Room-temperature-protonation-driven on-demand metal-insulator conversion of a transition metal oxide

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Room-temperature protonation and metal-insulator conversion of a transition metal oxide (TMO) was demonstrated by all-solid-state thin-film transistor with vanadium dioxide using a water-infiltrated nanoporous glass as a solid electrolyte. This promising result can provide a novel route for TMO-based solid-state electro-optical devices, in particular, smart windows for on-demand infrared shielding.

Keywords: protonation, solid state electrochemistry, transition metal oxide, thin film transistor
Hydrogen in transition metal oxides (TMOs) commonly exist as protons (H+) through covalent O-H bonding with the surrounding oxide ions (O^{2-})\textsuperscript{[1]} and act as shallow donors that donate an electron to TM cations,\textsuperscript{[2]} resulting in a dramatic change in the electro-optical properties.\textsuperscript{[3]} Although H+ has historically been viewed as the most ubiquitous impurity,\textsuperscript{[4]} recent studies suggest that it may reveal the potential characteristics in TMOs. Protonation of TMOs is the most ideal technique to modulate their functions, even as compared with state-of-the-art modulation techniques,\textsuperscript{[5,6]} due to their intrinsic nonvolatile operation,\textsuperscript{[7,8]} but protonation is not typically utilized for solid-state devices because of imperative high-temperature annealing treatment in hydrogen source. Although one solution for room temperature (RT) protonation of TMOs is liquid-phase electrochemistry through electrolysis of an aqueous solution, which has been a facile method to protonate TMOs at RT,\textsuperscript{[9,10]} it is unsuited for practical purposes due to liquid-leakage problem. Hence, protonation/deprotonation in solid-state devices has yet to be realized in practical applications.

Herein, we focus on vanadium dioxide (VO\textsubscript{2}) to demonstrate solid-state protonation and conversion of the electronic states from an insulator to a metal at RT. VO\textsubscript{2} is classically well-known thermochromic TMO, which shows metal-insulator (MI) transition at the transition temperature (T_{MI}) of 68 °C.\textsuperscript{[11]} The MI transition accompanies a structural change from a low-temperature monoclinic to a high-temperature tetragonal (rutile-type) structure, which causes reconstruction of electronic structures to open up a charge gap of \textasciitilde0.6 eV,\textsuperscript{[12]} resulting in the abrupt change of electrical and optical properties at the MI transition. In particular, the dramatic change of optical transmittance in infrared region while maintaining visible transparency has potential for heat-blocking smart window, which enables us to intelligently regulate and utilize sunlight, leading to energy saving in architectures. These features of VO\textsubscript{2} offer several advantages compared to visible-color switching of conventional
electrochromic devices. However, the relatively high $T_{\text{MI}}$ of VO$_2$ makes it awkward to use at appropriate temperatures for practical applications.

Protonation of VO$_2$ ($\text{H}_3\text{VO}_2$) is one of the effective ways to reduce $T_{\text{MI}}$ and modulate the electronic state from an insulator to a metal via hydrogen spillover through thermal annealing of the VO$_2$ nanobeam in H$_2$ / vacuum conditions.$^{[13]}$ MI phase modulation has also been achieved by electrostatic-charge doping with ionic-liquid-gated transistors$^{[14,15]}$ and epitaxial strains in thin films,$^{[16]}$ but protonation of VO$_2$ via a chemical route is the most ideal to engineer the MI transition characteristics due to the intrinsic non-volatile operations similar to a conventional electrochromic device based on $\text{H}_3\text{WO}_3.$$^{[3]}$ However, protonation of VO$_2$ requires a high-temperature heat treatment,$^{[17-19]}$ and the uptake of H$^+$ into VO$_2$ was extremely slow at RT, i.e. the chemical solubility of $\text{H}_x\text{VO}_2$ was very small at $x = 0.08.$$^{[17]}$ Controlling the MI phase transition by RT protonation has technological importance as a step toward practical uses.

