# Metal–insulator transition of $VO_2$ thin films grown on $TiO_2$ (001) and (110) substrates

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The effect of uniaxial stress along the $c$ axis on the metal–insulator transition of $VO_2$ has been studied in the form of epitaxial thin films grown on $TiO_2$ (001) and (110) substrates. A large reduction in the transition temperature $T_{MI}$ from 341 K for a single crystal to 300 K has been observed in the film on $TiO_2$ (001) where the $c$-axis length is compressed owing to an epitaxial stress, while the $T_{MI}$ has been increased to 369 K in the film on $TiO_2$ (110) where the $c$-axis length is expanded. The correlation between the $c$-axis length and $T_{MI}$ is suggested: the shorter $c$-axis length results in the lower $T_{MI}$. © *2002 American Institute of Physics.*
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Vanadium dioxide, $VO_2$, undergoes a metal-to-insulator (MI) transition at 341 K which is a first-order phase transition accompanied by a structural change from a high-temperature tetragonal form to a low-temperature monoclinic form.[1] Dramatic changes in electrical resistivity and infrared transmission occur across the phase transition, thus making the material useful for potential applications as switching devices.[2–5] There has been an enduring interest in modifying the MI transition temperature $T_{MI}$ of $VO_2$ by applying pressure or doping it with elements like Nb and W.[6,7] Hydrostatic pressure affected the $T_{MI}$ only slightly ($dT_{MI}/dP$ = 0.6 K/GPa), while a relatively large pressure dependence was reported under uniaxial stress along the $c$ axis ($dT_{MI}/dP = -12$ K/GPa).[8] On the other hand, a reduction in $T_{MI}$ down to 318 K was reported for reactively sputtered $VO_2$ films deposited on $Al_2O_3$ (0001) substrates.[9,10] These results suggest that in the form of a thin film the $T_{MI}$ of $VO_2$ can be modified through the control of stress along the $c$ axis induced by the lattice mismatch between the film and substrate.

In this work we prepared high-quality $VO_2$ thin films on $TiO_2$ (001) and (110) substrates. Table I shows the lattice parameters $a$ and $c$, and interplanar spacing of (110), $d_{110}$, of $VO_2$ and $TiO_2$ in a tetragonal form, together with the corresponding lattice mismatch. Since both the lattice parameters of $VO_2$ are smaller than those of $TiO_2$, the $c$-axis length should decrease for a $VO_2$ film epitaxially grown on $TiO_2$ (001) because of an in-plane tensile stress at the interface (lattice mismatch: 0.86%), while increase for a $VO_2$ film grown on $TiO_2$ (110) (mismatch: 3.6%). Therefore, a reduction or an increase in $T_{MI}$ is expected there, respectively.

Thin films of $VO_2$ were prepared using a pulsed laser deposition technique on $TiO_2$ (001) and (110) planes. A $V_2O_3$ pellet was used as a target, which was obtained by reducing $V_2O_5$ under $H_2$ atmosphere at 1173 K. During the deposition, the substrate temperature $T_s$ was kept at certain temperature between 523 and 743 K, and oxygen pressure

was maintained at 1.0 Pa. After deposition, the films were cooled down to 300 K in 30 min under the same oxygen pressure. A deposition rate was about 0.2 nm/min. The thickness of the grown films measured by a surface profilometer (Tencor, Alpha sensor 500) was 10–15 nm.

Figure 1(a) shows a typical x-ray diffraction (XRD) pattern for a $VO_2$ film on a $TiO_2$ (001) substrate which was prepared at $T_s = 643$ K. Two distinguished peaks at $2\theta = 62.74°$ and $65.55°$ are observed in the figure. The former is indexed to that from $TiO_2$ (002), and the latter is identified as the (002) diffraction from tetragonal $VO_2$. No other peaks are observed by XRD analysis, suggesting that the prepared film is an (001)-oriented single phase. The full width at half maximum of the (002) peak from the $VO_2$ film is 0.83°, from which the thickness of the film is calculated to be about 10 nm by using Scherrer's equation. This value is in good agreement with the result by surface profilometer measurements. The epitaxy of the film is confirmed by reflection high-energy electron diffraction observations and also by pole figures obtained by four-circle x-ray measurements. The lattice parameter $c$ of the film was determined to be 0.2847(1) nm, which is smaller by 0.28% than that of a bulk material [0.2855(1) nm]. This compression of the lattice parameter $c$ is plausibly due to an in-plane tensile stress (lattice mismatch: 0.86%). The XRD pattern of the $VO_2$ film deposited on $TiO_2$ (110) substrates is shown in Fig. 1(b). The film was prepared at $T_s = 583$ K. By XRD analysis, the film is found to be an (110)-oriented single phase. Assuming that the cell volume of $VO_2$ is the same as that of the bulk (59.22 $\times 10^{-3}$ $nm^3$), the lattice parameter $c$ can be estimated to be

