Strain-induced resistance change in V$_2$O$_3$ films on piezoelectric ceramic disks

I. INTRODUCTION

Among the various materials whose physical properties are strain dependent, vanadium sesquioxide (V$_2$O$_3$) has been of great interest for half a century because of its rich temperature-pressure phase diagram. It consists of three phases, namely, paramagnetic metal (PM), paramagnetic insulator (PI), and antiferromagnetic insulator (AFI). Pure V$_2$O$_3$ is in the PM phase at room temperature (RT) and under atmospheric pressure. Cr-doping converts the material into a PI phase in the same conditions, while the PM phase is recovered by applying hydrostatic pressure to Cr-doped V$_2$O$_3$. This reversible conversion from metallic to insulating phases and vice versa can be described with respect to the negative and positive pressure, respectively. It is also known that the $c/a$ ratio of V$_2$O$_3$ jumps at the transition, i.e., $c/a$ is high ($>2.815$) in the PM phase, while it is low ($<2.79$) in the PI phase, suggesting that the electrical properties of V$_2$O$_3$ are closely related to its strain. In a previous work, we prepared a series of V$_2$O$_3$ films on sapphire substrates with various deposition conditions, resulting in a wide range of $c/a$ ratios. Their physical properties, such as the PM–AFI phase transition temperature and resistivity ratio between high and low temperatures, were revealed to be clearly dependent on the $c/a$ ratio at RT.

The tendency was that the PM–AFI transition temperature is higher in films with a lower $c/a$ ratio at RT, indicating the stabilization of the insulating phase, and was qualitatively consistent with the change of $c/a$ ratio at the phase transition reported in bulk materials. This behavior suggests that one can expect to drive the V$_2$O$_3$ material from a metallic regime to an insulating one by artificially controlling its $c/a$ ratio. Preparing the material in a thin film form, especially in an epitaxial manner on a single crystal substrate, is convenient in order to realize a huge strain. However, in order to apply the mechanism to devices, the $c/a$ ratio must be modified in situ.

Some ideas for the in situ strain-induced conductivity control of V$_2$O$_3$ have been reported. Newns et al. have proposed a piezoelectric transistor, in which a piezoelectric layer and a so-called piezoresistive layer are confined in a rigid frame. Its operation principle is that the electric conductance in the piezoresistive layer are controlled in situ by means of mechanical stress applied from the electrically-driven piezoelectric layer. Cr-doped V$_2$O$_3$ was listed as one of the candidate materials for the piezoresistive

**ABSTRACT**

We prepared a stacked structure consisting of a quasi-free-standing functional oxide thin film and a ceramic piezoelectric disk and observed the effect of the piezoelectric disk deformation on the resistance of the thin film. Epitaxial V$_2$O$_3$ films were grown by a pulsed laser deposition method on muscovite mica substrates, peeled off using Scotch tapes, and transferred onto piezoelectric elements. In this V$_2$O$_3$/insulator/top electrode/piezoelectronic disk/bottom electrode structure, the resistance of the V$_2$O$_3$ layer is ascribed to the piezo-actuated evolution of $c/a$ ratios, which drives the material towards an insulating phase. A memory effect on the resistance, related to the hysteretic displacement of the piezoelectric material, is also presented.
layer in their proposal. Recently, we have used a conductive atomic force microscopy (C-AFM) system to apply a local pressure of sub-gigapascal to a c axis-oriented V₂O₃ film and achieved obvious metal–insulator transition. These two configurations are categorized as the approaches in which an external stress is applied along the out-of-plane direction to a film. In the present work, we attempted to apply an in-plane external stress to a V₂O₃ film. The structure simply consists of a quasi-free-standing V₂O₃ film fixed on an M–I–M-structured piezoelectric element, with neither a rigid frame nor an AFM tip. Such a design was inspired by a number of previous studies on strain-induced modification of magnetic properties of thin films placed on piezoelectric bases. Driving the phase-change properties of VOₓ by the piezoelectric force has also been reported, mainly in VO₂ films directly deposited on Pb(Mg₁/₃Nb₂/₃)O₃–PbTiO₃ (PMN-PT) single crystal substrates. Nevertheless, no study on the combination of a VOₓ film and a low-cost polycrystalline piezoelectric element has been reported so far.

