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Gate-tunable gigantic lattice deformation in VO$_2$


RIKEN Center for Emergent Matter Science (CEMS), Wako 351-0018, Japan
Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan
RIKEN SPring-8 Center, Hyogo 679-5148, Japan
National Institute of Advanced Industrial Science and Technology, Tsukuba 305-8562, Japan
Japan Synchrotron Radiation Research Institute, SPring-8, Hyogo 679-5198, Japan
Quantum-Phase Electronics Center and Department of Applied Physics, University of Tokyo, Tokyo 113-8656, Japan
Department of Advanced Materials Science, University of Tokyo, Kashiwa 277-8561, Japan

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We examined the impact of electric field on crystal lattice of vanadium dioxide (VO$_2$) in a field-effect transistor geometry by in-situ synchrotron x-ray diffraction measurements. Whereas the c-axis lattice parameter of VO$_2$ decreases through the thermally induced insulator-to-metal phase transition, the gate-induced metallization was found to result in a significant increase of the c-axis length by almost 1% from that of the thermally stabilized insulating state. We also found that this gate-induced gigantic lattice deformation occurs even at the thermally stabilized metallic state, enabling dynamic control of c-axis lattice parameter by more than 1% at room temperature.

The field-effect transistor (FET) is a key building block for modern information technology, enabling electrical switching of current flowing through a channel surface by external voltages. The essential feature of FET is to tune the number of electrons in a channel material electrostatically, the number of electrons in a channel material electrostatically, the number of electrons in a channel material electrostatically, or by external voltages. The essential feature of FET is to tune the number of electrons in a channel material electrostatically, or by external voltages.

We recently reported that a combination of EDLT and vanadium dioxide (VO$_2$) provides remarkable features relevant to the first-order MIT. VO$_2$ is a classic strongly correlated oxide showing characteristic MIT above room temperature with a resistance jump of more than four orders of magnitude. This MIT is of the first order, and hence, electronic states are strongly coupled with lattice structures; a half-filled metallic state is thermally stabilized in a tetragonal phase above the transition temperature ($T_M$), whereas a low-temperature insulating state is stabilized in a monoclinic phase with dimerized V$^{2+}$ ion pairs.

We fabricated EDLT with VO$_2$ thin films, and found that the low-temperature insulating state can be completely switched to the metallic state over the first-order MIT by application of gate voltages ($V_G$). Moreover, it turned out that an electrically induced conducting channel is extended to an entire region of the 70-nm thick film along c-axis direction beyond the fundamental electrostatic screening length, which is in marked contrast to conventional FETs that have a two-dimensional conducting channel. We have attributed these phenomena to electric-field induced collective phase transitions; electrostatic charge accumulation at a surface triggers long-range bulk lattice deformation to minimize interface energy, and subsequently, this bulk structural transformation drives a cascade of electronic phase transition inside bulk region of a film beyond the screening length. This distinguished function of electric-field induced bulk phase transition is particularly advantageous for optoelectronic device applications such as energy-saving smart windows as we recently demonstrated.

Due to its fundamental interest regarding the operation mechanism as well as its practical importance toward future ultralow-energy consumption electronics based on correlated oxides, VO$_2$-EDLT has attracted growing attention. Among a number of recent reports, Jeong et al. has also realized gate-induced metallization in VO$_2$ thin films by EDLT technique using ionic liquid, but they have proposed a different mechanism; electric-field induced oxygen vacancy formation. As direct evidence, they presented secondary ion mass spectrometry data using oxygen isotope, which indicates that in their case oxygen fills into a gate-induced metallic state at a surface of VO$_2$ film within 5 to 10 nm length scale upon applying negative $V_G$ under oxygen atmosphere. In addition, they noted that a gate-induced metallic state remains even after removal of ionic liquid, suggesting irreversible chemical reactions. These results may not be able to explain our results, where a gate-induced metallic state is not...
limited to a surface but extended to an entire region of the 70-nm thick film, and it can be reversibly switched on and off by application of $V_G$. This implies that the governing mechanism can differ depending on sample variations and/or experimental conditions, even though a metallic ground state can be induced by application of $V_G$ for both cases. There are even other mechanisms suggested by other groups; one group insists that hydrogen doping should play a major role, and another group claims that gating effect is limited only at a surface. Accumulation of experimental evidence from different aspects is highly desired to understand what is going on in VO$_2$-EDLT. In this report, we directly elucidate by *in-situ* x-ray diffraction (XRD) measurements that crystal lattice of VO$_2$ significantly deforms under the presence of electric field throughout a whole film over the screening length. We also show that this bulk lattice deformation can be dynamically controlled at room temperature by $V_G$ in a reversible isothermal process.

