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Author(s)
Katase, Takayoshi; Endo, Kenji; Ohta, Hiromichi

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Thermopower analysis of metal-insulator transition temperature modulations in vanadium dioxide thin films with lattice distortion

Takayoshi Katase,* Kenji Endo, and Hiromichi Ohta†

Research Institute for Electronic Science, Hokkaido University, N20W10, Sapporo 001-0020, Japan

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Insulator-to-metal (MI) phase transition in vanadium dioxide (VO₂) thin films with controlled lattice distortion was investigated by thermopower measurements. VO₂ epitaxial films with different crystallographic orientations, grown on (0001) α-Al₂O₃, (1120) α-Al₂O₃, and (001) TiO₂ substrates, showed significant decrease of absolute value of Seebeck coefficient (S) from ~200 to 23 µV K⁻¹, along with a sharp drop in electrical resistivity (ρ), due to the transition from an insulator to a metal. The MI transition temperatures observed both in ρ(T) and S(T) for the VO₂ films systematically decrease with lattice shrinkage in the pseudorutile structure along the c axis, accompanying a broadening of the MI transition temperature width. Moreover, the onset T₀, where the insulating phase starts to become metallic, is much lower than the onset Tₘ. This difference is attributed to the sensitivity of S for the detection of hidden metallic domains in the majority insulating phase, which cannot be detected in ρ measurements. Consequently, S measurements provide a straightforward and excellent approach for a deeper understanding of the MI transition process in VO₂.

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I. INTRODUCTION

Vanadium dioxide (VO₂), a strongly correlated oxide, shows an insulator-to-metal (MI) transition when heated to its transition temperature (Tₘ) of 68°C [1] due to crystal-structure and electronic-structure changes. In the high-temperature metallic phase at T > Tₘ, VO₂ has a rutile-type tetragonal structure, while in the low-temperature insulating one at T < Tₘ, the vanadium ions form a dimer along with the position shifting from linear chains to zigzag pattern, resulting in a monoclinic structure [2]. This structural transformation accompanies a dramatic change in the 3d-band configuration with appearance of bandgap ~0.6 eV [3], yielding abrupt changes of both electrical resistivity on the order of 10⁴−10⁶ and the optical transmission in the infrared region. Tₘ can be varied over a wide range below room temperature (RT) by ionic doping [4], external strain [5], and an electric field application [6]. These features of the MI transition in VO₂ have proved to be useful in electrical and optical switching devices [7,8].

However, the nature of the MI transition in VO₂ is still quite unclear [9,10] and, consequently, potential device applications remain underdeveloped. One reason for this situation is that VO₂ has an electronic phase separation at the nanoscale region [11] and a complicated phase diagram with internal strain [12], which significantly makes it difficult to understand and control the MI transition characteristics. In a temperature range around the Tₘ, the metallic tetragonal and insulating monoclinic phases coexist randomly, where the electronic-transport properties are largely influenced by the domain configuration [13]. Especially in thin films, the polycrystalline domains with epitaxial strains and defects cause discontinuous and irregular phase domain structures, which result in the complex and broad MI transition [14].

The phase domain structures and their electronic behaviors have been experimentally investigated by electrical-transport measurement using nanowires at the nanoscale [15] or nanoscopic imaging on thin-films during the MI transitions [16]. In the electrical-transport measurement on VO₂ nanowires, discrete resistivity jump was observed, which suggests the important role of the electronic behaviors of each domain in the electrical properties. The nanoscopic imaging on thin films revealed that both electronic and structural changes exhibit phase coexistence leading to percolation conduction depending on the domain distribution. It is therefore critically important to understand the evolution of coexisting metallic and insulating domains with spatial phase inhomogeneity at the nanoscale, and further characterization that combines several experimental techniques is necessary to unveil and control the MI transition process.

