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Control of metal-insulator transition temperature in VO$_2$ thin films grown on RuO$_2$/TiO$_2$ templates by strain modification

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ABSTRACT
Ruthenium dioxide (RuO$_2$) is an ideal buffer layer for vanadium dioxide (VO$_2$) heterostructures due to its high electrical conductivity and matching crystal structure with metallic VO$_2$. VO$_2$ thin films were deposited on single crystal TiO$_2$ (001) substrates with RuO$_2$ buffer layers via pulsed laser deposition. The metal-insulator transition temperature ($T_{MIT}$) in VO$_2$ films can be controlled by the epitaxial strain between the VO$_2$ film and RuO$_2$ buffer layer by adjusting the buffer layer thickness (10 - 50 nm). We observed a decrease in the $T_{MIT}$ of VO$_2$ films from 59$^\circ$C to 24$^\circ$C as the RuO$_2$ thickness decreased from 50 nm to 10 nm. Additionally, we show that the RuO$_2$ buffer layer can sustain an intermediate strain state in VO$_2$ films up to 100 nm in thickness with a subsequently lower $T_{MIT}$ (30$^\circ$C). The 10 nm thick RuO$_2$ buffer layer can reduce the $T_{MIT}$ in VO$_2$ films by providing a pathway to relieve the strain through grain boundaries.

I. INTRODUCTION
Vanadium dioxide (VO$_2$) undergoes a sharp metal-insulator transition (MIT) above room temperature at ~67$^\circ$C, which is associated with a structural phase transformation (SPT) between a low-temperature insulating monoclinic phase and a high-temperature metallic tetragonal phase. The MIT and SPT can be controlled by external parameters such as temperature, electric field, or photo-excitation, and the switching time of the transition can be on ultrafast timescales (~100 fs) when the transition is induced optically. As the temperature of the VO$_2$ increases above 67$^\circ$C, the electrical resistivity decreases by several orders of magnitude and the infrared transmittance decreases by ~60%. These unique properties have made VO$_2$ an attractive candidate in many promising applications such as ultrafast switches, thermal optical modulators, field effect transistors, bolometric photodetection, plasmonic metamaterials, thermal actuators, and smart radiators for spacecraft.

The nature of the MIT and SPT in VO$_2$ has been a long-standing debate. It is generally acknowledged that the mechanism of the MIT in bulk VO$_2$ is considered to be a collaborative Mott–Peierls transition. The SPT from monoclinic (M1) phase to tetragonal rutile (R) phase is most commonly reported; however, some intermediate phases, such as M2-phase, B-phase, A-phase, have also been recognized during the phase transition. On the other hand, recent reports have revealed that ultrathin VO$_2$ films deposited on lattice matched TiO$_2$ substrates show no monoclinic phase at room temperature, suggesting that the VO$_2$ films are tetragonal rutile in both the insulating and metallic states, i.e., the films undergo an electronic phase transition without the structural phase transition.

