Persistent M2 phase in strongly strained (011)-oriented grains in VO₂ films grown on sapphire (001) in reactive sputtering

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ABSTRACT

We report on the first observation of the persistent M2 phase in strongly strained (011)-oriented grains in VO₂ films grown on Al₂O₃ (001) substrates by means of conventional rf reactive sputtering under adequate deposition conditions. Spatially resolved micro-Raman spectra clearly showed that (011)-oriented large crystalline grains with the *c_R*-axis parallel to the substrate resulted in the appearance of the M2 phase over a wide temperature range of 30 °C. A close correlation of the appearance range of the M2 phase with the in-plane tensile stress of (011)-oriented grains was revealed by X-ray diffraction. We present a phase diagram for the M1, M2, and R phases in relation to the stress of (011)-oriented grains and temperature. It was shown that (011)-oriented micrometer-sized long grains play a crucial role in the emerging structural phase transition (SPT) via an M2 phase even in a film grown on Al₂O₃ (001), which is ordinarily reserved for the (020)-oriented VO₂ growth. The results shown here will contribute to make clear the conditions for obtaining VO₂ films with the appearance of the M2 phase in their SPT process.

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I. INTRODUCTION

A strongly correlated oxide, called vanadium dioxide (VO₂), has been generating a wide range of interest because of the drastic changes taking place in physical properties that are concomitant with the insulator-metal transition (IMT) phenomenon and the utilization of such changes in engineering applications.^{1–3} Attempts have been made over several decades to study the correlation between the IMT and the structural phase transition (SPT) in order to realize the desired properties of VO₂.^{4,5} In addition, recently, growing interest for the application of the IMT to electrical, optical, and thermal devices has been related to the controllability of the IMT in VO₂ thin films.^{6–11} New attempts to apply the IMT for neuromorphic computing and terahertz switching require further understanding of the physics of the thin film VO₂.^{3,12–15}

So far, a number of studies on VO₂ single crystals and VO₂ films have suggested that the distance of V atoms along the *c_R*-axis

(in the high-temperature tetragonal phase, R phase) determines the IMT temperature.^{16–18} VO₂ films grown on TiO₂ (001) substrates, in which the IMT occurs at room temperature (around 300 K), contribute to enhancing the applicability of VO₂ films.¹⁹ However, the appearance of an intermediate phase in the SPT pathway between the monoclinic M1 phase and the tetragonal R phase, especially, in VO₂ thin films, remains unresolved.^{20–25} Conditions for the appearance of the intermediate M2 phase with a monoclinic symmetry have been intensively investigated by many authors by using VO₂ single-crystalline nanorods (usually called nanobeams).^{26–31} Phase diagrams as functions of temperature and stress along the *c_R*-axis have been displayed for the SPT of single-crystalline VO₂.^{28,30} As for VO₂ films grown on various substrates, the appearance of the M2 phase strongly depends on deposition conditions, which affect the stress on the VO₂ films.^{32,33} Polycrystalline VO₂ films have grain boundaries, even though they are composed of highly oriented grains, giving rise

to a complicated situation of stress state acting on the grains.^{33,34} In addition, the coexistence of the $V_{n-1}O_{2n-1}$ and V_nO_{2n+1} phases different from that of the stoichiometric VO_2 invites difficulties for considering the relation between the stress and the M2 phase.^{35,36}

Al_2O_3 (001) substrates are frequently utilized for the growth of VO_2 films in which b_M -axis (in the low-temperature monoclinic M1 phase) oriented VO_2 grains are grown with in-plane three directions based on the lattice matching between the hexagonal plane of Al_2O_3 (001) and the a_M - c_M plane of VO_2 .³⁷ Since the c_R -axis (a_M -axis) is parallel to the Al_2O_3 (001) plane, stress on the VO_2 film acts on the V-V chains, giving rise to the possibilities of inducing the M2 phase if strong tensile stress remains in the film. Thery *et al.* reported the SPT via an M2 phase in relatively thin VO_2 films on Al_2O_3 (001) deposited by electron-beam evaporation due to the tensile stress, which originates in the difference of the thermal expansion coefficient between VO_2 and Al_2O_3 .³² We also reported that the SPT with the intermediate M2 phase was observed in the VO_2 film on Al_2O_3 (001) deposited by biased reactive sputtering.^{36,38} The films we obtained were dominated by (011)-oriented large crystalline domains, which underwent SPT with the M2 phase. The temperature range of the appearance of the M2 phase was as narrow as 10–15 °C. Based on these studies, the fact that the tensile stress on the c_R -axis induces SPT with the M2 phase even in thin films was observed. However, the correlation between the stress strength and the temperature range of the appearance of M2 phase was unclear due to the presence of a disorder and the grain boundaries in the VO_2 film on the substrate. Grain boundaries reduce stress on the VO_2 grains, especially, in the case of VO_2 on Al_2O_3 (001), because of restricted small grain sizes. Thus, it is highly desirable to observe the effect of tensile stress on the appearance of the M2 phase directly in the VO_2 film on Al_2O_3 (001).