Here we propose a new solid-state device for on-demand-protonation of VO$_2$ thin films at RT using a thin film transistor (TFT) combined with water-electrolysis.$^{[20]}$ Figure 1a schematically illustrates the device structure of a water-electrolysis TFT composed of water-infiltrated nanoporous glass as a gate insulator, which serves as solid electrolyte.$^{[20]}$ The gate insulator consists of an amorphous 12CaO·7Al$_2$O$_3$ (a-C12A7) thin film with nanoporous structure (Hereafter this film is abbreviated as CAN). C12A7 is hydrosopic material, and water vapor in air is automatically absorbed into the CAN film due to the capillary effect of the interconnected nanopores.$^{[20]}$ A gate bias application induces water electrolysis in the CAN gate insulator, and produced electro-active H$^+$ ($\text{H}_3\text{O}^+$) and OH$^-$ ions can be used to protonate and deprotonate the VO$_2$ channel layer, respectively. The water-electrolysis TFT can be considered as a nanosized electrochemical cell that enables reversible
protonation/deprotonation in a high-electric field. Consequently, the ~10-nm-thick VO$_2$ layer was reversibly altered from an insulator to a metal by changing the external gate voltage up to 35 V at RT. The protonation was clearly accompanied by the structural change from monoclinic VO$_2$ to tetragonal H$_x$VO$_2$ phase. The MI phase modulation in protonated VO$_2$ under an applied voltage at RT offer a new route to all-solid-state smart windows for on-demand infrared shielding, and the present results lead to a universal approach to modulate the electrical and optical properties of TMOs via water-electrolysis-induced protonation.

The TFT structure was fabricated on 20-nm-thick VO$_2$ epitaxial films (channel size: 800-μm long and 400-μm wide) grown on (11$ar{2}$0) sapphire substrates by pulsed laser deposition. Crystallographic characterization of the VO$_2$ epitaxial film is summarized in Figure S1 in Supporting Information. $T_{\text{MI}}$ of as-grown VO$_2$ films was 65 °C, which is similar to 68 °C of bulk VO$_2$.[11] Figure 1b shows an optical micrograph of the VO$_2$-based water-electrolysis TFT. Metallic Ti films were used for Source (S), Drain (D) and Gate (G) electrodes. A 200-nm thick CAN film was used for a gate insulator as solid electrolyte, where the film was deposited at RT under an oxygen pressure of 5 Pa to realize a nanoporous structure. (The relative density of the CAN film was 71 % with respect to 2.92 g cm$^{-3}$ of a dense C12A7 film).[20] Figure 1c shows Z-contrast, high-angle, annular dark-field scanning transmission electron microscope (HAADF-STEM) image of the cross-sectional TFT structure. The numerous dark spots with 10–20 nm diameters indicate that the high-density nanopores were incorporated in the CAN film. For the protonation of VO$_2$ by water-electrolysis TFTs, we focused on the electronic structure of parent (insulating) VO$_2$. The energy-band diagram of VO$_2$[21] with respect to the electric potentials of oxidation and reduction of H$_2$O (Figure S2 in Supporting Information) shows that the conduction band minimum is below the electric potential of cathode reaction ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$) and the valence band maximum is above that of anode reaction ($\text{H}_2\text{O} \rightarrow 1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$). Thus, the proton
can be expected to move into and get out from VO$_2$ channel layer without the gas generation by applying positive and negative electric-fields, respectively.