The ability to tune $T_{MIT}$ is important in many device applications. Doping with high-valence metal ions into the VO$_2$ lattice is a commonly used method to achieve tuning of the $T_{MIT}$ in VO$_2$ films. Introducing epitaxial strain between...
VO$_2$ and the substrate has also been realized as an effective way to control the $T_{\text{MIT}}$ in VO$_2$ films. TiO$_2$ rutile substrates are most commonly used for the growth of epitaxial VO$_2$ films due to rutile’s matching crystal structures and similar lattice parameters with metallic VO$_2$ (P42/mmm). Muraoka et al. reported that ultrathin VO$_2$ films show a reduced $T_{\text{MIT}}$ (299 K) when grown on TiO$_2$ (001) substrates, while the $T_{\text{MIT}}$ increased up to 369 K for VO$_2$ films grown on TiO$_2$ (110) substrates.\textsuperscript{27} In the former case, the compressive strain in the c-axis of the VO$_2$ films resulted in the reduced $T_{\text{MIT}}$ while in the latter, the tensile strain in the c-axis led to the increased $T_{\text{MIT}}$. Fan et al. also reported the thickness-dependent interfacial strain dynamics of epitaxial VO$_2$ films grown on TiO$_2$ (001) substrates, demonstrating that a large epitaxial strain occurred in the initial growth stage of the VO$_2$ films and the epitaxial strain was relaxed as the film thickness increased, leading to an increase in the $T_{\text{MIT}}$.\textsuperscript{21} In addition, various buffer layers have been introduced between VO$_2$ films and substrates in order to control the strain and MIT properties in VO$_2$ films.\textsuperscript{28–31} Among them, RuO$_2$ was proposed as an excellent buffer because it has the same crystal structure and space group as both TiO$_2$ and metallic VO$_2$.\textsuperscript{31} In this report,\textsuperscript{3} they showed that the $T_{\text{MIT}}$ of thin VO$_2$ films can be changed continuously by epitaxial strain in a buffer layer of varying thickness. Here we report a systematic study on the epitaxial strain of VO$_2$ films by varying RuO$_2$ and VO$_2$ film thickness using X-ray reciprocal space mapping analysis. Furthermore, the a-axis lattice parameter of VO$_2$ (a = 4.54 Å, c = 2.88 Å, JCPDS #71-4821) is smaller than the TiO$_2$ (a = 4.59 Å, c = 2.96 Å, JCPDS #21-1276) but bigger than the RuO$_2$ (a = 4.49 Å, c = 3.11 Å, JCPDS #40-1290), indicating that the VO$_2$ film can be compressively strained along the in-plane direction when deposited on bulk RuO$_2$ whereas it would be tensile-strained on the TiO$_2$ (001) substrate. Thus, the $T_{\text{MIT}}$ in VO$_2$ films can be tuned by adjusting the epitaxial strain of the RuO$_2$ buffer layer. Another advantage of using a RuO$_2$ buffer layer is that it can be used as a bottom oxide electrode for VO$_2$ based devices with out-of-plane configurations, which would considerably reduce the switching voltage and current (compared to VO$_2$-based planar type devices).

In this work, we demonstrate control of the MIT temperature in VO$_2$ thin films by adjusting the epitaxial strain in conducting RuO$_2$ buffer layers. Using a 10 nm thick RuO$_2$/TiO$_2$ template, we were able to sustain the intermediate strain states even with large VO$_2$ film thicknesses (~100 nm), resulting in relatively low $T_{\text{MIT}}$ (~30 °C).

II. EXPERIMENTAL METHODS

VO$_2$/RuO$_2$ thin films were epitaxially grown on single crystal TiO$_2$ (001) substrates by pulsed laser deposition. A pulsed laser beam generated by a KrF excimer laser (LPX300, 248 nm, and pulse duration of 30ns) was introduced into a deposition chamber through a quartz window and focused on the target. The energy density of the laser beam was 2 J/cm$^2$ at the target surface. A RuO$_2$ target (American Elements) was used for the buffer layer growth and the VO$_2$ films were grown from a V$_2$O$_5$ target (Kurt J. Lesker). Before thin film deposition, the chamber was evacuated to a background pressure of 10$^{-5}$ Torr. The RuO$_2$ buffer layers (10 ~ 50 nm) were deposited at 500 °C and at 10 mTorr of oxygen partial pressure, followed by VO$_2$ layers (20 ~ 100 nm) grown at 390 °C and at 10 mTorr of oxygen. The structure of deposited films was characterized by x-ray diffraction (XRD) $\theta$-2$\theta$ scans using a Rigaku x-ray diffractometer with Cu Kα radiation. The electrical properties of the VO$_2$/RuO$_2$ heterostructures were characterized in a probe station equipped with a heating stage (Linkam) at temperatures between 0 and 100 °C using a Keithley 4200 semiconductor characterization system.

III. RESULTS

In order to investigate the effect of the RuO$_2$ film thickness on the epitaxial strain of VO$_2$/RuO$_2$ heterostructures, RuO$_2$ buffer layers (10 ~ 50 nm) were prepared on TiO$_2$ (001) substrates while holding the VO$_2$ film thickness constant at 50 nm. Figure 1a shows the $\theta$-2$\theta$ XRD patterns of the VO$_2$/RuO$_2$/TiO$_2$ thin films with various RuO$_2$ film thicknesses (10, 30 and 50 nm). The strong peak at 62.8° is assigned to the TiO$_2$ (002) substrate whereas the peak at ~60° is indexed...
to rutile RuO$_2$ (002), and the peak at $-65^\circ$ is indexed to the tetragonal VO$_2$ (002) plane. No other peaks were observed, indicating that pure VO$_2$ was formed during film growth. With increasing RuO$_2$ buffer layer thickness, the RuO$_2$ (002) peak moves to lower 2$\theta$ angles (approaching the bulk RuO$_2$ (002) angle) and the VO$_2$ (002) peak moves to lower 2$\theta$ angles (approaching the bulk VO$_2$ (002) angle). This result suggests that the c-axis lattice parameter of both the RuO$_2$ buffer layers and the VO$_2$ thin films increases as the RuO$_2$ thickness increases, meaning that the epitaxial strain can be adjusted using different thicknesses of the RuO$_2$ buffer layer.