In this article, we show the case in which (011)-oriented long platelike grains were grown on Al_2O_3 (001) substrates under adequate deposition conditions in conventional reactive sputtering. We demonstrate that the (011)-oriented grains underwent SPT with a persistent M2 phase over 30 °C through the micro-Raman observations for the particular grains. A phase diagram for M1, M2, and R phases in relation between the stress on the (011)-oriented grains and the temperature is shown. We discuss the correlation of the appearance of the M2 phase in VO_2 films grown on Al_2O_3 (001).

II. EXPERIMENTAL METHODS

VO_2 films were deposited by conventional radio frequency (rf) magnetron sputtering. In this study, we did not utilize substrate biasing that we introduced before.³⁶ Polished Al_2O_3 (001) was used as the substrate and was placed at the center position on the lower electrode. The temperature of the substrate and the rf power fed to the metal vanadium (99.9%) target with a diameter of 100 mm were 450 °C and 200 W, respectively. The flow rates of Ar and O_2 gases were 38 and 1 sccm, respectively. The total pressure of Ar and O_2 gases was 0.5 Pa. We varied the deposition period as 10, 20, and 30 min.

Crystalline structures of VO_2 films were analyzed by X-ray diffraction (XRD; Philips, X'pert MRD) with $CuK\alpha$ X-ray source ($\lambda = 1.5418$ Å). Temperature-dependent micro-Raman measurements were also done to investigate the SPT at a particular

crystalline region. The Raman setup utilizes a 514 nm Ar ion laser with a power of 0.5 mW as the light source. The incident laser light was focused by a $\times 50$ lens (0.50 NA), which realizes the spatial resolution of around 2 μm .³⁹ Reflex device (Renishaw, inVia) and a temperature controller (Linkam, THMS 600) were introduced for temperature-controlled Raman measurements. Field emission scanning electron microscopy (FE-SEM; Hitachi, S-4800) was used for observing both the surface and the cross-sectional morphologies of the VO_2 films. Atomic force microscopy (AFM; Shimadzu, SPM-9700) was also utilized to observe crystalline growth aspects and minute surface roughness. Electron probe microscopy analysis (EPMA; Shimadzu, EPMA-1610) was introduced to investigate spatial difference of the atomic concentration. Resistance changes against temperature were measured by two electrical probe tips, which are made of tungsten carbide (WC). Film thickness was evaluated by cross-sectional SEM images.

III. RESULTS AND DISCUSSION

Figure 1 shows XRDs for VO_2 films deposited for different periods of 10, 20, and 30 min. We named these samples as S1 (10 min), S2 (20 min), and S3 (30 min). Film thicknesses were 100, 290, and 340 nm for S1, S2, and S3, respectively. In all samples, we see diffraction from the VO_2 (020) plane at around $2\theta = 39.8^\circ$, whose FWHM of rocking curves was 0.09° , 0.14° , and 0.11° for S1, S2, and S3, respectively. The growth of (020)-oriented VO_2 films on Al_2O_3 (001) is commonly known in addition to the in-plane three growth directions based on lattice matching between a_M and c_M plane with a β angle of 122° and the hexagonal Al_2O_3 (001) plane. A large shift ($2\theta = 39.98^\circ$, $d_{(020)} = 2.255$ Å against bulk $2\theta = 39.83^\circ$, $d_{(020)} = 2.263$ Å) of the XRD peak position for (020) in the sample S1 means the occurrence of a strong in-plane tensile stress, which is basically caused by the thermal stress. As suggested by many researchers, a large difference of the thermal expansion coefficient between VO_2 ($29.7 \times 10^{-6}/K$ along the c_R -axis in the tetragonal phase) and Al_2O_3 ($5.0 \times 10^{-6}/K$) results in a large tensile stress.³² A simple estimation of the in-plane thermal stress of a VO_2 film with the c_R -axis parallel to the Al_2O_3 (001) substrate gives -1.10 GPa at a temperature of 70 °C for the deposition temperature of 450 °C when we use Young's modulus E of 140 GPa. Thery *et al.* showed the relaxation of the in-plane tensile strain with an increase of VO_2 film thickness deposited by the electron-beam evaporation method, where residual stress is dominated by thermal stress, with relaxation occurring with increasing thickness.³² However, in our experiment using reactive sputtering, where energetic ions assist crystalline growth, the (011)-oriented VO_2 growth also appeared at deposition periods of 20 and 30 min, as shown in Fig. 1.

