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Large mobility modulation in ultrathin amorphous titanium oxide transistors

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Recently, ultrathin metal-oxide thin film transistors (TFTs) have shown very high on-off ratio and ultra-sharp subthreshold swing, making them promising candidates for applications beyond conventional large-area electronics. While the on-off operation in typical TFTs results primarily from the modulation of charge carrier density by gate voltage, the high on-off ratio in ultrathin oxide TFTs can be associated with a large carrier mobility modulation, whose origin remains unknown. We investigate 3.5 nm-thick TiO_x -based ultrathin TFTs exhibiting on-off ratio of $\sim 10^6$, predominantly driven by ~ 6 -decade gate-induced mobility modulation. The power law behavior of the mobility features two regimes, with a very high exponent at low gate voltages, unprecedented for oxide TFTs. We find that this phenomenon is well explained by the presence of high-density tail states near the conduction band edge, which supports carrier transport via variable range hopping. The observed two-exponent regimes reflect the bi-exponential distribution of the density of band-tail states. This improved understanding would be significant in fabricating high-performance ultrathin oxide devices.

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Thin film transistors (TFTs) made of semiconducting metal oxide have been extensively investigated over the past decades, primarily as a higher-mobility, low-cost alternative to conventional amorphous Si in large area electronics applications such as active matrix displays^{1–3}. On the other end of the spectrum, in the domain of high-performance computing, the single-crystalline Si-based technology is approaching its physical limits, and atomically thin two-dimensional material systems have been garnering extensive interests in pursuit of gaining ultimate electronic control on the transistor channel. As a matter of fact, fully depleted Si-on-insulator (FD-SOI) technology, using ultrathin Si layer has shown profound impacts on low-power computing devices⁴. To this end, complex oxide materials have also been used to fabricate TFTs based on two-dimensional electron gas (2DEG), where the carrier transport is highly confined near the insulator-semiconductor interface⁵. Primarily, such reports have been focused on epitaxially grown oxides, limiting their scalability in practical applications. However, the 2DEG formation has been reported recently in a rather simple $\text{TiO}_2/\text{Al}_2\text{O}_3$ interface fabricated by atomic layer deposition (ALD)^{6,7}, showing promises for scaling up this device architecture for more practical applications. In addition, sputter-deposited 1-nm-thick indium tin oxide transistors have shown to reach near-ideal subthreshold swing and nearly no drain-induced barrier lowering⁸. These recent reports clearly indicate growing interests in ultrathin oxide TFTs.

An interesting observation among the ultrathin channel devices and 2DEG transistors is that they typically exhibit sharp and very high on-off ratios in the transfer characteristics with extremely low off currents; the channel is essentially fully depleted of charge carriers in the off-state, and the gate induced charge accumulation leads to many decades of increases in the drain current, driving the transistor into on-state. In general, the working of conventional TFTs exhibit many orders of gate-dependent charge carrier density modulation, while the extent of gate-induced mobility modulation has been limited to only a few decades^{9–12} or has not been studied in detail^{13–15}. A large gate-dependent mobility modulation is uncommon in conventional amorphous Si TFT devices, and a clear picture elucidating the origin of mobility modulation in ultrathin metal oxide TFTs has not been reported so far^{11,16}. Since the on-off current modulation in TFTs is essentially from the combined effect of both carrier density and mobility modulations, it is worth examining if such mobility modulation is a universal phenomenon in amorphous-oxide TFTs. Moreover, it may have general implications on further improving the performance of the ultrathin oxide devices.

TiO_2 as a semiconductor is extensively used in solar cells^{17–20} and photocatalysis^{21–24}, but its application as a TFT channel material has not been much explored. For those reported so far, TiO_2 layers were mostly thicker than ~ 10 nm and crystalline^{9,25–34}, with only a few reporting the mobility modulation^{9,10}. A large extent of mobility modulation, as high as ~ 9 decades, has been recently reported from mixed amorphous-crystalline TiO_x TFT³⁵, with its origin remaining unexplained nevertheless.

In this report, we utilize ultrathin (3.5 nm) amorphous TiO_x film deposited by low-temperature ALD to fabricate TFT devices and investigate the origin of large gate-induced mobility modulation. Based on the analysis of gate-dependent mobility and control experiments involving post-ALD thermal treatments, we find that the mobility modulation is caused by the presence of high density of band-tail states that mediate the variable range hopping (VRH) of charge carriers near the mobility edge of conduction band.

Results and discussion

Performance of ultrathin TiO_x TFT. We fabricated bottom-gate TFTs based on the 3.5-nm-thick ultrathin amorphous TiO_x thin

film deposited on Si substrates with 300 nm SiO_2 by low-temperature ALD at 85 °C using titanium (IV) isopropoxide and water as reactants. The deposited film was subjected to a two-step forming gas annealing at 400 °C and 600 °C (each for 15 min), and Al-based source and drain electrodes with channel length of 5 μm and width 500 μm were patterned by electron-beam lithography as shown in the schematic in Fig. 1a. The ultrathin TiO_x film, after the default forming gas annealing treatment, was found to be nearly amorphous with minor nano-crystallinity, as it can be seen in the X-ray diffraction (XRD) spectra depicted in Fig. 1b. Despite using slow acquisition rate of the XRD spectra (scan rate of $0.38^\circ \text{min}^{-1}$; total scan time of 3 h), no significant crystallinity could be observed, except for the two very weak scattering peaks likely originating from either rutile or anatase TiO_x ^{17,24}. Moreover, the highly surface-sensitive, low-energy electron diffraction (LEED) pattern acquired from the TiO_x (inset in Fig. 1b) shows uniform, diffused background with no discernable diffraction features, further confirming the amorphous nature of prepared ultrathin TiO_x film.