TABLE I. Lattice parameters $a$ and $c$, and interplanar spacing of (110), $d_{110}$ of $VO_2$ and $TiO_2$ in the tetragonal form. The lattice mismatch between them is presented.

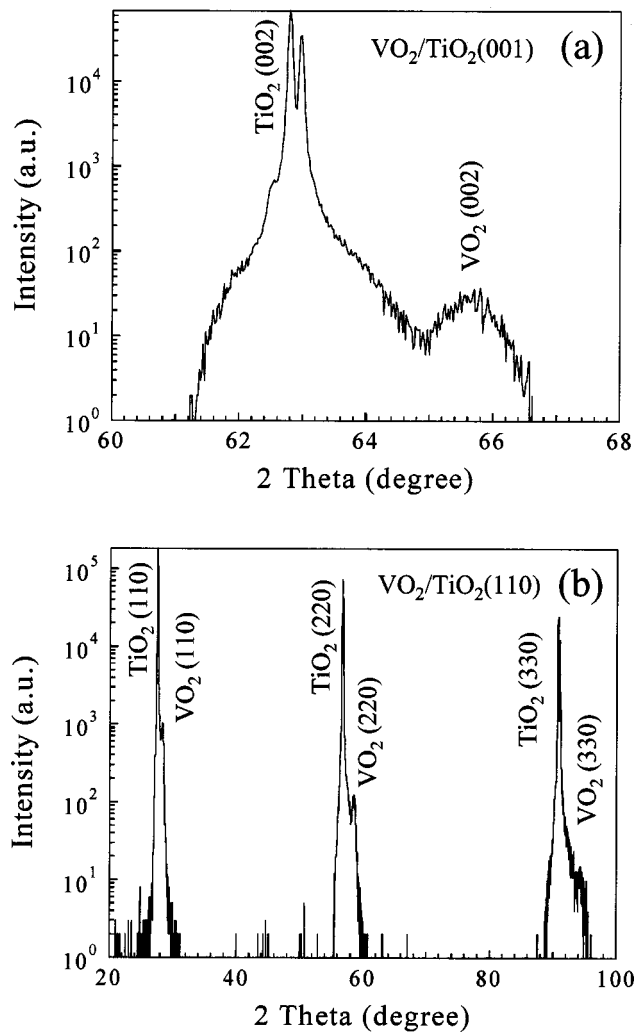| Lattice parameter/ material | $a$ (nm) | $c$ (nm) | $d_{110}$ (nm) |
|---|---|---|---|
| $VO_2$ | 0.455 40 | 0.285 57 | 0.322 01 |
| $TiO_2$ | 0.459 33 | 0.295 92 | 0.324 79 |
| Lattice mismatch (%) | 0.863 | 3.62 | 0.863 |

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FIG. 1. x-ray diffraction pattern for an epitaxial $VO_2$ film deposited on $TiO_2$ (001) prepared at $T_s = 643$ K (a) and on $TiO_2$ (110) prepared at $T_s = 583$ K (b).

0.2890 nm. Thus, the $c$ axis was expanded compared with bulk.