We have focused on thermopower measurement as a physical property to investigate electronic structure change around the MI transition of VO₂ [17] because Seebeck coefficient (S) changes significantly due to the electronic structure reconstruction across the Tₘ. The general expression for the electronic contribution to the S is

\[ S = -\frac{k_B}{e} \int \left( \frac{E - E_F}{k_B T} \right) \frac{\sigma(E)}{\sigma} dE, \]  

where \( k_B \) is the Boltzmann constant and \( E_F \) is the Fermi energy [18]. Here, \( \sigma \) is described as an integral over the single carrier without electron correlation effects

\[ \sigma = \int \sigma(E) dE = e \int g(E) \mu(E) f(E) [1 - f(E)] dE, \]

where \( g(E) \) is the density of states (DOS), \( \mu(E) \) is the mobility, \( f(E) \) is the Fermi distribution function, and \( \sigma(E) \) is energy-dependent conductivity.

The S of semiconductors is expressed as

\[ S = -\frac{k_B}{e} \left( \frac{E_F - E_c}{k_B T} + A \right), \]
considering Eqs. (1) and (2) in the framework that only electrons contribute to the $S$, and $E_F$ lies near the conduction band edge $(E_c)$. By using the relation of $n_e = N_e e^{-\frac{E_c-E_F}{k_B T}}$, in Eq. (3), the $S$ can be simplified to

$$S = \frac{k_B}{e} \left[ N_e - \frac{N_e}{n_e} + A \right]$$

where $N_e$ is the effective DOS of the conduction band, $n_e$ is the carrier concentration, and $A$ is a transport constant that depends on the dominant scattering mechanism [19]. Meanwhile, $S$ for metals or degenerate semiconductors at low temperature ($E_F \gg k_B T$) is basically expressed as

$$S = \frac{\pi^2 k_B^2 T}{3} \left( \frac{\partial \log \alpha(E)}{\partial E} \right)_{E=E_F}$$

in Mott’s equation [20,21].

The $S$ of metals are typically small and keep constant by reflecting the energy differential of DOS around the $E_F$, but those of the semiconductors drastically change, depending on $n_e$, by reflecting the shape of the DOS around the conduction band bottom due to the $E_F$ shifts by carrier doping [22]; the doped carriers may be unintentionally caused by the existence of oxygen vacancies for VO$_2$ thin film [23]. Previously, we systematically measured the $S$ of electron-doped V$_{1-x}$W$_x$O$_2$ epitaxial films with different doping levels [17] and clarified that the metallic electronic structure clearly changes into an insulating electronic structure with a parabolic DOS around the conduction band bottom, where the $S$ for insulating phase systematically changes by reflecting the derivative of the DOS around the $E_F$.

$S$ measurements have been actively performed to investigate the MI transition characteristics of bulk [24,25], nanowires [26], and thin-films [27] of VO$_2$, where the $S$ significantly change from 200–400 $\mu$V K$^{-1}$ for the insulating phase down to $\sim$20 $\mu$V K$^{-1}$ for the metallic phase. In addition, $S$ measurements were recently applied to investigate the metal-insulator domain arrays in single-crystal microbeams [26] and the effect of the domain inhomogeneity in thin films [27], which demonstrates the unusual $S$: the complications of the phase coexistence near the domain wall may cause a deviation of the $S$ from a normal behavior in each pure domain. The ability of sensitive detection of the metallic and insulating phases around the $T_{MI}$ should make $S$ measurements suitable to investigate the MI transition process of VO$_2$.

In this paper, we investigate the MI phase transition of VO$_2$ thin films with regulated lattice distortion via $S$-measurements. We controlled the epitaxial orientations of the VO$_2$ films grown on single crystalline substrates of (0001) $\alpha$-Al$_2$O$_3$, (1120) $\alpha$-Al$_2$O$_3$, and (001) rutile-TiO$_2$. Then we compared their MI transition process by simultaneously measuring the $S$ and electrical resistivity ($\rho$).