The transistor output characteristics measured from the fabricated ultrathin TiO_x TFT shown in Fig. 2a display linear ohmic characteristics at low drain voltage (V_d) across the entire range of gate voltages (V_g), whereas toward the high V_d the drain current (I_d) tends to saturate. Accordingly, the transfer characteristics measured in the saturation regime ($V_d = 70$ V), as depicted in Fig. 2b, shows ~ 6 decades of on-off ratio, the subthreshold swing of 3.6 V/dec, the turn-on voltage (V_{on}) of ~ 24.6 V, and the threshold voltage (V_{th}) of ~ 48.5 V, with the

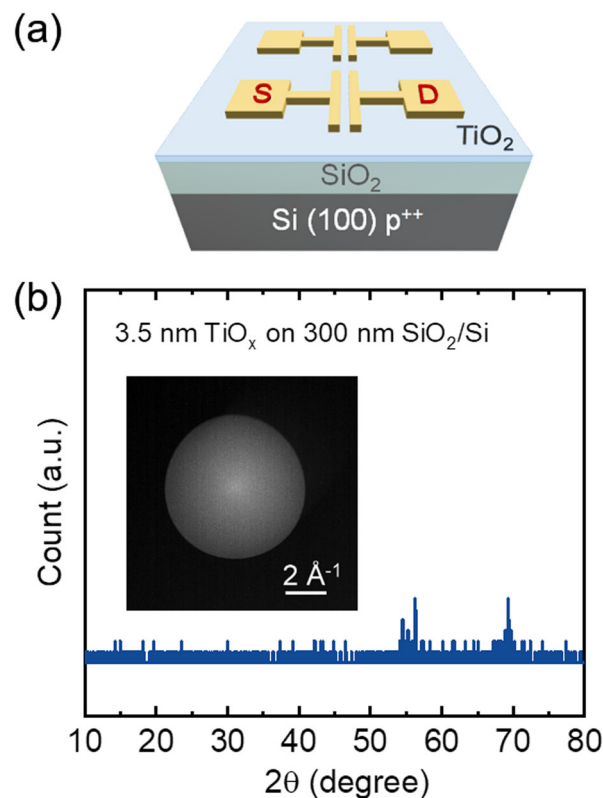


Fig. 1 Design of the ultrathin TiO_x TFT and its structural characterization.

a Schematic of the TiO_x TFT device investigated; **b** XRD pattern acquired from 3.5-nm-thick TiO_x thin film displaying no significant crystallinity except for weak scattering peaks potentially corresponding to anatase/rutile phases. The inset shows LEED image of the TiO_x thin film where the lack of any discernable crystalline peaks confirms the near amorphous structure of ultrathin TiO_x .