VO$_2$-based water-electrolysis TFTs were characterized at RT by measuring sheet resistance ($R_s$) and thermopower ($S$) after applying and subsequently switching off gate bias. It should be noted that $S$-values can be used to easily evaluate the metal-insulator conversion because they basically reflect the energy differential of density of state at Fermi energy and are sensitive to significant changes in the electronic structure of VO$_2$ at $T_{MI}$.[22] Figures 2a and b plot the gate voltage ($V_g$) dependence of $R_s$ and $S$-values at RT for VO$_2$-based water-electrolysis TFTs, respectively. The dependence was measured immediately after the bias application for 10 minutes at each positive voltage from +5 V to +35 V. A double-digit decrease in $R_s$ from the virgin state (68 kΩ sq$^{-1}$) to 0.5 kΩ sq$^{-1}$ at +35 V was clearly observed, and the $R_s$ continued to decrease by positive $V_g$ application. Meanwhile, $|S|$-value drastically decreased form 200 μV K$^{-1}$ of insulating parent VO$_2$ phase[22] as the positive $V_g$ increased up to +30 V and became saturated at 43 μV K$^{-1}$, which is close to that of metallic H$_x$VO$_2$ bulk (~35 μV K$^{-1}$). [19] These results are discussed by comparing the electronic structures of insulating H$_x$VO$_2$ ($T < T_{MI}$) and metallic H$_x$VO$_2$ ($T > T_{MI}$). Schematic electronic structures around Fermi energy are shown in Figure S3 in Supporting Information. H$^+$ doping into insulating H$_x$VO$_2$ provides electrons to the conduction band, and the gradient of DOS becomes moderate, resulting in the consequent reduction of $|S|$-values. On the other hand, $|S|$-values of metallic H$_x$VO$_2$ are constant at ~35 μVK$^{-1}$ at $T > T_{MI}$. Therefore, the decrease in $|S|$-values and their saturation as $V_g$ increases reflect a change in the electronic state from an insulator to a metal. The inset in Figure 2a summarizes the $V_g$ dependence of $I_g$ during the bias application at each $V_g$. Although $I_g$ at $V_g = +5$ V was small bellow 10 pA, $I_g$ exponentially increased with respect to $V_g$ from +10 V to +35 V, suggesting that $I_g$ originates from the ion current of water-electrolysis in the CAN film and electrochemical reaction of VO$_2$ film.
These findings suggest the device operation mechanism as follows. First, $V_g$ application at +5 V accumulates charge carriers at the VO$_2$ film surface via a pure electrostatic field effect due to the negligible leakage current, resulting in the formation of parallel-plate capacitor (i.e. the electric field starts to be well applied on the surface of VO$_2$ channel). Using a capacitance ($C$) of 160 pF for the CAN gate insulator,$^{[20]}$ the accumulated sheet carrier density is estimated to be $1.6 \times 10^{12}$ cm$^{-2}$ at $V_g = +5$ V. A further gate bias application generates dissociated H$^+$ and OH$^-$ ions in the solid gate insulator, which are attracted to the surface of VO$_2$ and Ti, respectively. H$^+$ ions penetrate into the VO$_2$ crystal (H$_x$VO$_2$), while OH$^-$ ions form an oxidized TiO$_2$ passivation layer on the Ti film surface or become O$_2$ gas at the interface, where the electrostatic potential with linear distribution should be formed across CAN layer. Therefore, threshold voltage of the device operation for the water-electrolysis TFTs can be considered to be much higher than the H$_2$O dissociation potential of 1.23 V. The high electric field formed in the nanosized electrochemical cell should achieve RT protonation of the VO$_2$ thin film, as illustrated in Figure 1a. It should be noted that the protonated VO$_2$ film is stable under ambient and vacuum conditions at RT. The retention time dependence of $R_s$ monitored after switching the gate bias (+20 V) off is shown in Figure S4a in Supporting Information. Although slight decrease of $R_s$ was observed in air, $R_s$ are almost persistent following the removal of $V_g$, confirming the non-volatility of device operation due to the chemical reaction.

Then, we performed reversible operation of VO$_2$-based water-electrolysis TFTs, i.e. protonation and deprotonation by changing positive and negative gate bias. Figure 2c shows the temperature dependences of $R_s$ before and after applying $V_g$ alternately at +20 V and −20 V at RT, where $R_s$–$T$ was measured after switching off $V_g$. The inset plots logarithm of $R_s$ versus $T$ to show the MI transition clearly. $R_s$–$T$ were reversibly modulated and recovered to
initial state, where the ON/OFF ratio was ~30 at RT. However, unlike the previous report on bulk H₃VO₂,[¹³] Tₘᵢ did not shift to lower temperature and was almost unchanged.