We see strong diffraction peaks from VO_2 (011) at around $2\theta = 27.9^\circ$ for S2 and S3, in Fig. 1(b). As shown in Fig. 1(c), rocking curves for the (011) plane showed small values of FWHM of 0.13° and 0.10° for S2 and S3, respectively, indicating a superior orientation of the grains. In addition, the higher peak position of (011) of S2 ($2\theta = 27.955^\circ$, $d_{(011)} = 3.1916$ Å, against bulk $2\theta = 27.85^\circ$, $d_{(011)} = 3.2034$ Å) suggested a strong in-plane tensile stress on the (011)-oriented grains. The fact that the in-plane tensile stress estimated by the shift of the (020) peak was rather relaxed in S2 compared to that in S1 suggested the difference of stress between

FIG. 1. (a) X-ray diffraction patterns for VO_2 films with the deposition time of 10, 20, and 30 min, namely, S1, S2, and S3. (b) Enlarged XRD patterns for the (011) peak. (c) X-ray rocking curves for the (011) peak in S2 and S3.

$\text{VO}_2(020)$ and (011) crystalline grains. It is known that the stress in polycrystalline films differs between crystallite and grain boundaries.⁴⁰ We elucidate that the stress of sample S2 depends on crystallites with different sizes as evidenced later by SEM images. The higher peak position of (011) at $2\theta = 27.955^\circ$ in S2 corresponds to the out-of-plane compression ε_z of -0.37% , which is caused by the in-plane tensile stress $\sigma_{\parallel}$ based on the elastic-body approximation. We adopted the well-known relationship of $\sigma_{\parallel} = -E\varepsilon_z/2\nu$, where ν is Poisson's ratio, for deriving the in-plane stress. By using the reported values of E and ν of 140 GPa and 0.30,^{42,43} a tensile stress of 860 MPa was obtained for the (011)-oriented grains. On the other hand, the peak position of (011) in S3 was almost in accordance with that of the bulk VO_2 , suggesting that the stress on the (011)-oriented grains was relaxed in this sample through the increase of film thickness.

Figure 2 shows FE-SEM images of VO_2 films for S1, S2, and S3. Noticeable grains cannot be seen in S1, as shown in Fig. 2(a),

FIG. 2. FE-SEM images for samples S1 (a), S2 (b) and (c), and S3 (d). An AFM image (e1) and the surface profile (e2) for S2. The backscattered electron microscopy (BSE) image (f1) and corresponding EPMA mapping for oxygen concentration (f2) for S2.

suggesting that the thinnest film is composed of (020)-oriented fine crystalline grains. In Fig. 2(b), we found micrometer-sized large crystalline grains in S2 in addition to conventional smaller grains with the (020)-orientation. In the inset of Fig. 2(b), we show another SEM image that clearly shows the platelike crystalline grain with width and length of around $1\mu\text{m}$ and $6\mu\text{m}$, respectively. The cross-sectional SEM image for S2 also evidences the presence of a platelike crystallite in Fig. 2(c). When we increased the deposition time to 30 min in S3, as can be seen in Fig. 2(d), large crystalline grains with a dark contrast were enlarged to more than several tens of micrometer square, although many grain boundaries were present. Such large crystalline grains were confirmed to be

FIG. 3. Temperature-dependent micro-Raman spectra for (a) (011)-oriented and (b) (020)-oriented grains in S2. Color plots of Raman spectra for (c) (011)-oriented and (d) (020)-oriented grains in S2. Temperature-dependent micro-Raman spectra for (e) (011)-oriented and (f) (020)-oriented grains in S3.

corresponding to the (011)-oriented VO₂ by area-restricted XRD measurements, as shown in Fig. A in the [supplementary material](#). Figure 2(e1) shows an AFM image for S2, in which rod-shape crystallites are grown in the fine matrix grains. Height analysis shown in Fig. 2(e2) evidences a flat surface of the crystallite in contrast to matrix grains with rough surfaces and deep grain boundaries. Based on the results of SEM and AFM images, characteristic micrometer-sized large crystalline grains in S2 were attributed to (011)-oriented crystallites. It can be elucidated that with increasing film thickness, (011)-oriented rod-shape crystallites coalesced and resulted in the formation of large grains. Rod-shape crystallites are no longer observed in S3, suggesting the relaxation of in-plane stress on a particular direction.

