However, the high performance ZnO-based TFTs of InGaZnO⁷, bi-layer InSnO/InGaZnO¹¹, InZnO¹³, and GaZnON¹⁸ compounds usually contain Indium (In) or Gallium (Ga), which are rare elements in earth's crust. In addition, device performance is sensitive to the moisture degradation and atomic composition of these compound. Alternatively, high mobility, high transistor on-current (I_{ON}), and low off-current (I_{OFF}) TFTs are found in two-dimensional metal-chalcogenide^{21–28}. However, chemical vapor deposition (CVD)-grown MoS₂^{25–28} shows a considerably lower mobility compared with peeled-off flakes from crystals^{21–28}. To further increase the display pixel density and drive organic light-emitting diodes (OLED), higher mobility and I_{ON} than those of ZnO-based TFTs are needed. The low DC and switching power consumptions are other technological trends for displays that require a low I_{OFF} and low operation voltage. In this study, a remarkably high field-effect mobility (μ_{FE}) of 147 cm²/Vs was demonstrated experimentally in tin-oxide (SnO₂) TFT. This TFT also showed a high I_{ON}/I_{OFF} of 2.3×10^7 , low sub-threshold swing (SS) of 0.11 V/decade, low threshold voltage (V_T) of 0.27 V, low drive voltage of 2.5 V for low switching power, and ultra-thin layer with a thickness of 4.5 nm. Such ultra-thin thickness is comparable with that of multilayered MoS₂²⁷ for low DC standby power consumption. Notably, Sn (Group IV) has ns²np² electron configuration and directive sp³ orbitals, which differ from those of Zn⁷. According to first principle quantum-mechanical calculations, the considerably high μ_{FE} in SnO₂ TFT is caused by its overlapped s-orbitals even in an ns²np² configuration.

Results

To increase the transistor I_{ON} and reduce the operation voltage, a high-dielectric-constant (high- κ) gate insulator^{12,15} was used for the TFT. Figure 1(a) shows the current-voltage (I - V) and capacitance-voltage (C - V) characteristics of a gate capacitor with top Aluminum (Al) electrode, high- κ hafnium-oxide (HfO₂), and bottom n⁺-Si. In the Al/HfO₂/n⁺-Si capacitor, a small leakage current of 5.7×10^{-7} A/cm² at 2 V was obtained at a capacitance density of 0.38 μ F/cm². The high capacitance density yielded a low equivalent-oxide-thickness (EOT) of only 9.1 nm, which was due to the high- κ HfO₂ with a κ of 17. Figure 1(b) shows the transistor's drain current versus gate voltage (I_{DS} - V_{GS}) characteristics of the SnO₂/HfO₂ TFTs with 4.5 ~ 20 nm thick SnO₂. The device with thick 20 nm SnO₂ failed to show proper pinch off I_{OFF} due to very high conductivity, although the device has very high I_{ON} . The device with 4.5 nm thick SnO₂ shows the best I_{ON}/I_{OFF} performance. Figure 1(c,d) show the transistor's drain current versus drain voltage (I_{DS} - V_{DS}), I_{DS} - V_{GS} , and μ_{FE} - V_{GS} characteristics of the SnO₂/HfO₂ TFT with 4.5 nm thick SnO₂, respectively. The device was operated in the enhancement mode of an n-channel metal-oxide-semiconductor field-effect transistor (nMOSFET) at a low operation voltage of 2.5 V. The device also showed a high I_{ON}/I_{OFF} of 2.3×10^7 , low SS of 110 mV/decade, and low V_T of 0.27 V. The V_T was extracted from the intercept of the linear $I_{DS}^{1/2}$ - V_{GS} curve in a saturation region. A high I_{ON} is crucial to drive the OLED and increase the display pixel density, whereas a