Resistivity measurements were carried out using a four-point probe method in a Quantum Design Physical Property Measurement System (PPMS). Figure 2 shows the results for $VO_2$ films on $TiO_2$ (001) and (110) substrates. The
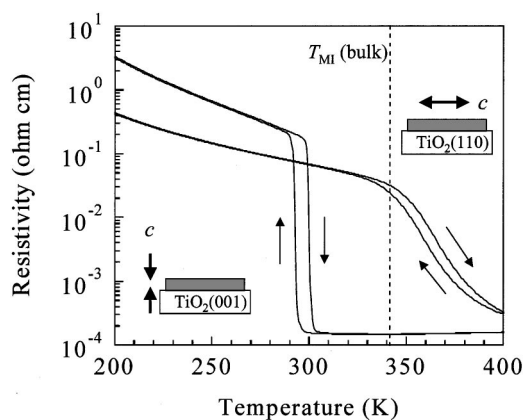


FIG. 2. Temperature dependence of resistivity for the $VO_2$ films formed on $TiO_2$ (001) and $TiO_2$ (110) substrates. The broken line represents the $T_{MI}$ in a $VO_2$ single crystal ($T_{MI} = 341$ K).
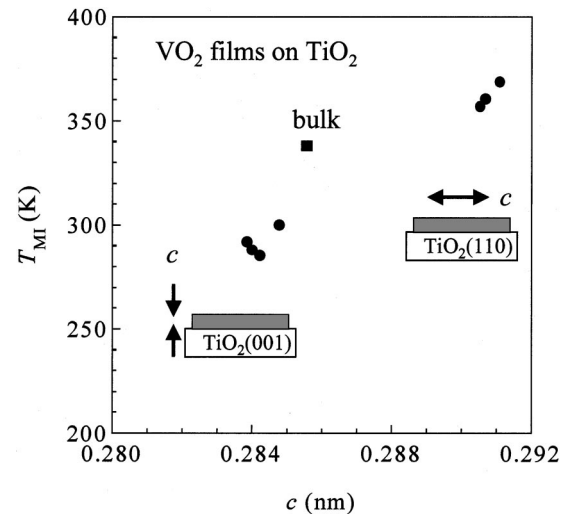


FIG. 3. MI transition temperature $T_{MI}$ vs lattice parameter $c$ for the $VO_2$ films deposited on $TiO_2$ (001) and $TiO_2$ (110) substrates. The single crystal $VO_2$ data is also plotted (closed square).

films were grown at 643 and 583 K, respectively. The MI transition temperature $T_{MI}$ is taken as the midpoint of the jump in the resistivity curve measured on heating. As seen in Fig. 2, the $T_{MI}$ is dramatically shifted from that of a single crystal (341 K) to 300 K in the film on $TiO_2$ (001). A large and sharp change in resistivity of $\Delta R \sim 10^3$ is observed at the transition, indicating a high quality of the film. A film with a further reduced $T_{MI}$ of 285 K is obtained when the $T_s$ is decreased down to 583 K, although the transition becomes rather broad ($\Delta R \sim 10^2$). On the other hand, the $T_{MI}$ increases up to 369 K for the film on $TiO_2$ (110) as shown in Fig. 2. The transition is relatively broad compared with the film on $TiO_2$ (001), which may be due to poor crystallinity arising from the large lattice mismatch between the film and $TiO_2$ (110) substrate (3.6%). These results are in good agreement with our expectation on the relation between the $c$-axis length and $T_{MI}$ in strained epitaxial $VO_2$ films. The $T_{MI}$ of $VO_2$ films with more than 100 nm thickness on $TiO_2$ (001) becomes close to 340 K. Moreover, the films with 20 nm thickness grown on $Al_2O_3$ (0001) show $T_{MI} \sim 340$ K. Both results also indicate a proof of lattice strain effect. The large modification of $T_{MI}$ in a wide temperature range is demonstrated in this work. In the previous work on $VO_2$ films deposited on $TiO_2$ buffer layers (12.5 nm thick), the $T_{MI}$ was reduced to 331 K.[11] This value is much smaller compared with our films. The difference may be interpreted due to the thickness of buffer layers. Since the thickness of layers (12.5 nm) is thin as well as $VO_2$ films and is much smaller than the substrate (0.5 mm for our case), the strain effect due to buffer layer is considered to be much smaller than our result. The difference may be also related to the quality of the films. The strain at the interface is considered to be retained in high quality films and thus to affect dramatically on the metal–insulator transition in $VO_2$.