Here, it should be noted that glancing incidence XRD (GI-XRD) showed the diffraction from V₆O₁₃ in all samples. V₆O₁₃, which is categorized as one of the Sharley phases with V_nO_{2n+1} like V₂O₅, is known to transform to VO₂ by annealing because of its quite low melting temperature of 680 °C.⁴¹ We elucidate that the (011)-oriented grains were nucleated and grown from the crystalline nuclei of highly oxidized V₆O₁₃ present with (020)-oriented VO₂ fine grains. In agreement with this, EPMA mapping images for oxygen (O) concentration in Figs. 2(f1) and 2(f2) show that (011)-oriented large grains contain less O compared to the surrounding matrix region.

Figure 3(a) shows the results of the temperature-dependent micro-Raman measurement on a particular rod-shape grain in the film S2. The superior crystallinity of the film at room temperature (20 °C) was evidenced by a series of intense peaks corresponding to the M1 phase VO₂. The continuation of the M1 phase until 65 °C was clearly recognized. At 70 °C, we recognized the onset of blue shift of the peak at 618 cm⁻¹ (V-O stretching mode in M1). A complete shift of the peak to 648 cm⁻¹ (V-O stretching mode in M2) was clearly observed at 75 °C. Characteristic splitting in the peaks at 220 and 229 cm⁻¹ (the V-V stretching mode in M2) was also recognized, suggesting that a superior crystalline M2 phase VO₂ was formed at this temperature. The M2 phase continued to occur clearly until 100 °C and then transformed to the R phase completely at 110 °C. Structural phase transition from M1 to M2 with such superior crystallinity and persistent M2 phase for a range of over 30 °C is the first observation made in VO₂ films grown on Al₂O₃ substrates. On the other hand, Fig. 3(b) shows micro-Raman spectra taken for the matrix region, where several tens of nanometer grains with (020)-orientation were grown. We also recognize the superior crystallinity of the M1 phase VO₂ at room temperature (20 °C), similar to Fig. 3(a). It can also be seen that the peak at 618 cm⁻¹ showed a blue shift to 648 cm⁻¹ at 75 °C, indicating the appearance of the M2 phase. However, characteristic spectra for M2 phase soon disappeared until 85 °C.

Figures 3(c) and 3(d) show the color plots of temperature-dependence of Raman peak position reproduced from the data shown in Figs. 3(a) and 3(b). An abrupt peak shift from 618 to 648 cm⁻¹ at 75 °C was clearly demonstrated in Fig. 3(c). On the other hand, the appearance of the M2 phase was hardly recognized for the (020)-oriented area in Fig. 3(d). In order to evaluate the quantitative evolution of the M1, M2, and R phases, we calculated the intensity of Raman peaks by adopting Lorentzian fittings for both (011) and (020)-oriented grains shown in Figs. 3(a) and 3(b). We focused on Raman mode of 619 cm⁻¹ for M1 and 648 cm⁻¹ for M2 phases as

representatives. To represent the R phase, which has a strong background for a wide wavenumber range [see Figs. 3(c) and 3(d)], we integrated the intensity for $900\text{--}1100\text{ cm}^{-1}$, where no Raman mode exists in any phase. Through the curve fittings, it was confirmed that the M2 phase appeared simultaneously with the R phase after 65°C in both cases. We show the evolution of each phase for both (011) and (020)-grains in Fig. B in the [supplementary material](#).