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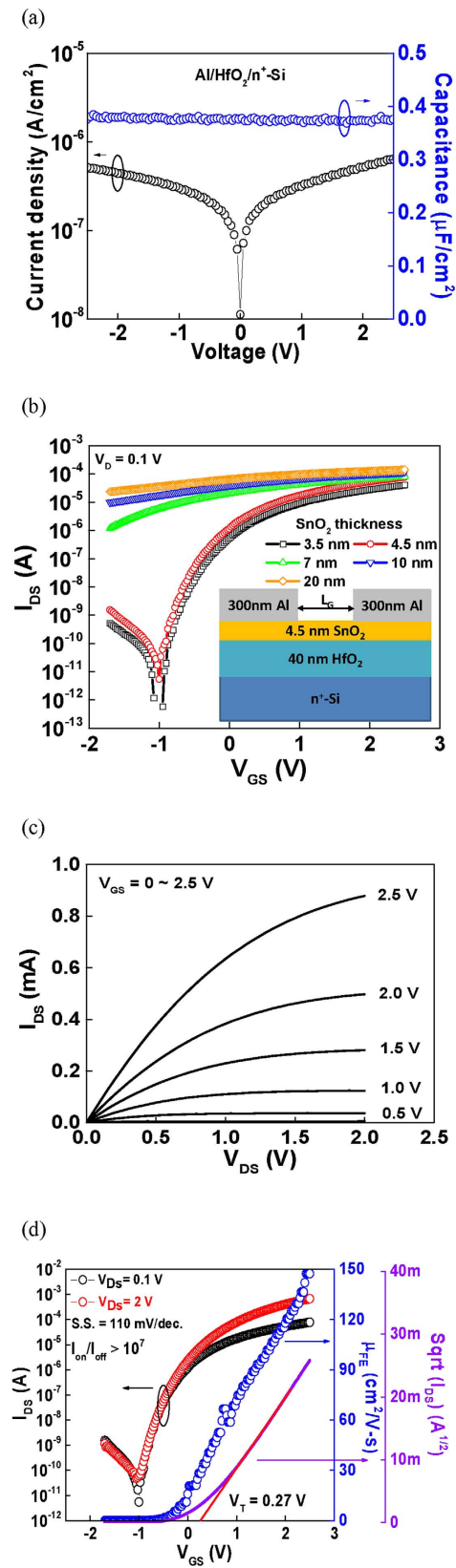


Figure 1. (a) *I*-*V* and *C*-*V* characteristics of gate capacitor, (b) *I*_{DS}-*V*_{GS} characteristics of Al/SnO₂/HfO₂/n⁺-Si TFTs with 20 ~ 3.5 nm SnO₂ layers, (c) *I*_{DS}-*V*_{DS} and (d) *I*_{DS}-*V*_{GS}, *μ*_{FE}-*V*_{GS} and Sqrt(*I*_{DS})-*V*_{GS} characteristics of Al/SnO₂/HfO₂/n⁺-Si TFTs at 4.5 nm SnO₂ thickness. The gate length is 50 μm.

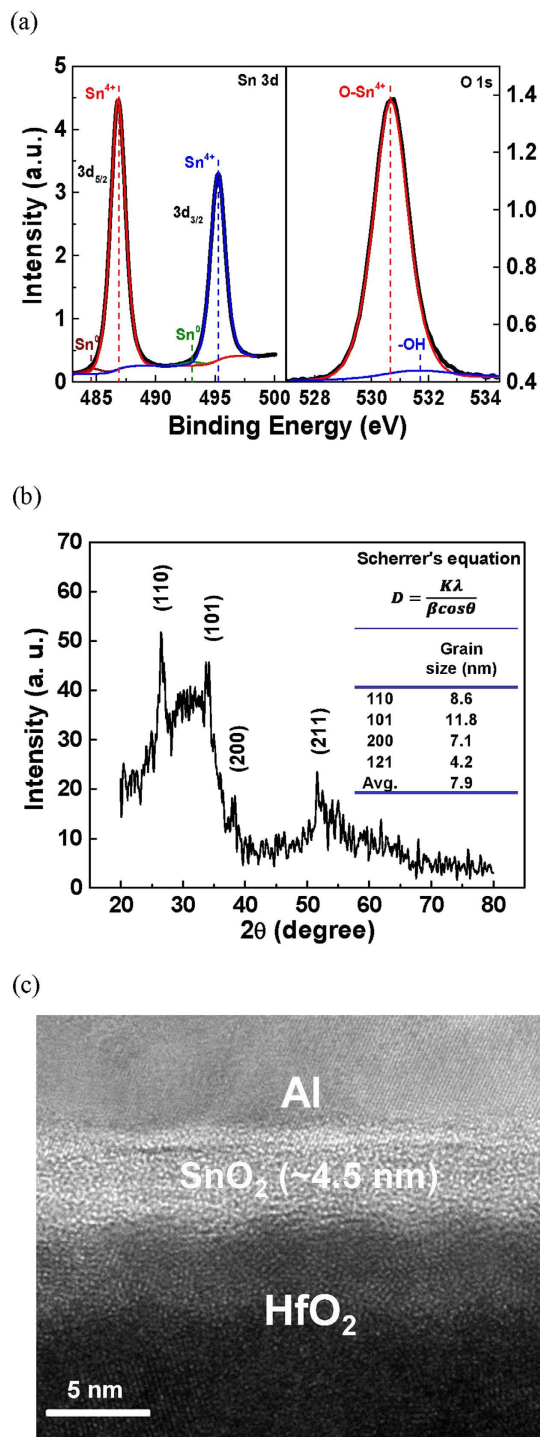


Figure 2. (a) XPS, (b) XRD, and (c) TEM analysis of SnO₂ formed on HfO₂/n⁺-Si. The SnO₂ thickness is 20 nm for XPS and XRD analysis, while 4.5 nm for TEM.