We prepared two VO$_2$-based (001) epitaxial thin films having different thicknesses of 10 nm (sample #1) and 40 nm (sample #2), both of which were grown on TiO$_2$ (001) single crystal substrates by pulsed laser deposition. The growth condition of the films and the device fabrication process were nominally the same as the previous reports. Sample specifications are listed in Fig. 1(a). The 40-nm thick film (sample #2) was doped with 2% of tungsten in order to reduce $T_{MI}$ below 300 K due to limitation of the maximum temperature available with the measurement systems used in this study. Both films were grown at around 400 °C under the oxygen pressure of 10 mTorr, and then patterned into a standard Hall-bar geometry by combining conventional photolithography and Ar-ion etching techniques. Source/drain electrodes, voltage probes, and a side gate electrode were made with Ti/Au deposited by electron-beam evaporation. The dimensions of a channel were 60 μm in width and 500 μm in length. Both a channel and a gate electrode were finally covered by an organic ionic liquid, $N,N$-diethyl-$N$-(2-methoxyethyl)-$N$-methylammonium bis-(tri-fluoromethylsulfonyl)-imide (DEME-TFSI). The sample #1 was then loaded in a standard cryostat and its electronic and structural properties were characterized in high vacuum ($P < 10^{-5}$ Pa), whereas those properties of the sample #2 were evaluated under N$_2$ flow. The XRD measurements on the sample #1 and #2 were performed by a commercially-available four-circle diffractometer and the home-made x-ray microrobe system, respectively, both of which are installed on the
Beam Line 19 LXU in SPring-8.\textsuperscript{23} The energy of the incident x-ray was tuned to 12.4 keV. The sheet resistance (\(R_s\)) was simultaneously recorded during XRD measurements using semiconductor parameter analyzer (Agilent Technologies, 4156C).

Figure 1(c) shows the temperature dependence of \(R_s\) for the samples #1 and #2 both at the ungated OFF states and at the gated ON states evaluated under dark condition when the x-ray beams were off. At OFF states, clear MITs were observed for both samples around room temperature with abrupt resistance jumps of a few orders of magnitude accompanied by thermal hysteresis, whereas MITs were completely suppressed at ON states in spite of the presence or absence of tungsten. \(R_s\) of the sample #2 at ON state (red data) was much lower than that of the sample #1 (green data), indicating that the gate-induced conducting channels were extended to the whole films in three dimensions for both cases irrespective of the thickness as we previously reported.\textsuperscript{11} In order to directly verify that the whole film underwent phase transitions in the light of crystal structure, we next performed XRD measurements at different conditions labeled as A to F in Fig. 1(c).

\(\text{VO}_2\) transforms its crystal structure across the thermally-driven MIT from the low-temperature insulating monoclinic phase to the high-temperature metallic tetragonal phase with a dramatic change in a \(c\)-axis length by almost 1\% in a bulk single crystalline form.\textsuperscript{24} This significant lattice deformation along \(c\)-axis direction is also seen in a strained \(\text{VO}_2\) (001) thin film grown on a lattice-matched TiO\(_2\) (001) substrate. Figure 2(a) displays the (002) XRD patterns taken exactly at the channel region of the sample #1 at three different conditions labeled as A, B, and C on the \(R_s-T\) curves in Fig. 1(c), where the horizontal axis 2\(d\) is twice the spacing between the (002) planes. The black open and filled symbols correspond to the data taken at OFF states (\(V_G = 0.0\) V) below (B) and above (C) \(T_{\text{MI}}\), respectively, showing nearly 1\% change between the 2\(d\) values across the thermally-driven MIT, where the high-temperature metallic state has a smaller \(c\)-axis length as is the case with bulk \(\text{VO}_2\).