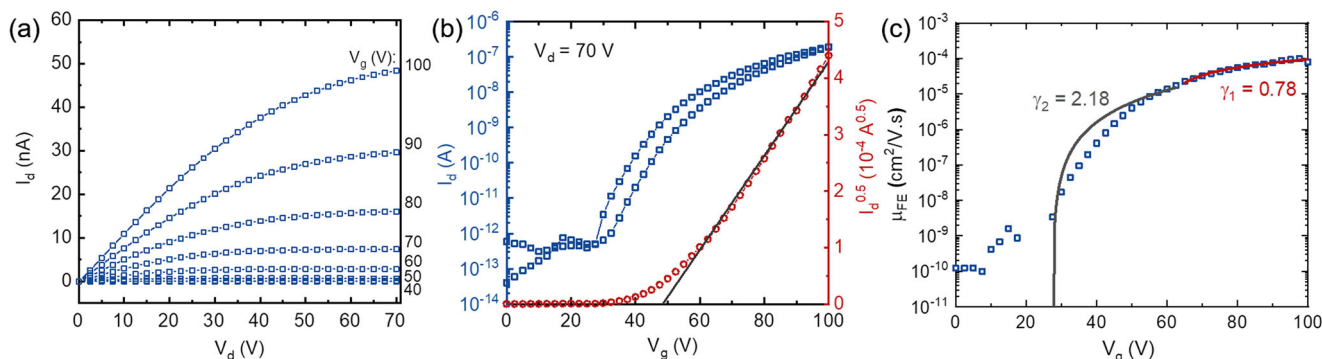


Fig. 2 Performance of ultrathin TiO_x TFT and μ_{FE} . Electrical characteristics of the TiO_x TFT ($W/L = 500 \mu\text{m}/5 \mu\text{m}$) fabricated using ultrathin TiO_x film annealed in forming gas (15 min at 400 °C followed by 15 min at 600 °C). **a** Output characteristics depicting linear-ohmic behavior at low V_d evolving into hard saturation at high V_d ; **b** Transfer characteristics at $V_d = 70 \text{ V}$ showing high on-off ratio (~ 6 decades), V_{on} of $\sim -24.6 \text{ V}$, and V_{th} of $\sim -48.5 \text{ V}$; **c** V_g -dependent μ_{FE} with power law fitting for $V_g > 60 \text{ V}$ and $V_g < 60 \text{ V}$, respectively. The exponent value of 0.78 for $V_g > 60 \text{ V}$ corresponds to the TLC, whereas the value of 2.18 for $V_g < 60 \text{ V}$ suggests VRH transport.

relatively large difference between V_{on} and V_{th} hinting the presence of a large population of trap states³⁶. The saturation mobility (μ_{sat}) of the TFT was then calculated using the standard expression,

$$\mu_{sat} = \frac{2L}{WC_i} \left(\frac{\partial \sqrt{I_d}}{\partial V_g} \right)^2, \quad (1)$$

where L represents channel length, W channel width, and C_i insulator capacitance per unit area. The μ_{sat} in the device under the discussion was $\sim 1.6 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. While the acquired mobility is lower than the crystalline TiO₂ TFTs reported previously^{25,27,29,32}, it is comparable to those reported from the TFTs fabricated using lower crystallinity TiO₂^{10,33,37}. We further evaluated the gate dependence of field-effect mobility (μ_{FE}) using the general expression (Eq. (2))^{38,39} and observed a large, ~ 6 -decade gate-dependent modulation of μ_{FE} (Fig. 2c).

$$\mu_{FE} = \frac{L}{V_d WC_i} \left(\frac{\partial I_d}{\partial V_g} \right). \quad (2)$$

Interestingly, as seen in Fig. 2c, the TFT also exhibits ~ 6 decades of mobility modulation. While the magnitude of mobility modulation generally observed in TiO_x TFTs has been 2–3 decades or less^{9,10}, modulation of ~ 9 decades has also been reported for sputter-deposited 20-nm-thick TiO_{2-x} TFTs followed by vacuum annealing³⁵.

Power law behavior of charge mobility. Given the ~ 6 decades of on-off ratio observed in our ultrathin TiO_x TFT, the current modulation is thus predominantly originating from the gate-induced mobility modulation while the carrier density modulation by gate providing only a minor contribution. We can safely exclude possible effects of contact Schottky barrier on the observed mobility modulation considering the choice of Al electrode that has been shown to form an ohmic contact on TiO_x^{26,29,33,37,40} and the negligible barrier height lowering effected by gate bias (Supplementary Note 1). The origin of gate-induced mobility modulation has been previously speculated to be related with the sub-bandgap trap states (localized tail states)^{41,42}, typically present near the conduction band edge (E_c) of amorphous semiconductors with an exponential decrease in their density of states. Particularly, Lee et al. have proposed a power law dependence of the saturation-regime μ_{FE} on V_g with

the following expression^{16,42}:

$$\mu_{FE} = K(V_g - V_{T,P})^\gamma, \quad (3)$$

where the exponent γ was correlated to the assumed carrier transport mode, and $V_{T,P}$ to the threshold voltage or charge percolation threshold at a given temperature. Based on the less than a decade of gate-dependent μ_{FE} modulation observed from amorphous InZnO/InGaZnO TFTs, they described the charge transport at low V_g as a trap-limited conduction (TLC) with the associated exponent of 0.7 and the high- V_g transport as mediated by percolation transport with the related exponent of 0.1. Similar gate-dependent μ_{FE} and exponents have been observed in the case of polycrystalline ZnO TFTs^{11,12}.

Upon utilizing the power law relationship to empirically analyze the μ_{FE} vs. V_g dependence, two different regimes are similarly identified in our gate-dependent mobility data obtained from the ultrathin TiO_x TFT, but, with very different exponent values as shown in Fig. 2c; at high V_g ($> 60 \text{ V}$), the exponent of 0.78 was obtained, indicating that the transport lies around the TLC according to the model proposed by Lee et al. However, at $V_g < 60 \text{ V}$, the obtained exponent is 2.18, far outside of the previously observed upper limit of 0.7¹⁶; in fact, such a high exponent value has never been reported for metal oxide TFT to our knowledge. As discussed, next, we attribute this to a high density of band-tail states that mediate the charge transport via VRH with the varying position of Fermi level (E_F) prescribed by given V_g accessing different distributions of band-tail states capable of supporting the VRH.