XRD $\phi$-scans were performed to establish the epitaxial relationship in the VO$_2$/RuO$_2$/TiO$_2$ layers. Figure 1b shows XRD $\phi$-scans on VO$_2$ (101), RuO$_2$ (101) and TiO$_2$ (101) for the 50 nm thick VO$_2$ film on RuO$_2$ (10 nm) buffered TiO$_2$ substrate. The $\phi$-scan of the TiO$_2$ exhibits four peaks separated by a $90^\circ$, suggesting fourfold symmetry about the out-of-plane axis. The $\phi$-scans of the RuO$_2$ buffer layer and VO$_2$ film also show fourfold symmetry with the same azimuth angles of the TiO$_2$ substrate, thus showing the epitaxy of the VO$_2$ film on the RuO$_2$/TiO$_2$ template with a relationship of [010]VO$_2$ || [010]RuO$_2$ || [010]TiO$_2$ along the in-plane direction and [001]VO$_2$ || [001]RuO$_2$ || [001]TiO$_2$ along the out of plane direction. Four-fold symmetry of all peaks suggests that all of these materials show their characteristic tetragonal symmetry at room temperature.

In order to understand the epitaxial strain of VO$_2$/RuO$_2$/TiO$_2$ heterostructures we performed x-ray reciprocal space mapping (RSM) measurements. Figures 2a–d show the RSMs data for various thicknesses of VO$_2$ films grown on 10 nm thick RuO$_2$ buffer layers. Figures 2e–h show the RSMs for various thicknesses of VO$_2$ films grown on 10 nm thick RuO$_2$ buffer layers. The square symbols mark the bulk TiO$_2$, RuO$_2$ and VO$_2$ peaks, while the triangle symbols mark the bulk TiO$_2$ (112), and the circular symbols mark the bulk RuO$_2$ (112) spot.

![Figure 2: (a-d) XRD RSMs of VO$_2$ films (50 nm) deposited on various thicknesses of RuO$_2$ buffer layers; (a) 10 nm, (b) 20 nm, (c) 30 nm and (d) 50 nm.](image-url)
Thickness-dependent electrical properties of the RuO$_2$ buffer layers were measured in order to examine the feasibility of the RuO$_2$ thin films as a bottom electrode. Figure 3a shows the room temperature resistivity and sheet resistance data of the RuO$_2$ thin films grown on TiO$_2$ (001) substrates as a function of the film thickness (10 - 50 nm) while the film growth temperature and oxygen pressure were fixed at 500 °C and 10 mTorr, respectively. The room temperature sheet resistance decreases from 225 to 43 Ω/□ with increasing RuO$_2$ film thickness from 10 to 50 nm while the film resistivity remains almost constant (∼220 µΩ·cm), which is similar to that of commercial indium tin oxide (ITO) electrodes [50 nm-thick ITO films with ∼50 Ω/□, ∼250 µΩ·cm]. Thus, the RuO$_2$ buffer layers with a thickness range from 10 to 50 nm can be used as a bottom electrode for VO$_2$-based devices with out-of-plane configurations.