low I_{OFF} is required to reduce the DC standby power. The low SS with the mean value and standard deviation of 100.2 ± 19.4 mV/decade indicates the good oxide/semiconductor interface to turn on the transistor fast. The I_{ON} showed an inversely proportional relation with gate length in a wide gate length TFT, a typical method to extract mobility correctly for Si MOSFET and metal-gate/high- κ MOSFET^{29–31}. A remarkably high μ_{FE} of 147 cm²/Vs is obtained with the mean value and standard deviation of 141.6 ± 11.5 cm²/Vs, which is higher than that of ZnO-based TFTs^{3–20} and even higher than that of a CVD-grown multilayered MoS₂ MOSFET^{21–24}. To reach high mobility, epitaxial growth of crystalline MoS₂ on a crystal substrate is needed. Unfortunately, the mobility is lower for CVD-grown MoS₂^{25–28} than peeled-off flakes from crystals^{21–28}. The lattice mismatch caused defects are the other major concern for circuit yield. In contrast, high mobility SnO₂ TFT is achievable on the amorphous substrate

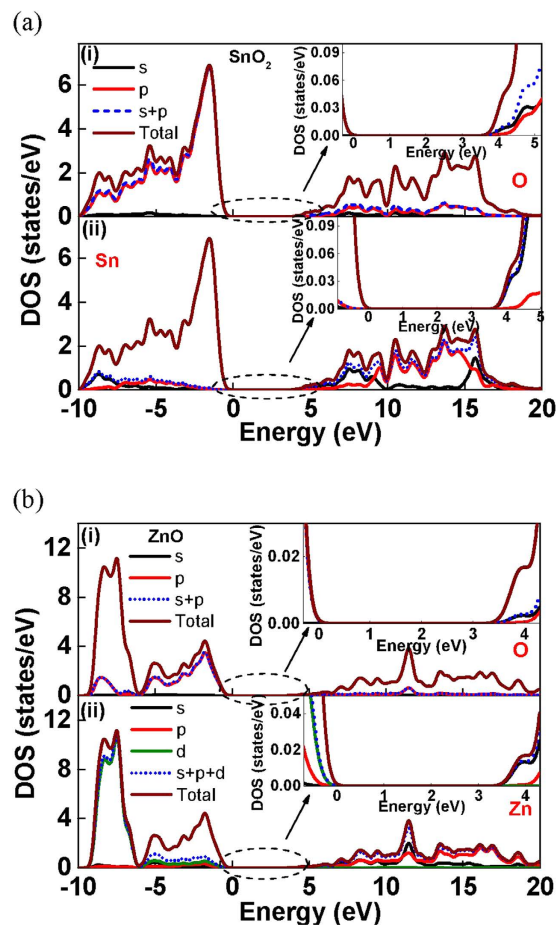


Figure 3. (a) DOS of (i) O, and (ii) Sn in SnO₂, and (b) DOS of (i) O, and (ii) Zn in ZnO.

and free from lattice-mismatch defects. Such metal-oxide has already been used to manufacture TFT circuit for display. It is crucial to notice that the mobility of metal-oxide increases with increasing carrier density⁷. In the 4.5-nm-thick SnO₂ TFT, the high mobility is due to the high V_G -induced carrier density³¹ of $\sim 10^{13} \text{ cm}^{-2}$ to screen out charged defects. This is also supported by the higher mobility with larger V_G , where induced carrier density increases with V_G . In the thicker 7–20 nm SnO₂ devices with poor pinch off, the mobility is lowered by extra parallel conduction from non-depleted bulk SnO₂. The mobility is lowered in 3.5 nm SnO₂ TFT due to stronger roughness scattering from top surface. Here the SnO₂ surface roughness is 0.39 nm, close to the HfO₂ roughness of 0.41 nm.

The high mobility SnO₂ TFT was further investigated using material analysis. Figure 2(a) shows the X-ray photoelectron spectroscopy (XPS) spectra from the Sn 3d and O 1s core level of the SnO₂ thin film. The Sn 3d peak corresponded to the oxidation state of Sn⁴⁺, and the O 1s peak was attributed to the O-Sn and O-H bonds. Thus, the chemical composition was determined to be Sn⁴⁺O₂²⁻. The X-ray diffraction spectroscopy (XRD) pattern in Fig. 2(b) reveals the presence of a rutile phase in SnO₂. An average grain size of 7.9 nm was obtained using the Scherrer's equation. Figure 2(c) shows the cross-sectional transmission electron microscopy (TEM) image of the SnO₂/HfO₂ stack. A relatively uniform SnO₂ layer with an ultra-thin thickness of 4.5 nm was observed.