II. EXPERIMENTAL

VO$_2$ epitaxial films were grown on (0001) $\alpha$-Al$_2$O$_3$, (1120) $\alpha$-Al$_2$O$_3$, and (001) TiO$_2$ substrates by pulsed laser deposition. A KrF excimer laser with a laser energy fluence of 3 J cm$^{-2}$ was used to ablate a V$_2$O$_5$ target disk. The growth temperature was fixed at 500°C, and the oxygen pressure ($P_{O_2}$) was optimized at 2.0 Pa because the resistivity-change ratio from an insulator to a metal across the $T_{MI}$ is extremely sensitive to $P_{O_2}$ during thin film growth [28]. After deposition at a rate of approximately 2 nm min$^{-1}$, the films were cooled to RT under the same oxygen pressure. The film thickness was set at 30–40 nm, which was characterized by x-ray reflectivity measurements. The crystal structures, including the crystallographic orientation and the mosaicity of the crystallites, were investigated by high-resolution x-ray diffraction (XRD; anode radiation: monochromatic CuK$_{\alpha}$, ATX-G, Rigaku Co.) at RT. The film surface structures were observed by atomic force microscopy (AFM).

$S$ was measured by giving a temperature difference ($\Delta T$) of $\sim$4 K in the film with In-Ga alloy electrodes. Here we used two Peltier devices placed under the film, where one side cooled and the other side heated a sample, without changing the temperature at the center [29]. We used two Cu leads to measure the thermoelectromotive force ($\Delta V$). Thus, the observable slope of $\Delta T/\Delta V$ plots should be expressed as $SV_{O_2}\text{film} + SCu$ (see Supplemental Material [30] for the calculation of $SV_{O_2}\text{film} + SCu$). Since $S$ of Cu is very small ($\sim$1.5 $\mu$V K$^{-1}$) as compared to that of VO$_2$, $S$ of the Cu leads was ignored in this study. The actual temperatures of both sides of the VO$_2$ film surface were monitored by two tiny thermocouples separated by a gap $\sim$7 mm. The thermoelectromotive force ($\Delta V$) and $\Delta T$ were simultaneously measured at almost the same positions, and the $S$ were obtained from the linear slope of the $\Delta V$–$\Delta T$ plots [17]. It should be noted that the sapphire substrate is not suited for $S$ measurements because of high thermal conductivity, but we measured the $\Delta V$ at the highly steady state after making the $\Delta T$ up to 10 K in sapphire substrate, which enables accurate $S$ measurements of VO$_2$ thin films prepared on sapphire substrates. Meanwhile, $\rho$ was measured by a dc four probe method using Au electrodes.

III. RESULTS

A. Epitaxial orientation control of VO$_2$ thin films

Figure 1 shows the (a)–(c) out-of-plane and (d)–(f) in-plane XRD patterns of VO$_2$ films grown on the substrates of (a) and (d) (0001) $\alpha$-Al$_2$O$_3$, (b) and (e) (1120) $\alpha$-Al$_2$O$_3$, and (c) and (f) (001) TiO$_2$. In addition, Fig. 2 summarizes (a)–(c) AFM images and reflection high-energy electron diffraction (RHEED) patterns, and (d)–(f) schematic epitaxial relation models of each film. For the out-of-plane XRD pattern of VO$_2$ film grown on (0001) $\alpha$-Al$_2$O$_3$ substrate [Fig. 1(a)], diffraction peaks of 0k0 ($k = 2$ and 4) for monoclinic VO$_2$ are observed along with those of the (0001) $\alpha$-Al$_2$O$_3$ substrate. The average crystallite tilt angle, full width at the half maximum (FWHM) value of the 020 diffraction peak [20–fixed $\omega$ scan, inset of Fig. 1(a)], is 0.17°. For the in-plane XRD pattern [Fig. 1(d)], 200 VO$_2$ and 1120 $\alpha$-Al$_2$O$_3$ diffraction peaks are observed, which confirms the epitaxial relationship of (010)[100] VO$_2$$||$(0001)[1120] $\alpha$-Al$_2$O$_3$. These results are also consistent with the RHEED pattern [Fig. 2(a)]. However, the in-plane 2$\theta$–fixed $\phi$ scan of the 200 diffraction peak [inset of Fig. 1(d)] shows six diffraction peaks instead of the twofold rotational symmetry of a monoclinic lattice, indicating that
the VO₂ film has three domain structures with 60° rotational periodicity, presumably due to domain matching between the film and substrate. Meanwhile, the broad 2θ diffraction peaks, which indicate a weak in-plane orientation, should originate from the misaligned orientations between (100) VO₂ and (1120) α-Al₂O₃ by 2.1° due to the monoclinic structure, as shown in the schematic epitaxial relation model [Fig. 2(d)]. Reflecting the rotational domain structure, small crystalline grains with size of ~20 nm are observed in the topographic AFM image [Fig. 2(a)].