Temperature-dependent electrical transport properties were measured for VO$_2$ (50 nm)/RuO$_2$ heterostructures with varying RuO$_2$ buffer layer thicknesses (10 – 50 nm). The effective sheet resistance ($R_{\text{eff}}$) of the VO$_2$/RuO$_2$ heterostructures is shown in Fig. 4a. It shows that the $T_{\text{MIT}}$ of all VO$_2$/RuO$_2$ films is lower than that of typical bulk VO$_2$ (∼67 °C). The $T_{\text{MIT}}$ surely decreases from 59 to 24 °C as the RuO$_2$ buffer layer thickness decreases from 50 nm to 10 nm. This reduction in $T_{\text{MIT}}$ can be explained by a difference in epitaxial strain between the VO$_2$ and RuO$_2$ films. In general, when VO$_2$ films have the highest in-plane tensile epitaxial strain, the lowest $T_{\text{MIT}}$ in the VO$_2$ would be expected. Therefore, the 10 nm RuO$_2$ seems to be an ideal buffer layer to produce the largest epitaxial strain in VO$_2$ films, growing on thicker RuO$_2$ buffer layers (>10 nm) all showed higher $T_{\text{MIT}}$, indicating that these films are less strained than the VO$_2$ film on 10 nm RuO$_2$ buffer. It is noted that the magnitude of resistance change diminishes with increasing RuO$_2$ thickness. This
is primarily due to the low resistivity (∼220 μΩ·cm) of the RuO$_2$ layer and the associated current shunting through the RuO$_2$ layer as the RuO$_2$ sheet resistance decreases from 225 to 43 Ω/□ with increasing RuO$_2$ thickness from 10 to 50 nm (shown in Fig. 3a).

The electrical transport properties were also affected by the VO$_2$ film thickness. Figure 4b shows temperature-dependent sheet resistance plots of VO$_2$ films with varying thickness (20, 50, 75 and 100 nm) while the thickness of the RuO$_2$ buffer layers was fixed at 10 nm. As the film thickness increases from 20 nm to 100 nm, the resistance change amplitude increases threefold, while the $T_{\text{TRIT}}$ of VO$_2$ films slightly increases from 23 $^\circ$C to 30 $^\circ$C. For comparison, the sheet resistance curves of 100 nm VO$_2$ films on TiO$_2$ substrates with and without the RuO$_2$ buffer layer are plotted in the same figure (Fig. 4c). Without the RuO$_2$ buffer layer, the $T_{\text{TRIT}}$ of the VO$_2$ film increases from 30 $^\circ$C to 60 $^\circ$C. It is clear that the 10 nm RuO$_2$ buffer layer is responsible for lowering the $T_{\text{TRIT}}$ by preventing relaxation of the strain on the 100 nm thick VO$_2$ film. Furthermore, this low $T_{\text{TRIT}}$ (30 $^\circ$C) for 100 nm thick VO$_2$ films is ideal for operating switching devices because the transition occurs near room temperature. The $T_{\text{TRIT}}$ of VO$_2$ films are deduced from the derivative curves in Fig. 4d–i and are summarized in Table I.

### IV. DISCUSSION

The $T_{\text{TRIT}}$ in VO$_2$ has been observed to be dependent on epitaxial strain in thin films.$^{27,33}$ In general, compressive strain along the c-axis of VO$_2$ (i.e., in-plane tensile strain) leads to a reduced $T_{\text{TRIT}}$ in epitaxial VO$_2$ films. Furthermore, since the a-axis lattice parameter of RuO$_2$ ($a = 4.49$ Å) is smaller than TiO$_2$ ($a = 4.59$ Å), the initial epitaxial RuO$_2$ film layers are subject to tensile-strains at the RuO$_2$/TiO$_2$ interface. As the thickness of RuO$_2$ increases, its lattice parameter monotonically decreases due to relaxation by misfit dislocations. Thus, the $T_{\text{TRIT}}$ in VO$_2$ films can be modified efficiently by the epitaxial strain in RuO$_2$ buffer layers. Figure 5a shows the axial ratio (c/a) for 50 nm-thick VO$_2$ films with varying RuO$_2$ thickness. The a- and c-axis lattice parameters of VO$_2$ films were calculated from RSM data. Clearly, the tendency of the c/a ratio is similar to that of the $T_{\text{TRIT}}$ in strained VO$_2$ films. The c/a ratio in VO$_2$ films decreases as the RuO$_2$ thickness decreases which, in turn, results in a lower $T_{\text{TRIT}}$. The lowest $T_{\text{TRIT}}$ (24 $^\circ$C) is observed in the VO$_2$ film having the smallest c/a ratio (for a 10 nm RuO$_2$ buffer layer), indicating that the VO$_2$ film is under tensile strain along the in-plane axis and under compressive strain along the out-of-plane axis. However, as the RuO$_2$ buffer layer thickness increases, its epitaxial strain becomes more relaxed and the induced strain in the VO$_2$ film is relieved, thus increasing the VO$_2$ c/a ratio, leading to an increased $T_{\text{TRIT}}$ (59 $^\circ$C), closer to the bulk VO$_2$ value (67 $^\circ$C).