Origin of band-tail states. First, in order to ascertain the stoichiometry of the TiO_x film and examine the presence of defects such as oxygen vacancies, high-resolution X-ray photoelectron spectroscopy (XPS) spectra were obtained from the prepared TiO_x film subjected to the post-ALD forming gas annealing (Fig. 3a, c) and compared with the data from a control TiO_x film after similar post-ALD annealing carried out in pure O₂ (Fig. 3b, d). The defect states in metal oxides, typically originating from oxygen vacancies or interstitial hydrogen, are by nature shallow states generally existing very close to the conduction band edge. In the case of TiO₂, various reports have estimated that such shallow states exist at ~ 10 – 260 meV below the conduction band edge, among which those related with hydrogen interstitials are relatively closer to the conduction band edge than the oxygen vacancy states^{43–46}. When the TiO_x ALD is carried out at lower

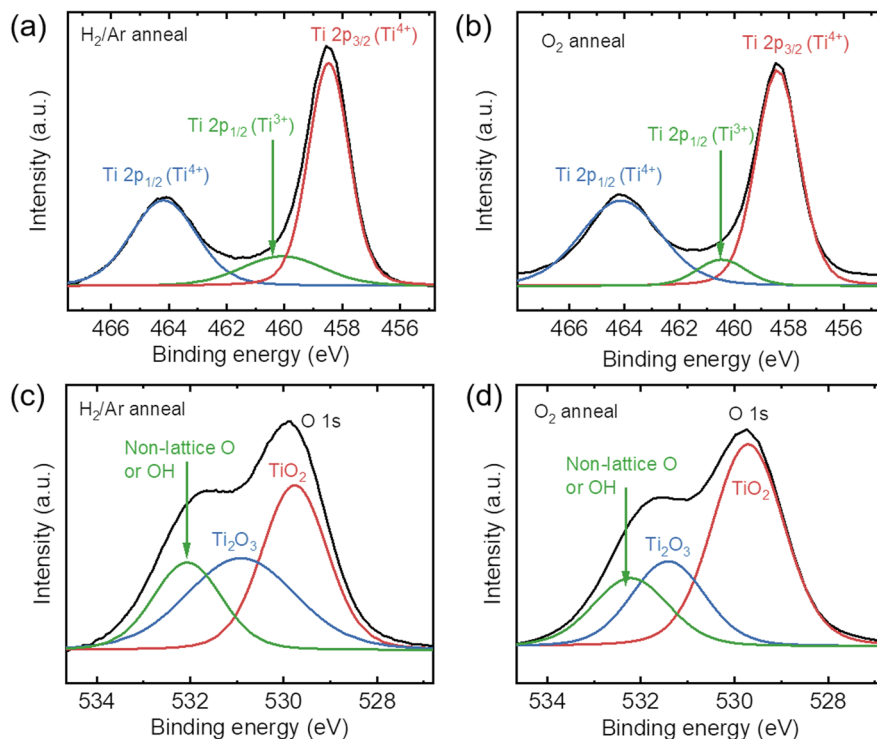


Fig. 3 Processing-dependent stoichiometry and oxygen vacancies in ultrathin TiO_x . High-resolution XPS spectra of Ti 2p (top row) and O 1s (bottom row) of ultrathin TiO_x film annealed in: **a, c** forming gas (4% H_2/Ar); **b, d** TiO_x film annealed in O_2 .

temperatures, such as 85 °C in our case, a high density of defect states is generally expected to exist within the deposited film.

As seen in the XPS spectra (Fig. 3a, b), both the Ti^{4+} peaks, viz. $\text{Ti}^{4+} 2p_{3/2}$ and $\text{Ti}^{4+} 2p_{1/2}$, correspond to TiO_2 lattice, whereas the Ti^{3+} peak ($\text{Ti}^{3+} 2p_{1/2}$) is related to a reduced, Ti_2O_3 lattice structure. The change in the peak intensities can be attributed to the difference in the electronic states of Ti in the two different samples. The sample annealed in forming gas (Fig. 3a) exhibited ~90 % larger area for Ti^{3+} peaks and ~17 % area decrease for Ti^{4+} peak, in comparison with oxygen-annealed sample (Fig. 3b). This observation indicates that the annealing in forming gas removes oxygen atoms from the TiO_2 lattice, reducing the concentration of Ti^{4+} , resulting in the increase in Ti^{3+} and the fraction of Ti_2O_3 ^{47–49}. The difference in the composition of the above samples was cross-confirmed by the peak shift and estimating the change in area of the O 1s XPS spectrum (Fig. 3c, d). The as-acquired O 1s peak was deconvoluted into three peaks with binding energies of 529.73, 531.22, and 532.23 eV, each corresponding to lattice oxygen (TiO_2), reduced Ti_2O_3 , and non-lattice oxygen (e.g., –OH, wherein hydrogen can originate from water used as an oxidant during ALD or forming gas annealing), respectively. In the forming-gas-annealed sample (Fig. 3c), the lattice oxygen peak (529.76 eV) exhibited a decrease in its area by ~28%, while the area of the Ti_2O_3 peak (530.92 eV) and non-lattice oxygen peak (532.03 eV) increased by ~55% and ~12%, respectively, compared with the oxygen-annealed sample (Fig. 3d). These data, along with the Ti 2p XPS spectral analysis, thus confirm that the forming gas annealing led to the formation of oxygen vacancies in the lattice by the consumption of lattice oxygen to form a larger proportion of reduced Ti_2O_3 ⁴⁷.