The $T_{MI}$ was plotted against the lattice parameter $c$ of $VO_2$ films in Fig. 3. As seen in the figure, an intimate relation between them is suggested: the $T_{MI}$ becomes low in the films with smaller $c$. This means that the stability of metallic phase in $VO_2$ depends on the $c$-axis length, i.e., the $V^{4+} - V^{4+}$ distance in the crystal structure. Since in a metallic state with the rutile structure $c$ expresses the distance
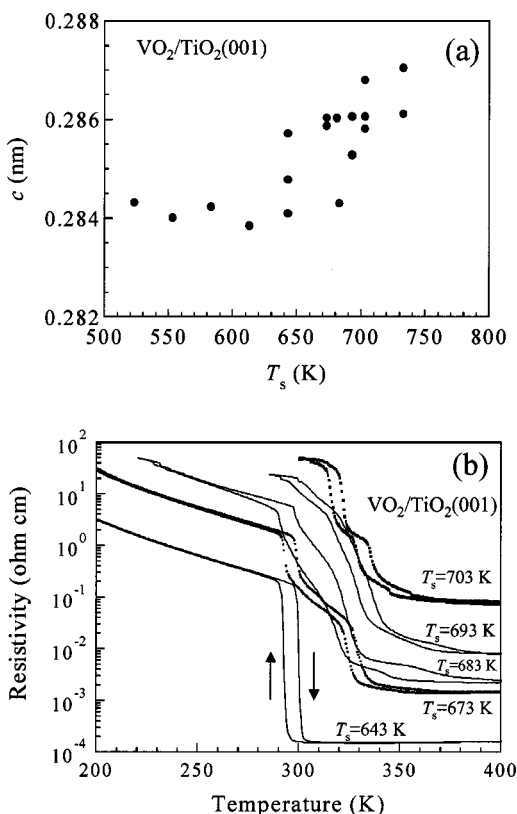
FIG. 4. (a) $T_s$ dependence of the lattice parameter $c$ in the VO$_2$ film deposited on TiO$_2$ (001) substrates. (b) Temperature dependence of resistivity for the VO$_2$ films deposited on TiO$_2$ (001) substrates prepared at $T_s$ above 643 K.

between the adjacent vanadium atoms lining up in the direction of the $c$ axis, the V$^{4+}$–V$^{4+}$ distance decreases with decreasing $c$. In this case, it is considered that the reduced V$^{4+}$–V$^{4+}$ distance results in direct overlapping of $d$ orbitals, which increases the width of the $d$ band and stabilizes the metallic phase of the rutile structure.

Figure 4(a) shows the substrate temperature dependence of the $c$-axis length of VO$_2$ films prepared on TiO$_2$ (001) substrates. The $c$-axis length changes little below $T_s$ = 643 K, while it increases with increasing $T_s$ above 643 K. Figure 4(b) shows the temperature dependence of resistivity of VO$_2$ films deposited on TiO$_2$ (001) at $T_s$ above 643 K. Interestingly, the MI transition occurs stepwise, suggesting the existence of multiphases with different MI transition tem-

peratures in the films. The resistivity values at 400 K increase with increasing $T_s$. Such a behavior is not observed in our experiments growing VO$_2$ films on Al$_2$O$_3$ (0001) substrates at the same condition as those on TiO$_2$ (001). Considering the facts that Ti ions in TiO$_2$ substrates are easy to diffuse into the deposited films at high temperature and that in the solid solution Ti$_x$V$_{1-x}$O$_2$ the $T_{MI}$ is increased with increasing the amount of Ti,[12] the most probable reason for the observed MI transition with several steps is the formation of (Ti,V)O$_2$ phases in the films. This must be related to the spinodal decomposition and raises an interesting problem on the unique phase separation in nanometer scale for very thin films. Detailed study will be reported elsewhere.

In summary, we have prepared VO$_2$ films on TiO$_2$ (001) and (110) substrates and studied the change of $T_{MI}$. A large decrease in $T_{MI}$ down to 300 K is observed in the film on TiO$_2$ (001), while the $T_{MI}$ is increased up to 369 K in the film on TiO$_2$ (110). This large modification of $T_{MI}$ in a wide temperature range has been demonstrated for the first time in this work. An intimate correlation between $T_{MI}$ and the $c$-axis length is suggested, which may be important to elucidate the mechanism of the MI transition in VO$_2$.

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