On the other hand, in the case of the VO₂ film on the (1120) α-Al₂O₃ substrate, h00 (h = 2, 3, and 4) diffraction peaks of monoclinic VO₂ are observed along with intense peaks from the (1120) α-Al₂O₃ substrate in the out-of-plane XRD pattern [Fig. 1(b)]. Because the double lattice spacing (h = odd numbers) along the a axis of monoclinic VO₂ originates from the formation of the vanadium-ion dimer, the existence of the 300 diffraction peak confirms that the structural transition temperature (monoclinic-to-tetragonal phase transition) is above RT. The average crystalline tilt angle is 0.16° [inset of Fig. 1(b)]. The in-plane XRD pattern [Fig. 1(e)] shows clear diffraction peaks of 020 VO₂ and 0006 α-Al₂O₃. The in-plane φ scan of the 020 diffraction shows a twofold rotational symmetry with 180°, originating from the monoclinic symmetry of the VO₂ lattice. These results substantiate that the VO₂ film is grown on the (1120) α-Al₂O₃ substrate with an epitaxial relationship of (010)[010] VO₂||[1120][0001] α-Al₂O₃ [Fig. 2(e)], which is also confirmed in the RHEED pattern [Fig. 2(b)]. For the film surface structure of the VO₂ film on the (1120) α-Al₂O₃ substrate, reflecting the anisotropic crystal structure of VO₂ along the [102] direction, rectangular shaped grains are observed in the AFM image [Fig. 2(b)].

For the out-of-plane XRD pattern of VO₂ film grown on (001) TiO₂ substrate [Fig. 1(c)], the 402 diffraction peak of VO₂ is observed along with the 002 diffraction peak of TiO₂. The 402 diffraction corresponds to 002 diffraction of tetragonal VO₂, which has the same rutile structure with the TiO₂ substrate. For the in-plane XRD pattern [Fig. 1(f)], the 022 diffraction of monoclinic VO₂, corresponding to the 220 diffraction peak of tetragonal VO₂, overlaps with the 220 diffraction peak of the TiO₂ substrate. The asymmetric φ scan for the 420 (monoclinic) [222 (tetragonal)] diffraction peak, shown in the inset, exhibits a fourfold rotational symmetry with 90°, confirming that VO₂ film grows on isostructural TiO₂ (001) substrates with an epitaxial relationship between the film and TiO₂.