To identify the effect of oxygen vacancies on the gate-dependent mobility, transfer characteristics were measured from a control TFT fabricated on the oxygen-annealed ultrathin TiO_x film (Fig. 4a). Compared with the forming-gas-annealed TiO_x TFT (Fig. 2b), the on-state drain current was decreased by 2 decades even at higher V_d (=100 V), whereas the off-state current

was also increased by 2 decades, rendering the current modulation ratio significantly decreased down to only 2 decades. The observed increase in off-state currents is consistent to the notion that annealing the defective ultrathin TiO_x film in oxygen environments reduces the concentration of oxygen vacancy (i.e., charge trap) and the number of trapped charge carriers within the TiO_x film. Moreover, the oxygen-annealed device featured a markedly smaller difference between V_{th} (~55.2 V) and V_{on} (~46.4 V) compared with the forming-gas-annealed TiO_x device (i.e., V_{th} = ~48.5 V and V_{on} = ~24.6 V), reaffirming the reduced charge trap density, given that the difference between V_{th} and V_{on} can be majorly attributed to the charge trap concentration within the channel of a TFT, since within the $V_{on} < V_g < V_{th}$ regime, most charge carriers are induced into trap states and/or tail states that exhibit low mobility³⁶. Meanwhile, as we have postulated earlier, the primary charge transport in the on-state is likely mediated by the defect states associated with oxygen vacancies, and, thus, the decreased oxygen vacancy concentration should decrease the on-state current, as observed in the oxygen-annealed TiO_x TFT (Fig. 4a). Likewise, the field-effect mobility was decreased by ~3 decades (Fig. 4b) with mobility modulation decreased to 4 decades compared with the forming-gas-annealed TiO_x device (Fig. 2c) with ~6 decades of mobility modulation, strongly suggesting the role of defect states in the V_g -induced mobility modulation.

Considering the ultrathin thickness of the TiO_x film, it is also possible that the surface defects and associated states may have an impact on the TFT characteristics. In order to test this premise, we spin-coated 300 nm of poly(methyl methacrylate) (PMMA) on top of the TFT devices fabricated from the forming-gas-annealed ultrathin TiO_x film. While the PMMA-topcoat is expected to only passivate the surface defects, the device characteristics of the PMMA-topcoat TiO_x TFT (Fig. 4c) displayed only a marginal improvement in the transfer characteristics. For instance, both on- and off-state currents were only slightly increased, resulting in a minor increase in the maximum

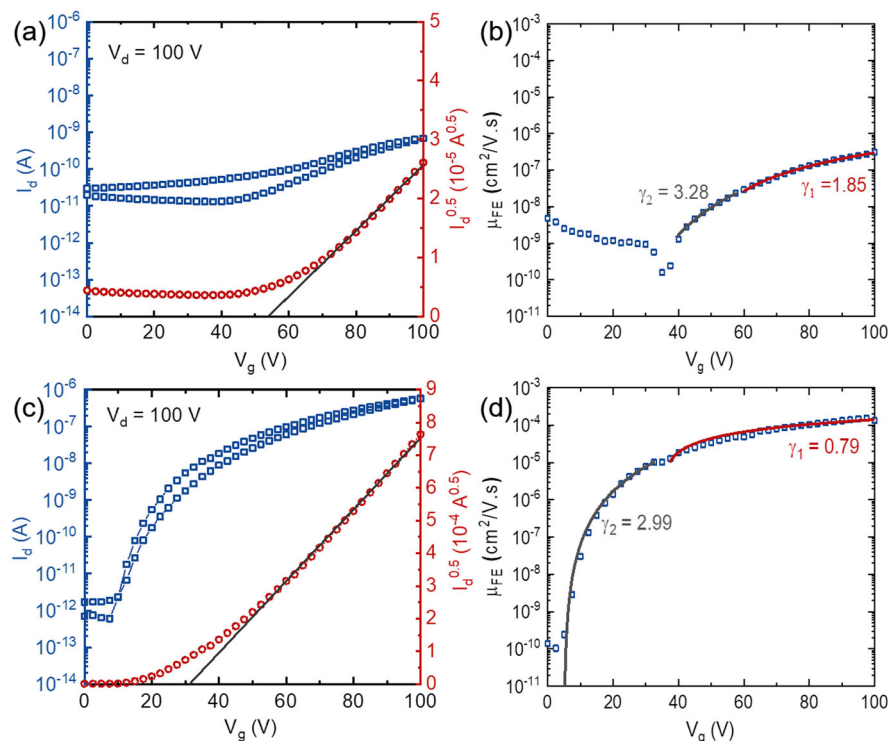


Fig. 4 Role of oxygen vacancy defects in mediating VRH transport. **a** Transfer characteristics of the TiO_x TFT (W/L = 500 μm/5 μm) fabricated using ultrathin TiO_x film annealed in oxygen atmosphere (15 min at 400 °C followed by 15 min at 600 °C); **b** μ_{FE} variation with V_g with power law fits for $V_g > 50$ V and $V_g < 50$ V. The exponent values of 1.85 and 3.28 indicate that the carrier transport occurs via VRH. The decrease in the number of available defects states however restricts the charge mobility. **c** Transfer characteristics of the TiO_x TFT (W/L = 500 μm/5 μm) fabricated using forming gas annealing and the PMMA top-coat, leading to the passivation of surface defects and, consequently, a small increase in the on-state current due to decreased carrier scattering. **d** μ_{FE} variation with gate voltage and power law fit for $V_g > 40$ V and $V_g < 40$ V with the exponents of 0.79 and 2.99 indicating the VRH transport at low V_g changing toward TLC transport at high V_g .