We found that applying electric field yields an opposite effect. The filled green symbol in Fig. 2(a) denotes the XRD pattern taken at ON state (\(V_G = 1.5\) V) well below the original \(T_{\text{MI}}\) (A), indicating more than 1\% increase of the 2\(d\)
value from the low-temperature insulating monoclinic phase (B). The obtained profile is constituted with a single Gaussian distribution function without any shoulder components at the position of the thermally-stable insulating state (B). This suggests that a whole film has a single crystal structure, directly evidencing from structural viewpoint that the gate-induced MIT occurs throughout an entire film as we concluded previously in the lights of transport and optical spectroscopy measurements.11,16 This bulk lattice deformation upon electrically driven MIT is also confirmed in the sample #2, which consists of the 40-nm thick film, as shown in Fig. 2(b). We note that the linear thermal expansion coefficients of VO2 below and above TMI and that of TiO2 are approximately 6, 17, and 9 × 10⁻⁶ K⁻¹, respectively,25,26 suggesting negligible contribution of these thermal effects to the obtained data on the length scale discussed here.

Surprisingly, we found that this gigantic change in a c-axis lattice parameter can be induced even above TMI, where the high-temperature “metallic” state is originally stabilized at OFF state. Figure 3 demonstrates dynamic control of lattice deformation in VO2 by electric field at room temperature (T = 305 K) examined for the sample #2. From our previous studies, we have known that the application of VG above TMI results in a slight increase of RS, which is essential for a decrease of TMI and eventual emergence of the gate-induced three-dimensional metallic ground state.11 We focus on this behavior as a measure of the change in the electronic state of VO2 during gating process. Starting from the high-temperature metallic state (F), positive VG was firstly applied while monitoring RS in order to get to the gate-induced “metallic” state [{Set} region in Figs. 3(a) and 3(b)]. RS monitoring was then interrupted to do optical alignment for the XRD experiments [gray “Alignment” region in Figs. 3(a) and 3(b)]. After that, simultaneous characterizations of the XRD patterns and RS were started while VG was gradually altered from positive to negative so as to release electrical charges accumulated at the surface of VO2 [{“Reset/Measure” region in Figs. 3(a) and 3(b)}]. Figure 3(c) illustrates the snapshots of the XRD patterns collected during this “reset” process, showing significant shift of the 2d value by more than 1% from the start point (G) to the end point (M) according to the change in VG and corresponding change in RS [see Figs. 3(a) and 3(b)]. There was a linear relationship between the 2d002 value and RS as shown in Fig. 3(d), implying that the electronic state and the structural phase are strongly coupled with each other at the gated state. The XRD pattern and RS eventually returned to those of the high-temperature metallic state, verifying the reversible device operation.

We note that the obtained results on the gating effects at the thermally stable metallic state, in particular, increase of RS upon applying VG is unusual and cannot be understood within the framework of a standard parallel capacitor model. One of possible interpretations is that a gate-induced metallic state has a larger resistivity than that of a thermally stable metallic state due to strong deformation in lattice structure throughout an entire film under the presence of extremely large electric field. On the length scale of this gate-induced lattice deformation, we speculate that it should be considered separately from the electrostatic screening length; it should not be limited by the screening length, but rather governed by the size of the metal/insulator domains of two different structures, which is known to be fairly large (in the order of a few tens micrometers) for VO2 (001) epitaxial thin films grown on lattice-matched TiO2 (001) substrates.27

In summary, we revealed by in-situ synchrotron XRD experiments that the gate-induced metallic states in VO2-EDLT have larger c-axis lattice parameters than those of the thermally stable insulating and metallic states, and that this gate-induced lattice deformation is extended to a whole film. A gate sweep measurement above TMI enabled dynamic control of lattice deformation at room temperature in a reversible process, where a remarkable shift of a c-axis lattice parameter by more than 1% was achieved. The obtained results suggest the formation of unidentified phases in VO2 under the presence of electric field both below and above TMI. Further structural analysis including in-plane reflection measurements in a wider VG-T parameter space as well as x-ray spectroscopic measurements will give us further insights into the origin of these phases, and eventually, into the device operation mechanism and physics behind.

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