Considering that the $R_s$ continues to decrease as $V_g$ increases and the $|S|$-values reaches at that of metal H₃VO₂ at $V_g = +30$ V (Figures 2a and b), only the film surface region becomes metal due to an insufficient H⁺ migration from the surface into bulk region. To estimate the thickness ($d$) of metal H₃VO₂ layer, we used a simple bi-layer model of thermopower,[²³] where the parallel circuit composed of metal (M) and insulator (I) layers was considered to calculate the combined electromotive force. (The electromotive force depends on both the conductivity and thickness of each layer.) The observed $|S|$-value ($|S|_{obsd.} = 43$ μV K⁻¹) of the present TFTs can be expressed by the equation of $|S|_{obsd.} = (\sigma_M|S|_M + \sigma_I|S|_I)/(\sigma_M + \sigma_I)$, where sheet conductance $\sigma_M$ and $\sigma_I$ are defined as $\sigma_M \times d$ and $\sigma_I \times (20-d)$, respectively. The physical properties of conductivity and $|S|$-values for the M and I phases are used from those of reported bulk H₃VO₂[¹⁹] and virgin VO₂ TFTs (Figures 2a and b), respectively. As a result, maximum thickness of metallic layer, after the $V_g$ application at +35 V, is estimated to be 11 nm, confirming that the VO₂ film surface was changed from an insulator to a metal state.

The MI transition of VO₂ is strongly coupled with crystal structure change from an insulating monoclinic phase to a metallic tetragonal phase, which is accompanied by the disappearance of V⁴⁺-ion dimer.[¹²] To validate the crystal structure change of protonated VO₂ film, structural analysis was performed by electron diffraction with TEM at RT. Figures 3a and b present the nano-beam electron diffraction (ED) patterns observed at about 5 nm in depth from surface region of VO₂ film, before (a) and after protonation (b) with an incident electron beam along the [010] direction of VO₂. The initial ED pattern (a) is consistent with the monoclinic structure, where the diffraction spots of superstructures, indicated by arrows,
originate from the formation of $V^{4+}$-ion dimer. Following the protonation (b), the diffraction spots due to the superstructures disappear, demonstrating a transformation from the monoclinic to the tetragonal phase (Figures 3c and d). This result indicates that crystal structure was changed by water-electrolysis-induced protonation of VO$_2$, which provides evidence of metal-insulator conversion. It should be noted that, for heavily-protonated H$_x$VO$_2$ nanobeams$^{[24]}$ and ionic-liquid-gated VO$_2$ TFTs$^{[25]}$ their metallic phases were recently found to have the partially retained V$3d$ orbital ordering. However, the pairing of V ions was not confirmed in the present ED patterns. Additional investigation is necessary to verify this inconsistency in the future.

The metal-insulator conversion must be reversibly controlled in a practical time for the application to electronic devices. Figures 4a and 4b present $I_g$ under $V_g$ application and $R_s$ at the OFF state versus number of gate pulses of +20 V and −20 V at RT, where each pulse duration is 1 min. Upon the application of $V_g$ within 1 min, a large $I_g$ of $\pm 160$ μA was observed and consequently reversible switching of $R_s$ was realized. The voltage switching of metal-insulator conversion demonstrates great potentials especially for on-demand operating smart windows advanced electronic devices based on protonated VO$_2$. Here, we like to discuss a typical time scale of the switching process and its $V_g$ dependence of VO$_2$-based water-electrolysis TFTs. The switching speed of metal-insulator conversion can be considered to depend on water-electrolysis, ion migration in the solid electrolyte, and proton diffusion into VO$_2$ film under $V_g$ application. In particular, the proton diffusion should limit the operation speed in this case because of the low diffusion constant of proton at RT. Therefore, the device-operation speed should strongly depend on the density of protons accumulated at the surface of VO$_2$ channel. Therefore, the speed of metal-insulator phase switching should basically depend on $V_g$, because the density of protons ($\equiv I_g$) exponentially increases with $V_g$. 
There has been a considerable debate concerning the field-induced MI phase conversion of ionic-liquid-gated VO₂ TFTs, in which it results from a collapse of the Mott insulator due to electrostatically accumulated electrons at the film surface[14] or arises from the formation of oxygen vacancies due to an electric-field-induced oxygen migration during the gating process.[15] The latter one might be valid for CAN-gated water-electrolysis TFTs, but, in this case, the DC of \( I_g \) keeps unchanged, during \( V_g \) application, at extremely large value of 0.1–1 mA without the decay for 60 sec at least (Fig. 4(a)) and it is hard to consider the CAN forms the capacitor structure. The present device seems to operate like rechargeable Ni-H₂ battery with constant ionic current, where linear electric-field induces the penetration of ions into each electrode. Therefore, electric-field effect on VO₂ film surface should not be so high to induce oxygen vacancies in the film because of the lack of electric double layer at the interface. In addition, it is known fact that H⁺ can penetrate into VO₂ crystal and H⁺ with smallest ionic radii \( (i.e. \) just proton without electron shell)\[^{26}\] is easily considered to penetrate into VO₂ crystal, compared to the large cations of ionic liquids \( (~10^{2} \text{ pm}) \) such as HMIM-TFSI\[^{15}\] (in this case, the oxygen vacancy mechanism might work.) Therefore, protonation should tend to take place more than electric-field-induced oxygen migration in the present device.