FIG. 1. (Color online) (a)–(c) Out-of-plane and (d)–(f) in-plane XRD patterns at RT for VO₂ films grown on single crystalline substrates of (a) and (d) (0001) α-Al₂O₃, (b) and (e) (1120) α-Al₂O₃, and (c) and (f) (001) TiO₂. Crystalline phases and diffraction indices are noted above the corresponding diffraction peaks. Insets of (a)–(c) show out-of-plane rocking curves (2θ-fixed ω scans) and those of (d)–(f) show in-plane rocking curves (2θχ-fixed φ scans) for each diffraction peak of VO₂ film.
substrate (i.e. (20\bar{1}|011) (monoclinic)|[001]|110] TiO₂ or (001)[110] VO₂ (tetragonal)|[001]|110] TiO₂ [Fig. 2(f)]. For the film surface of the VO₂ film on the (001) TiO₂ substrate [Fig. 2(c)], the film has a polycrystalline structure composed of small grains (∼40 nm diameters), although epitaxial growth is confirmed in the RHEED patterns. From these results, we successfully controlled the crystal orientations of the VO₂ films by the choice of substrates.

B. Metal-insulator transition characteristics

Figures 3(a) and 3(b) summarize ρ−T curves normalized by ρ at 35 °C (ρ/ρ₃₅°C) and S−T curves of the VO₂ epitaxial films, respectively, where it should be noted that there has been no report on the comparison of the MI transition characteristics for the VO₂ films with different crystallographic orientations. Here we normalized ρ to show the change of Tₘ clearly, because ρ of the VO₂ epitaxial films were scattered as shown in the inset of Fig. 3(a), where ρ should be influenced by grain-boundary scattering due to different grain sizes and different epitaxial orientations of the VO₂ films. The average ρ₃₅°C was 1.95 Ω cm with a standard deviation of 1.12 Ω cm. The average ρ was confirmed to be consistent with previously reported values of VO₂ films [27]. Meanwhile, S is a physical property that is not affected by grain boundary scattering and makes it easy to directly compare MI transition characteristics. Both ρ−T and S−T were measured along the [100], [010], and [011] directions for monoclinic VO₂ films grown on (0001) α-Al₂O₃, (1120) α-Al₂O₃, and (001) TiO₂, respectively. As the temperature increases, all the VO₂ films show a sharp drop (a three-digit decrease) in ρ−T [Fig. 3(a)] due to the transition from an insulator to a metal. For the S−T curves [Fig. 3(b)], |S| of all the VO₂ films start to decrease from 220 − 240 μVK⁻¹ for the insulating phase down to 23 μVK⁻¹ for the metallic phase [17]. The |S| of the insulating phase at low temperature around RT increases linearly with temperature, indicating that the insulating phase is a degenerate semiconductor, while the constant S for the metallic phase (−23 μVK⁻¹) agrees well with the previously reported S of −20 μVK⁻¹ for those of undoped VO₂ bulks [24,25], microbeams [26], and thin films [27].

To visualize the MI transitions clearly, Figs. 3(c) and 3(d) plot the temperature derivative curves of d[log ρ/ρ₃₅°C]/dT and dS/dT, respectively. The arrows in Fig. 3(c) denote the MI transition temperatures observed in ρ(T), which are defined as the peak position in the d[log ρ/ρ₃₅°C]/dT versus T. Tₚ for the VO₂ films depends on the substrate [i.e., Tₚ of the VO₂ film on (0001) α-Al₂O₃ is 64 °C, which is close to 68 °C of VO₂ bulks [1], but decreases to 59 °C on (1120) α-Al₂O₃ and 50 °C on (001) TiO₂]. The difference in Tₚ should be related to the interfacial strain effect between the films and the substrates because it has been reported that strains imposed on VO₂ films by substrates significantly affect Tₚ [31]. In general, Tₚ depends on the c axis length of the rutile structure in VO₂ because the V-V chain length along the c axis plays an important role in the MI transition [5,32]. It should be noted that the transition from an insulator to a metal in bulk VO₂ simultaneously induces shrinkage by 1% along the c axis of the rutile structure [2,33], indicating that the lattice shrinkage would drive the electronic phase toward the metal.