Figure 5b shows the axial ratio (c/a) for VO$_2$ films as a function of film thickness while the RuO$_2$ thickness is fixed at 10 nm. As the VO$_2$ thickness increases from 20 to 100 nm, the c/a ratio in the VO$_2$ films slightly increases from 0.621 to 0.628, which is still much smaller than that of a fully relaxed VO$_2$ film (0.634). This low c/a ratio results in a reduced $T_{\text{TRIT}}$ (23–30 $^\circ$C) for 20–100 nm thick VO$_2$ films, indicating that a significant portion of strain is still present even in 100 nm thick VO$_2$ films. In general, the VO$_2$ film is coherently strained below its critical thickness, and above the critical thickness the strained film is relaxed by the formation of misfit dislocations until it becomes fully relaxed.$^{34}$ VO$_2$ films grown

### TABLE I. Transition temperatures of VO$_2$:RuO$_2$:TiO$_2$ heterostructures during heating and cooling processes. $T_{\text{heal}}$ and $T_{\text{cool}}$ are the transition temperatures determined from the derivative curves during heating and cooling, respectively. $T_{\text{TRIT}}$ is determined by the average between $T_{\text{heal}}$ and $T_{\text{cool}}$.

<table>
<thead>
<tr>
<th>Transition temperature</th>
<th>50 nm-VO$_2$ grown on TiO$_2$ with various thicknesses of RuO$_2$ buffer</th>
<th>Various thicknesses of VO$_2$ films grown on TiO$_2$ with 10 nm RuO$_2$ buffer</th>
<th>100 nm-VO$_2$ on TiO$_2$ with/without 10 nm RuO$_2$ buffer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 nm</td>
<td>20 nm</td>
<td>30 nm</td>
</tr>
<tr>
<td>$T_{\text{heal}}$ ($^\circ$C)</td>
<td>28.3</td>
<td>41.6</td>
<td>56.2</td>
</tr>
<tr>
<td>$T_{\text{cool}}$ ($^\circ$C)</td>
<td>22.9</td>
<td>38.4</td>
<td>52.4</td>
</tr>
<tr>
<td>$T_{\text{TRIT}}$ ($^\circ$C)</td>
<td>25.6</td>
<td>40.0</td>
<td>54.3</td>
</tr>
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</table>
on single crystal TiO$_2$ (001) substrates are well explained by this strain relaxation mechanism: where below 15 nm the VO$_2$ film is fully strained but when its thickness reaches 100 nm it is completely relaxed due to the formation of misfit dislocations. However, it is difficult to explain our results on VO$_2$ films grown on RuO$_2$/TiO$_2$ templates using this classical strain mechanism. Instead, the strain relaxation behavior in our films can be explained by grain boundaries. The grain size of the RuO$_2$ buffer layer was determined by atomic force microscopy to be ~ 30 - 40 nm as shown in Fig. S3 in the supplementary material. The boundary between RuO$_2$ grains is a favorable region for dislocation nucleation. Thus, high density boundaries in RuO$_2$ buffer layers can provide an alternative pathway to relieve the strain at the VO$_2$/RuO$_2$ interface. This explains why our VO$_2$ films can sustain intermediate strain states for thicker films up to 100 nm. Similar results (strain relaxation through grain boundaries) have been reported for other epitaxial oxide systems.

Epitaxial VO$_2$ thin films were deposited on conductive RuO$_2$/TiO$_2$ templates by pulsed laser deposition. The MIT temperature of VO$_2$/RuO$_2$/TiO$_2$ heterostructures can be tuned from 59 °C to 24 °C by adjusting the strain state of the films by decreasing the RuO$_2$ thickness from 50 nm to 10 nm. The boundaries between RuO$_2$ structures are favorable regions responsible for the nucleation of dislocations, which can partially relieve the strain in the film, thereby sustaining intermediate strain states even with large thicknesses (~ 100 nm). This allows lowering of the MIT temperature to near room temperature. These results suggest that the strain generated by the RuO$_2$ buffer layer can provide an effective way for tuning the MIT of VO$_2$ films and provide a route to realizing out-of-plane electrical switching devices.

V. CONCLUSIONS

See supplementary material for the RSMs data, electrical properties and AFM images.

ACKNOWLEDGMENTS

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