To investigate the pure electric-field effect on this VO₂-TFT, we fabricated TFT structure with water-free gate insulator of a fully dense a-C12A7 film \( (i.e. \) the relative density of a-C12A7 film is 100% \( (2.9 \text{ gc} \text{m}^{-3}) \) and there is no water-containing nanopores in the film).\[^{27}\] The TFT characteristics at RT with the results of CAN-gated VO₂ TFT are summarized in Supporting Information Fig. S5. The \( I_g \) for dry a-C12A7-gated VO₂ TFT was \(<1 \text{nA} \) at most, which is \(~10^{6} \) times smaller than that of CAN-gated VO₂ TFT, indicating that pure electric field effect is dominant. Although the \( C \) of 210 pF for a-C12A7 film is higher than that \( (160 \text{ pF}) \) of CAN film,\[^{20}\] both the \( R_s \) and \( S \)-values have kept almost unchanged even at \( V_g = +40 \text{ V} \) (The maximum \( R_s \) modulation ratio was \(~0.1\%\)). The MI phase conversion by
electric-field effect was not observed in dry a-C12A7-gated VO₂ TFTs and should originate from water-electrolysis in the CAN gate insulator.

To further confirm that the metallization of VO₂ based water-electrolysis TFTs originates from protonation rather than the formation of oxygen vacancies, the protonated TFT was heated in a vacuum. Annealing temperature dependence of $R_s$ for the protonated TFTs, measured at RT, is shown in Figure S4b in Supporting Information. $R_s$ was nearly constant at annealing temperatures below 100 °C, but significantly increased at 150 °C and $R_s$ returned to the insulating state. These observations indicate that thermal deprotonation of H₄VO₂ occurred at 150 °C, which is consistent with the result for bulk H₄VO₂ (87 °C). The increase of $R_s$ in the TFTs upon heating in a vacuum supports that the device operation does not originate from the formation of oxygen vacancies.

Additionally, protonation of VO₂ TFTs is further supported by the change of ED patterns on electron beam irradiation (Figure S6 in Supporting Information for ED patterns of the protonated VO₂ TFTs as a function of irradiation time of electron beam). The ED patterns of protonated VO₂ films changed and the diffraction spots of superstructures appeared as the irradiation time ($t$) increased, where the ED pattern of VO₂ TFTs at $t = 90$ sec can correspond to M2-type monoclinic structure. These observations indicate that the tetragonal structure (metal) changed to monoclinic structure (insulator) upon electron beam irradiation at RT, which can be explained if thermal deprotonation occurs in a vacuum. A similar result was observed for p-type GaN:Mg thin films grown by MOCVD; the obstacle hydrogen produced by NH₃ dissociation can be removed from GaN:Mg film by electron beam irradiation in a vacuum and accordingly p-type conduction was realized. Although it is difficult to completely rule out the contribution of oxygen vacancies, these results should support the water-electrolysis-induced protonation of VO₂ film at RT.