To estimate the c axis length, the monoclinic structure was converted into the pseudorutile structure. Figure 4(a) depicts the relations between Tₚ and the c axis lattice parameters estimated from the XRD patterns of the VO₂ films (Fig. 1) as well as that of bulk VO₂ [34]. Tₚ of VO₂ films with different crystallographic orientations monotonically decreases as the c axis lattice parameters shrink in the pseudorutile structure compared to those of bulk VO₂. Because the film on (0001) α-Al₂O₃ should be structurally relaxed as a result of the large lattice mismatch and different crystallographic symmetry, Tₚ is comparable to that of bulk VO₂. On the other hand, the films on (1120) α-Al₂O₃ and (001) TiO₂ are partially strained, and Tₚ consequently decreases. Meanwhile, the transition temperatures observed in S(Tₛ), which are determined as peak positions in dS/dT versus T [Fig. 3(d)], also decreases as the c axis length decreases [Fig. 4(b)]. These results indicate that the distortion along the c axis of the rutile
FIG. 3. (Color online) (a) and (b) Temperature dependences of electrical resistivity ($\rho$) and Seebeck coefficient ($S$) for VO$_2$ epitaxial films grown on (0001) $\alpha$-Al$_2$O$_3$ (blue), (1120) $\alpha$-Al$_2$O$_3$ (red), and (001) TiO$_2$ (green), respectively. (a) $\rho$–$T$ curves normalized by $\rho$ at 35 °C ($\rho/\rho_{35°C}$) and (b) $S$–$T$ curves measured by increasing $T$ from RT. Temperature derivative plots of (c) $d[\log\rho/\rho_{35°C}]/dT$ and (d) $dS/dT$. The arrows indicate the positions of $T_\rho$ and $T_S$. The onset and offset temperatures of the transition from an insulator to a metal are marked by open and closed triangle symbols, respectively, and the color bars indicate the temperature range of the MI transition.

structure is the dominant factor for reducing $T_\rho$ and $T_S$ in the present VO$_2$ films.

FIG. 4. (Color online) The relations of (a) $T_\rho$ and (b) $T_S$ with estimated $c$–axis lattice parameters in the pseudorutile structure for VO$_2$ epitaxial films. Those of the monoclinic-VO$_2$ bulk are also shown for comparison [1,25,34]. $T_\rho$ and $T_S$ of the VO$_2$ films decreased with shrinkage of the $c$–axis lattice parameters from those of bulk VO$_2$.

IV. DISCUSSION

To more clearly show the MI transition process, onset and offset temperatures of $T_\rho$ and $T_S$ for the transition from an insulator to a metal are denoted by open and closed triangles, respectively, in Figs. 3(c) and 3(d). Color bars indicate the temperature range of the MI transition width where the metallic and insulating phases should coexist. It is noteworthy that the MI transition temperature width becomes broader as $T_\rho$ and $T_S$ decrease, presumably due to the distortion of the $c$–axis length in the rutile structure of the films, which leads to an inhomogeneous domain distribution. Although the offset $T_\rho$ and $T_S$ are almost the same, the onset $T_\rho$ is much higher than the onset $T_S$, (i.e., the transition temperature where the insulating phase begins to transform into metallic phase is higher for the $\rho$ measurement compared to that for the $S$ measurement).

One plausible reason for this difference should come from the domain distribution of the metallic and insulating phases at the nanoscale [15]. Figure 5 schematically depicts the domain configurations at each temperature (a)–(d) around the MI transition according to a previous report [15] and the corresponding changes in $\rho$–$T$ and $S$–$T$ as functions of temperature. As the temperature increases from (a) to (d), the majority phase changes from (a) an insulator to (d) a metal, where the metallic and insulating domains coexist at (b) and (c); metallic domains first form inside the insulating phase, then some domains connect with each other, and finally, the entire region becomes a metallic phase. It has been reported that VO$_2$ films show percolation conduction, depending on the domain configuration, and $\rho$ significantly decreases when the metallic domains are connected with each other at (c).