To thoroughly understand the cause of the high mobility in SnO₂ TFT, first principle quantum-mechanical calculations were used to investigate the electronic structures of SnO₂ and ZnO; ZnO has been extensively studied using the localized density functional theory (DFT) to reveal the mechanism that leads to its high mobility. The structures of both SnO₂ and ZnO semiconductors were successfully obtained using local density approximation plus U (LDA+ U) method with appropriate U^p and U^d value. The LDA+ U method compensates for the underestimation of the bandgap caused by a strong self-interaction by the DFT. The bandgaps of SnO₂ and ZnO were calculated to be 3.68 and 3.39 eV (Figure S1(a) and S1(b)), respectively, which are consistent with the experimental values of 3.6 and 3.4 eV, respectively. The contribution of each orbital in the conduction band minimum (CBM) of SnO₂ was investigated using density of state (DOS) analysis. The energy of valence band minimum was set to zero for convenience. As shown in Fig. 3(a), the utmost valence band was predominated by the O 2p orbitals, and the contribution from Sn was mostly from 5p orbitals. The lower conduction states near CBM were mostly derived from Sn 5s orbitals, whereas the O 2p orbitals contributed only in higher energy states. The Sn 4d orbitals did not give rise to the electron conducting property of SnO₂ because the antibonding interaction between Sn 4d and O 2p orbitals led only to the slight mixing of states at a deep valence band level. The DOS results of ZnO (Fig. 3(b)) were similar to those of SnO₂. The major difference between the valence bands of SnO₂ and ZnO is the contribution of d orbitals. The upper valence bands (from -6 to 0 eV) were composed of primarily of O 2p orbitals and slight

mixing states from Zn 4s, 4p and 3d, whereas Zn 3d orbitals dominated in deeper states. In conduction band, Zn 4s was the major component near CBM while O 2p orbitals had little contribution at levels lower than 5 eV. Therefore, the high mobility of SnO₂ was attributed to the overlapping of s-orbitals, as with ZnO, although it had ns²np² configuration. This is further supported by the charge density distribution of SnO₂ shown in Figure S2(a), which has highly overlapped orbitals similar with those of ZnO in Figure S2(b). The highly overlapped orbitals of SnO₂ is related to large atomic radius, one row below Zn in the periodic table. From the results of DOS and charge density distribution, the higher mobility than the state-of-the-art ZnO TFTs^{32–33} is attributed to the highly overlapped s-orbitals of SnO₂.

The carrier effective mass is a major factor that may explain the higher mobility of SnO₂ than that of ZnO. The high electron mobility of n-type materials is caused by a deep curvature in CBM of band structure shown in Figure S1(a) and S1(b), which leads to a low effective mass of electrons. The calculated electron effective mass of SnO₂ was approximately 20% lighter than that of ZnO, indicating a faster electron transport in the SnO₂ conduction band.

In conclusion, this SnO₂ TFT device had a considerably high mobility, high I_{ON}/I_{OFF} , low SS, low operation voltage, and ultra-thin thickness. The low operation voltage is due to the high- κ gate dielectric with a high capacitance density. The low SS indicates the good gate dielectric and SnO₂ interface. The high I_{ON}/I_{OFF} is related to the high mobility to increase I_{ON} and the ultra-thin thickness to decrease I_{OFF} , where the high mobility is caused by strongly overlapped s-orbitals.

Methods

The SnO₂ TFTs were fabricated on a heavily doped n-type silicon (100) substrate. The 40-nm-thick high- κ gate HfO₂ and 20–3.5-nm-thick SnO₂ films were deposited by physical vapor deposition. Thicker 20 nm SnO₂ film was also deposited for X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) pattern analysis. Then the high- κ layer and SnO₂ film was annealed at 400°C. Finally, the Al source-drain electrodes were thermally evaporated and patterned. The gate length and width are 50–150 μ m and 500 μ m, respectively. Therefore, the maximum process temperature for this device is 400°C. The fabricated devices were characterized by XPS, XRD, TEM, C-V, and I-V measurements. All quantum-mechanical calculations were performed by Cambridge Sequential Total Energy Package (CASTEP) code. Structural optimization was performed on each model prior to calculating their electrical properties. The LDA+U method is known to correct the strong correlation of metal oxides and is proven to be quite effective for ZnO. The calculations were carried out by using generalized gradient approximation (GGA) with LDA+U.

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Author Contributions

C.W.S. did the experiments; A.C. supervised the experiments and wrote the main manuscript text; C.F.L. and W.F.S. did the quantum-mechanical calculations. All authors reviewed the manuscript.

Additional Information

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