Furthermore, we performed micro-Raman measurements for the film S3. In Fig. 3(e), we recognize the shifted peak at 648 cm^{-1} at temperatures from 75 to 80°C . Also in Fig. 3(f), we recognize the shifted peak from 75 to 80°C . However, Raman spectra characteristics in the M2 phase were weak compared to those that appeared in the (011)-oriented grain in S2. In our previous paper, we reported the SPT through the M2 phase in VO_2 films deposited on Al_2O_3 (001) substrates by using biased reactive sputtering.^{36,38} We elucidated that the formation of (011)-oriented large crystalline grains was driven by a high-energy ion irradiation effect on the excess oxygen phases, which act as nuclei for the growth of (011)-oriented large domains. However, the appearance of the M2 phase was restricted to a narrower temperature range similar to that in Figs. 3(e) and 3(f). Thus, we emphasize that the enhanced crystallinity and persistency of the M2 phase was first demonstrated in this study by taking micro-Raman on the (011)-oriented long grains under high in-plane tensile stress. It is suggested that the appearance of the M2 phase in the course of SPT of VO_2 films strongly depends on aspects like crystalline orientation and grain size because they dominate the combined effect of stress on a particular c_R -axis direction.⁴² We elucidate that in a highly strained (020)-oriented VO_2 film, the appearance of the M2 phase over a wide temperature range is highly unlikely due to the small grain sizes in which the stress effect is relaxed by the grain boundaries. We also show the evolution of the Raman peak intensity of each phase for both (011) and (020)-grains of S3 in Fig. B in the [supplementary material](#).

FIG. 4. Stress-temperature phase diagram of structural phase transition (SPT) of M1-M2-R phases for (011)-oriented grains in VO_2 films grown on Al_2O_3 (001) substrate. Stress values were calculated from the XRD peak position of diffractions from (011)-oriented grains.

Based on the micro-Raman measurements, we drew the phase diagram for M1, M2, and R phases in relation between the stress on (011)-oriented grains and the temperature, as shown in Fig. 4. As mentioned before, we evaluated the in-plane stress values from the out-of-plane strain obtained by the peak position of (011), assuming elastic-body approximation with Young's modulus and Poisson's ratio of 140 GPa and 0.30 , respectively. The stress values for (011)-oriented grains for samples S2 and S3 are 860 and 165 MPa , respectively. From the results, it can be seen that increasing tensile stress induces a wider temperature window for the M2 phase. The high-temperature side was extended by the increasing stress, while the lowest temperature side for the M2 phase was rather constant at around 70°C . The added data for the VO_2 film with (011)-oriented large domains were based on the peak position of XRD presented in our previous paper,³⁶ supporting the validity of the proposed phase space regardless of the difference in the deposition method. The boundary between M2 and R phases obtained by the present study for sample S2 almost corresponds to the extrapolated line based on the result of Park *et al.*⁴³ The present result, in which the crystalline grain under a strong tensile stress of 0.86 GPa shows a persistent M2 phase until 100°C , suggested an invariant nature of SPT in VO_2 . On the other hand, it can be seen that the boundary from the M1 to M2 phases obtained by the present study was different from that using VO_2 nanobeams.^{28,30,43} SPT from M1 to M2 was observed at an almost constant temperature of around 70°C in our study. As shown in Fig. 3(b), (020)-oriented grains showed the onset of SPT at 70°C , the same as the onset of (011)-oriented grains.

Here, we consider the cause for a simultaneous onset for the appearance of the M2 phase for both (011) and (020)-oriented grains. When discussing the SPT of VO_2 , it is necessary to compare the lattice length toward the c_R direction. The monoclinic M2 phase has been reported to have a lattice length of $a_{M2} = 9.0664\text{ \AA}$, $b_{M2} = 5.797\text{ \AA}$, $c_{M2} = 4.5255\text{ \AA}$, and $\beta_{M2} = 91.88^\circ$.²⁰ Meanwhile, as is well known, the M1 phase has $a_{M1} = 5.753\text{ \AA}$, $b_{M1} = 4.526\text{ \AA}$, $c_{M1} = 5.383\text{ \AA}$, and $\beta_{M1} = 122.6^\circ$ and the tetragonal rutile phase has $a_R = 4.555\text{ \AA}$ and $c_R = 2.853\text{ \AA}$.²⁰ Thus, the corresponding lattice length of a_{M1} , $2c_R$, and b_{M2} are 5.753 , 5.706 , and $5.797\text{ \AA}$, respectively. The length would then be compressed by -0.8% upon M1 to R transition, while it would be tensiled by 0.76% upon M1 to M2 transition. As Zhang *et al.* suggested, the compression upon M1 to R phase transition induces tensile stress, which can locally stabilize the formation of the M2 phase with a large cell length of b_{M2} .²⁷ Thus, the formation of the M2 phase follows nucleation of the R phase. In addition, the onset of SPT of (011)-oriented grains will be strongly restricted by the surrounding (020)-oriented matrix grains. When VO_2 transforms from the M1 to the M2 phase, the unit cell volume increases by about 0.66% with in-plane enlargement for $2V_{M1} \rightarrow V_{M2}$. Then, the SPT of M1 to M2 would be severely restricted by the unchanged surrounding matrix. Therefore, we interpret that the (011)-oriented grains revealed the SPT from M1 to M2 at temperatures corresponding to that from M1 to R of (020) grains. Naturally, the SPT of (020) grains from M1 to M2 occurs simultaneously. As shown in Fig. 3, the peak intensity of the M2 phase in the (020) grains was smaller than that of the (011) grains in S2. Therefore, we interpret that a simultaneous onset of the appearance of the M2 phase for both (011) and (020)-oriented grains occurred at a temperature at which SPT from