In summary, we demonstrated a new solid-state device for water-electrolysis-induced
protonation and nonvolatile and reversible switching of metal-insulator conversion of VO$_2$ at RT. We fabricated a transistor structure on an insulating VO$_2$ thin film using water-infiltrated nanoporous glass (CAN) as a solid gate insulator, which acts as a solid electrolyte. A gate voltage application induced water electrolysis in the CAN gate insulator with large ion current i.e., nanosized electrochemical cell, and the produced protons were effectively incorporated and removed from VO$_2$ film, which results in a highly reversible alternation of the electronic state from an insulator to a metal. The reversible protonation clearly accompanied a change in the VO$_2$ crystal structure from insulating monoclinic to metal tetragonal phase. These findings provide a new pathway to realize all-solid-state electrochromic devices based on VO$_2$ for energy-saving applications that reversibly change the infrared transmission, while maintaining the visible-light transparency. At this stage, the modulation thickness is limited to be ~10 nm because the electric field is terminated at a thin layer of VO$_2$ channel and protons cannot penetrate deeper into insulating VO$_2$ layer. Indeed, it is difficult to apply this TFT structure to optical devices because, for practical use, a large change in transmittance is required and thus thicker film should be used. We consider that the all-solid state electrochromic device can be practical by changing the device structure to sandwich-type construction (e.g. ITO top electrode / CAN gate insulator / VO$_2$ film / SnO$_2$:F bottom electrode) on glass substrate, where the electric field can be applied over the thickness of VO$_2$ layer and the optical properties is largely modulated by RT protonation. The present approach should lead to the development of electro-optically active solid-state devices with TMO materials by engineering RT-protonation.

**Experimental section**

**Device Fabrication:** TFT structures (Figure 1a) were fabricated on 20 nm-thick VO$_2$ epitaxial films using metal shadow masks. The dimensions of the channel were 400 $\mu$m in width and 800 $\mu$m in length. The VO$_2$ channel layer was grown at 500 °C under O$_2$ pressure ($P_{O_2}$) of 2.0
Pa on (11̅20) α-Al₂O₃ substrates (10 x 10 x 0.5 mm³) by pulsed laser deposition (PLD). A KrF excimer laser (wavelength of 248 nm) was used to ablate a V₂O₅ polycrystalline target disk, where the laser energy fluence and the repetition rate were 3 J cm⁻² pulse⁻¹ and 10 Hz, respectively. Afterwards the films were cooled to RT under the same oxygen pressure. The VO₂ film with a monoclinic structure was heteroepitaxially grown on α-Al₂O₃ substrate with an epitaxial relationship of (100)[010]VO₂ || (11̅20)[0001]α-Al₂O₃, which was confirmed by high-resolution XRD at RT (Figure S1 in Supporting Information). Second, 20-nm-thick metallic Ti films, which served as both the source and drain electrodes, were deposited by e-beam (EB) evaporation in a vacuum (~10⁻⁴ Pa, no substrate heating). Then, 200-nm-thick CAN gate insulator was deposited by PLD (KrF excimer laser with energy fluence of 3 J cm⁻² pulse⁻¹) at RT under P_O₂ of 5 Pa to make CAN film nanoporous. The bulk density of the resultant CAN film was 2.07 g cm⁻³, evaluated by grazing incidence X-ray reflectivity, which corresponds to 71 % of fully dense amorphous C12A7 glass (2.92 g cm⁻³). AC conductivity of the CAN film was 3.7 x 10⁻⁸ S cm⁻¹ at RT, which was slightly smaller than 5.6 x 10⁻⁸ S cm⁻¹ of ultrapure water. Finally, a 50-nm-thick metallic Ti film, used as the gate electrode, was deposited by EB evaporation at RT.