saturation mobility. The device also featured ~6 decades of current on–off ratio, largely identical to the value obtained without the PMMA surface passivation while V_{th} and V_{on} exhibited a slight decrease (by ~10 V). As depicted in Fig. 4d, the field-effect mobility showed ~6-decade modulation with the power law exponents of 0.79 and 2.99, respectively, for high- V_g and low- V_g regimes, all nearly same as the values obtained from the TiO_x device without the PMMA-topcoat, highlighting that the surface defect states have a minor influence on the observed, large gate-induced modulation of charge mobility, not interfering with the inherent charge carrier transport in the ultrathin TiO_x thin film.

Bi-exponential density of states. Based on the correlations drawn between the transfer characteristics and XPS analysis discussed above, it can be established that the oxygen vacancies within the bulk of the TiO_x film mediate the charge carrier transport in the ultrathin TiO_x TFT. However, the meaning of the large power law exponent still remains unexplained, which to our knowledge has never been reported in the case of oxide semiconductors. During the postulation of Eq. (3) for TLC mode in oxide TFTs, Lee et al. have correlated the value of exponent to the characteristics of the band-tail density of states through $2(T_o/T - 1)$, where T_o is the characteristic temperature of band-tail states¹⁶. In fact, a similar empirical relationship has been discussed previously in other semiconductor systems such as organic TFTs^{50–52}. Interestingly, Meijer et al. have analytically derived the identical mobility vs. V_g power law relationship based on the VRH transport of charge carriers through the band-tail states in

organic semiconductors⁵⁰. They report the expression,

$$I_d = A(C_i(V_g - V_{on}))^{\left(\frac{2T_o}{T} - 1\right)}, \quad (4)$$

where T_o being the characteristic temperature of band-tail density of states, and A the proportionality constant dependent on T and other material parameters. Considering that $\sigma_d = en\mu$, where e is the elementary charge and $n = \frac{C_i(V_g - V_{on})}{et_s}$ with t_s being the thickness of the charge accumulation layer, the Eq. (4) becomes expressing the identical power relation to Eq. (3) suggested by Lee et al. Despite the fact that both the models originate from slightly different analytical approaches, they arrive at the same power law relation between mobility and V_g , especially with the identical power law exponent. Lee's model has presented the TLC transport in oxide semiconductors while Meijer et al. have formally referred the transport mode as VRH; the origin of both the transport mechanisms can be essentially attributed to localized band-tail states originating from the material being amorphous or highly defective. In TLC, the free electrons in the conduction band are responsible for the current flow with defect states acting as charge traps, whereas in the case of VRH, high density of trap states supports the hopping transport of charge carriers, thus effectively exhibiting the current flow. Our large exponent value suggests that VRH being the governing charge transport mechanism at low V_g . There are numerous past literatures studying VRH transport in organic TFT utilizing the same model and reporting similarly large exponents. The parameter T_o describes the width of exponential distribution of density of band-tail states⁵³. In the case of our device, the value of exponent at low V_g (2.18 in Fig. 2c) corresponds to $T_o = 622.8$ K (i.e. 53.6 meV).