the M1 to the R phase was initiated. On the other hand, the SPT from M2 to R is accompanied by a slight volume decrease of 0.40%, which enables (011)-oriented grains' transformation according to the stress-temperature phase diagram.

Kim *et al.* reported that single-crystal VO₂ wires with a length over 10 μm grown on an r-cut sapphire substrate possess M2 phase, which are stable from 19 to 100 $^{\circ}\text{C}$.⁴⁴ They expected that thicker wires with greater stress supplied sufficient driving force to nucleate the M2 phase in addition to the effect of substrate-mediated interaction. Thus, we interpret that the growth of large grains with superior crystallinity is a key issue to emerge persistent M2 phase. Furthermore, the occurrence of the M2 phase in VO₂ films on Al₂O₃ (001) substrates was reported by Ji *et al.*²² They mentioned that the temperature window for the M2 phase depends on the

tensile strain that is relevant to the film thickness. Thus, in the present study, the large in-plane tensile stress in (011)-oriented grains in S2 contributes to an enlargement of the window for the M2 phase, as shown in Fig. 4.

Finally, we show resistance (R)-temperature (T) characteristics for S1, S2, and S3 films in Fig. 5. Resistance was measured by two probe tips separated by 1 mm. As can be seen, change in resistance above three orders of magnitude was observed after the onset of the IMT in both S2 and S3. Values of the transition temperature defined by the peak of $-d(\log_{10} R)/dT$ against the rising temperature were 77 and 79 $^{\circ}\text{C}$ for S2 and S3, which were higher than those of S1 (75 $^{\circ}\text{C}$). Resistance started to decrease with the onset of SPT at around 70 $^{\circ}\text{C}$ in both S2 and S3. As shown in temperature-dependent Raman measurements, the R phase increases its domination in accordance with the decrease in the M1 phase at a temperature of 70 $^{\circ}\text{C}$. Although the M2 phase appeared at this temperature in both (011) and (020) grains, resistance continued to decrease due to the current flow through the R phase. It can be observed in both S2 and S3 that the resistance almost reached its lowest values soon after the M2 phase for the (020) grains disappeared. We marked the temperature ranges of the M2 phase for (011) grains based on the results of Fig. 3. Even in sample S2, the apparent influence of the M2 phase on resistance was not recognized because the current path between the two probe tips could be formed through the R phase area with a low resistivity. It is required to evaluate other physical properties such as optical reflectance and transmittance of infrared light with high spatial resolution in order to evaluate the effect of the persistent M2 phase in (011)-oriented grains. A combination of far-field infrared spectroscopy and near-field infrared microscopy will be effective for monitoring the coexisting insulating M2 and metallic R phases through the difference in optical characteristics including optical conductivity.⁴⁵

FIG. 5. Resistance (R)-temperature (T) characteristics for S1, S2, and S3 films. Numerical values of derivative of resistance against temperature $[d(\log_{10} R)/dT]$ were also plotted in the top part of the figure in which temperature axes are common with R - T panels.

IV. CONCLUSIONS

The persistent M2 phase in strongly strained (011)-oriented grains in VO₂ films grown on Al₂O₃ (001) substrates by means of conventional rf magnetron sputtering was first demonstrated. Temperature-dependent micro-Raman measurements showed the appearance of an M2 phase from 70 to 100 $^{\circ}\text{C}$ in (011)-oriented grains, in contrast to a narrower range of 10 $^{\circ}\text{C}$ in (020)-oriented matrix grains. It is suggested that the appearance of the M2 phase in the course of the SPT of VO₂ films strongly depends on factors like crystalline orientation and grain sizes because they dominate the combined effect of stress on a particular c_R -axis direction.

SUPPLEMENTARY MATERIAL

See the [supplementary material](#) for the (Fig. A) area-restricted XRD and SEM images for S3 and (Fig. B) integrated signal intensity of M1, M2, and R phases estimated by adopting Lorentzian fittings for Raman spectra of S2 and S3.

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