**Electrical transport measurement:** Gate current (I_g) was measured as a function of gate voltage (V_g) using a semiconductor device analyzer (B1500A, Agilent). Sheet resistance (R_s) was measured by d.c. four probe method in the van der Pauw electrode configuration. Thermopower (S-value) was measured by giving a temperature difference (ΔT) of ~4 K in the film using two Peltier devices while the actual temperatures of both sides of VO₂ film surface were monitored by two tiny thermocouples. The thermo-electromotive force (ΔV) and ΔT were simultaneously measured, and the S-values were obtained from the slope of the ΔV–ΔT plots. All the electrical property measurements were performed in an ambient atmosphere.
**Structural analysis:** TEM samples of the CAN-gated VO₂ TFTs were prepared by a focused-ion-beam (FIB) micro-sampling technique, in which the trilayer structure region of the TFTs was cutout and thinned by FIB (JIB-4600F, JEOL) to obtain samples for cross-sectional observation. The cross-sectional microstructure of VO₂ TFTs was examined at RT by HAADF-STEM (JEM-ARM200F, 200 kV, JEOL), where electron incident direction was sapphire [0001]. The ED patterns were observed by nanobeam electron diffraction with spot size of about 1.5 nm (JEM-2800, 200 kV, JEOL).

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Figure 1. Water-electrolysis-induced protonation of VO$_2$ thin film. (a) Schematic of the thin film transistor (TFT) structure composed of Ti electrodes / water-infiltrated CAN gate insulator / VO$_2$ epitaxial film on sapphire substrate. Magnified image illustrates the principle of electrolysis-induced protonation of the VO$_2$ film. During positive gate voltage ($V_g$) application, H$^+$ and OH$^-$ ions, which are produced by water electrolysis in the CAN film (nanosized electrochemical cell), move to the surfaces of VO$_2$ film and Ti gate electrode, respectively. H$^+$ ions penetrate into the VO$_2$ crystal (H$_x$VO$_2$) and OH$^-$ ions become O$_2$ gas at each interface. (b) Optical micrograph of the VO$_2$-based TFT. Channel width and length are 400 μm and 800 μm, respectively. (c) Cross-sectional HAADF-STEM image of Ti (50 nm) / CAN (200 nm) / VO$_2$ (20 nm) / sapphire substrate. Nanopores with 10–20 nm diameters appear as dark contrasts in the CAN film.
Figure 2. Protonation-driven metal-insulator conversion of VO\textsubscript{2} thin film. (a) Sheet resistance ($R_s$) as a function of $V_g$ up to +35 V, where $R_s$ was measured after holding the $V_g$ application for 10 minutes. Inset shows $V_g$ dependence of mean gate current (≡ion current, $I_g$) during the $V_g$ application. $I_g$ exponentially increased with $V_g \geq +10$ V due to water-electrolysis-induced protonation of VO\textsubscript{2}. $R_s$ simultaneously decreased with $V_g \geq +10$ V, indicating that the electronic state of VO\textsubscript{2} was altered from an insulator to a metal by water-electrolysis-induced
protonation. (b) Thermopower ($S$) as a function of $V_g$ at RT. $|S|$ decreased with $V_g \geq +10$ V and was saturated at 43 $\mu$V K$^{-1}$, which is close to that of metallic H$_x$VO$_2$ ($\sim$35 $\mu$V K$^{-1}$).[19] (c) Temperature dependence of $R_s$ measured before (blue closed circles) and after applying $V_g$ alternately at +20 V (red closed symbols) and −20 V (blue closed triangles) at room temperature (RT). Each curve was measured after switching off the $V_g$. Inset shows logarithmic $R_s$ vs. $T$. On/off ratio was ~30 at RT.
Figure 3 Structural analysis of protonated VO$_2$ thin film. Nano-beam electron diffraction patterns of (a) as-prepared and (b) protonated VO$_2$ films. The main diffraction indices are noted above the corresponding diffraction spots. Arrows in (a) indicate the diffraction spots due to vanadium-ion dimerization of monoclinic VO$_2$. Spots from the superstructure disappeared upon protonation (b), indicating the structural change from monoclinic to tetragonal phase. Schematic of the crystal structures for (c) monoclinic and (d) tetragonal phases. Brown and yellow denote vanadium and oxygen ions, respectively.
Figure 4 Reversible metal-insulator conversion of VO$_2$ thin film at room temperature. (a) Retention time dependence of $I_g$ during the $V_g$ application. VO$_2$ thin film was protonated at $V_g = +20$ V, whereas deprotonation occurs at $V_g = -20$ V. (b) $R_s$ modulation at room temperature, which was measured for each state in (a).