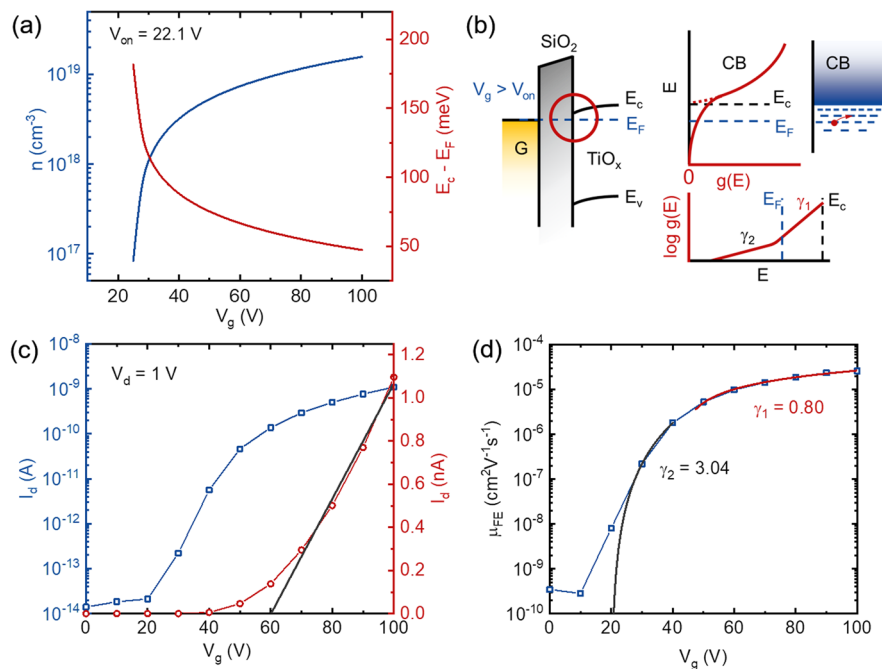


Fig. 5 Bi-exponential density of states and VRH transport. **a** Variation in n (blue line) and the position of E_F compared with E_c with respect to the V_g (red line) changed above V_{on} . **b** Schematic showing transistor band diagram across the gate-insulator-semiconductor stack (left); more details of the area marked by a red circle (top-middle) showing the electron energy (E) vs. density of states ($g(E)$), where CB denotes the conduction band with characteristic parabolic $g(E)$; bi-exponential variation of density of states ($g(E)$) with energy near E_c (bottom-middle); E_F is inside the band-tail and moving closer to E_c when $V_g > V_{on}$, thus supporting the charge (red dot) conduction via hopping through the localized states (indicated by the red arrow) depicting VRH phenomena (right). **c** Linear-regime transfer characteristics extracted from the output characteristics of ultrathin TiO_x TFT prepared by forming-gas annealing. **d** Corresponding linear mobility variation with gate voltage with the power-law exponent for VRH regime at low V_g exhibiting the value of 3.04 and the TLC transport regime at high V_g exhibiting the value of 0.8.

This value is comparable to the values reported for VRH in organic TFTs (~450–550 K for poly(3-hexylthiophene) (P3HT) and poly(p-phenylene vinylene)) which, similar to our system, is predominantly amorphous^{54,55}. This evidence supports that the VRH through localized band states is indeed mediating the charge transport in our system and suggests that it is also playing a role in exhibiting large mobility modulation.

Finally, it is possible to explain the observed two different power-law exponents in the V_g -dependent mobility data. Essentially, when V_g is varied in a given voltage range, the E_F in the transistor channel is sweeping through the density of band-tail states ($g(E)$) having a bi-exponential distribution⁵⁶. V_g causes the change in the carrier density, n , though $n = \frac{C_i(V_g - V_{on})}{e t_s}$, which in turn varies the E_F through $E_c - E_F = k_b T \log(N_c/n)$, with k_b being the Boltzmann constant and N_c the effective density of states of conduction band. These V_g -dependent n and E_F are illustrated in Fig. 5a. As V_g is increased, E_F is being moved closer to E_c (i.e., decreasing $E_c - E_F$ from 180 meV to 50 meV). During the course of this sweep, E_F is probing the exponential distribution of localized band-tail states with two different $k_b T_0$ regimes (Fig. 5b), which manifest themselves as the two linear regimes in the $\log(g(E))$ vs. E plot with the corresponding $g(E)$ expressed as:

$$g(E) = A \exp\left[-\frac{(E_c - E)}{k_b T_{o1}}\right] + B \exp\left[-\frac{(E_c - E)}{k_b T_{o2}}\right], \quad (5)$$

with A and B being proportional constants, and $\frac{-1}{k_b T_{o1}}$ and $\frac{-1}{k_b T_{o2}}$ indicating the two slopes in the schematic plot, respectively. In the mobility vs. V_g plots, a smaller γ_1 (at high V_g) gives a larger slope and a large γ_2 (at low V_g) a lower slope. Thus, our data shows that by sweeping V_g , we have surveyed $g(E)$ and revealed

the bi-exponential distribution of band-tail density of states, supporting the notion of the VRH charge transport mediated by localized band-tail states. Using the exponent values estimated in Fig. 2c, $\gamma_2 = 2.18$ and $\gamma_1 = 0.78$, the values for both the T_0 parameters can be calculated as $T_{o2} = 622.8$ K (53.6 meV) and $T_{o1} = 298.4$ K (25.7 meV), respectively. It should also be noted that over the course of V_g sweep assessed in this study, E_F is tracing the sub-bandgap region within 180 meV to 50 meV, which is much larger than the thermal energy at room temperature (~25 meV). Thus, at low- V_g when the E_F is residing in deeper trap states, the carriers do not have sufficient energy to get thermally released into the conduction band and VRH transport prevails. However, when E_F starts accessing the trap states much closer to 50 meV at high- V_g , a stochastic thermal release of the charge carriers into the conduction band starts taking place and the transport evolves towards majority TLC, which is also sometimes referred to as multiple trapping and thermal release (MTR) transport. Previously, exhibition of VRH at room temperature has been demonstrated in the case of amorphous organic semiconductors^{50,52}. In the case of amorphous oxide semiconductors, however, the prevalence of TLC or VRH has been reported to depend on temperature, where TLC prevails at room temperature and on decreasing the temperature VRH dominates the carrier transport⁴².

Meanwhile, it is worth noting that the T_0 values observed from the VRH model in organic TFTs have been estimated from the linear-regime mobility vs. V_g data⁵⁵, not from the saturation regime as discussed so far. To test whether the V_g -dependent, linear-regime mobility in the ultrathin TiO_x TFT still follows the VRH charge transport, we utilized the output characteristics of the ultrathin TiO_x TFT (Fig. 2a), extracting the linear-regime transfer characteristics at $V_d = 1$ V (Fig. 5c), which allows the evaluation of linear-regime μ_{FE} .

The resulting μ_{FE} vs. V_g plot in Fig. 5d clearly exhibits the two-exponent power law with 5-decade gate-dependent mobility modulation and the exponent values largely consistent with those observed in the saturation regime. This not only confirms the bi-exponential distribution of band-tail states but also further supports the correlation between the VRH transport and the large exponent at low V_g in the ultrathin TiO_x TFT regardless of the saturation or linear device operation regimes.

Conclusions

In summary, the ultrathin amorphous TiO_x TFT fabricated by low-temperature ALD was investigated to explore the origin of large gate-dependent mobility modulation observed in ultrathin metal oxide TFTs. The large ~ 6 -decade, gate-induced mobility modulation observed in the studied ultrathin TiO_x TFT could be associated with the presence of band-tail defects, such as bulk oxygen vacancies, based on the physicochemical analysis of TiO_x prepared under varying post-ALD thermal treatments and the accompanying TFT device characterization. By comparing the empirical power law relationship of the gate-dependent mobility in metal oxide TFTs with the analytic model previously derived for organic semiconductors, the large power-law exponent, which drives the large gate-induced mobility modulation, was identified to be originating from the VRH transport of charge carriers through the band-tail states of ultrathin TiO_x , with its bi-exponential density of states reflected on the two different power-law exponent regimes in the gate-dependent mobility. The results highlight rather unusual and counterintuitive roles of defect states within ultrathin metal oxides in possibly enabling some of the high performance parameters in associated TFT devices, as best exemplified by the increased off-state current accompanied by the reduced device on-off ratio upon the oxidative annealing of ultrathin TiO_x against the typical notion that such an oxidative annealing in metal oxide transistors would reduce the background carrier density while increasing the on-off ratio.

Methods

Fabrication of TiO_x TFT. The TiO_x thin film was deposited using Cambridge Nanotech Savannah S100 ALD system (base pressure ~ 0.45 Torr) at 85°C on oxygen-plasma-cleaned Si (p^{++}) substrate with 300 nm dry thermal oxide. During each ALD cycle, titanium (IV) isopropoxide and water vapors were alternatively pulsed each for 0.4 s with 5-s interval under continuous N_2 flow. In total, 75 cycles were used to deposit TiO_x film thickness of 3.5 nm (estimated by spectroscopic ellipsometry; J.A. Woollam M-2000FI). Unless otherwise stated, as deposited films were then annealed in forming gas (4% H_2/Ar) using a rapid thermal processor (RTP; Modular Process Technology, RTP-600S) at 400°C for 15 min followed by 600°C for 15 min. The TFT devices were fabricated with electron-beam lithography using the bilayer resist scheme (PMGI SF6 underlayer and ZEP 5200 A imaging layer) followed by lift-off of the evaporated contact metal stack consisting of 30 nm Al, 30 nm Ti, and 40 nm Au (bottom to top), to pattern source-drain electrodes with channel length of $5\ \mu\text{m}$ and width $500\ \mu\text{m}$. The schematic of the bottom gate top contact TFT device investigated in this study is shown in Fig. 1a.

Material characterization. The crystallinity of the TiO_x film was characterized by XRD (Rigaku Ultima III diffractometer), operating in the Bragg configuration using $Cu\ K_\alpha$ radiation ($1.54\ \text{\AA}$) with a scan range from 10° to 80° and a scan rate of $0.38^\circ\text{min}^{-1}$ to acquire the XRD spectra. The chemical bonding characteristics of prepared samples were characterized by XPS using a custom-built XPS system equipped with a hemispherical electron energy analyzer (SPECS) and Al K_α X-ray source (1.487 keV, SPECS). The sample crystallinity was also further examined by extremely surface-sensitive, LEED inside an ultra-high-vacuum (UHV) chamber (base pressure, 2×10^{-10} Torr) using a low energy electron microscope (LEEM) located at the Electron Spectro-Microscopy (ESM, 21-ID-2) beamline of the National Synchrotron Light Source II (NSLS-II). After being transferred to the UHV chamber, the samples were annealed at mild temperature of 250°C to remove adsorbed surface contaminants from air. All measurements were conducted at room temperature and using 30 eV incident electron energy.

Data availability

All the relevant data acquired or analyzed in support of the findings reported in this study are available from Materials Cloud Archive (<https://doi.org/10.24435/materialscloud:1t-g7>) or the corresponding author upon request.

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Author contributions

N.T. and A.S. prepared TiO_x samples. N.T. carried out device fabrication and electrical measurements. A.S. and S.S. carried out XPS measurements. A.S. conducted XRD measurements. Z.D. and J.T.S. performed LEED measurements. N.T. and C.-Y.N. planned experiments, analyzed data, assimilated and prepared initial draft. C.-Y.N. and J.T.S. conceptualized and supervised the study. All the authors discussed, commented on the draft and participated in finalizing the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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