The V₂O₅ film used in the present experiment should be single-oriented (most simply, c axis-oriented) in order to obtain the maximum strain effect. However, the commercially-available low-cost piezoelectric disks are made of polycrystalline ceramics with multi-oriented grains, meaning almost no chance for the V₂O₃ layer to grow single-oriented directly on it. One possible strategy to obtain a single-oriented film on a polycrystalline substrate is to place a free-standing crystalline buffer layer on the desired substrate and then grow the desired film. Another may be to epitaxially grow the desired film on a layered-structured crystalline substrate that is then peeled off and transferred onto the desired substrate. In this work, we adopted the latter strategy due to its simplicity. Mica was chosen as the substrate material because of its layered structure that is easily exfoliated with an adhesive tape (often referred to as a “Scotch tape method”). The in-plane lattices of both muscovite mica and V₂O₃ are regarded as quasi-hexagonal structures, with lattice parameters a = 5.19 and 4.95 Å, respectively, giving a lattice mismatch of about 5%. In samples with a stuck substrate of V₂O₃/insulator/top electrode/piezoelectric disk/bottom electrode, we measured the resistance of the V₂O₃ layer (Rᵥₒ₋ₒ) as a function of the piezoelectric disk bias (Vₚ). As a result, we observed a sizeable variation of Rᵥₒ₋ₒ that can only be explained by the resistivity change due to the piezo-induced modification of its c/a.

II. EXPERIMENTAL DETAILS

A. Films deposition process and crystallographic characterization

V₂O₃ films were deposited onto muscovite mica substrates by means of a pulsed laser deposition (PLD) method using a ceramic V₂O₅ target. Deposition conditions such as Ar ambient pressure (2 x 10⁻² mbar), repetition rate and deposition duration of the KrF excimer laser (Lambda Physik, COMPex 102; 5 Hz, 1800s), input energy, and fluence on the target surface (65 mJ, 2.0 J/cm²) are the same as those for V₂O₃ deposition on sapphire substrates previously reported. Only the substrate temperature was set lower (575 °C) considering a low melting temperature of mica. TiN layers for a control experiment were deposited on the muscovite mica substrates with a reactive dc sputtering method using a Ti target in an N₂ gas ambient of 5 mTorr. All the films for the Rᵥₒ₋ₒ-Vₚ experiments were deposited through a shadowing mask to pattern strips.

X-ray diffraction (XRD; Bruker, D8) measurements such as 2θ–ω, ω–ϕ-scans, and reciprocal space mapping (RSM) were performed for non-patterned V₂O₃ films with Cu Kα radiation. The thickness of the V₂O₃ film on mica was assumed to be identical to that of a V₂O₃ film deposited in the same run on a C-plane sapphire substrate, whose 2θ–ω profile contained Laue fringes that allow deducing its thickness. XRD 2θ–ω scans with a bias voltage to the piezoelectric disk were performed on a V₂O₃ film/thin mica/piezoelectric element stacked sample. The piezoelectric element was fixed on a glass plate with pieces of Scotch tape. Sample alignment along z (height), ω, and χ (tilting) axes was performed after every voltage change (at ω = 0° for the z axis, while around 2θ = 45.4°, a strong diffraction peak from mica, for ω and χ axes).

B. Transferring the film to the piezoelectric disk

The V₂O₃ layer, with a thin layer of mica, was exfoliated from the mica substrate and transferred to a commercial lead zirconate titanate (PZT)-based piezoelectric element by a Scotch tape. Prior to the transferring, Au (200 nm)/Ti (20 nm) electrode pads for a four-probe measurement were deposited on the V₂O₃ strips by a dc sputtering method using a shadowing mask. The V₂O₃ film was peeled off the mica substrate by a removable-type Scotch tape and pasted onto a commercial piezoelectric element (SPL, SPT08) with cyanacrylate glue. The piezoelectric element consists of a 0.2 mm-thick PZT-based piezoelectric disk, a 0.2 mm-thick metal plate as the bottom electrode, and a nickel (Ni) thin film as the top electrode. The layered structure of mica allows one to easily peel off the deposited layer, which is, however, inevitably accompanied by a very thin mica layer. This thin mica layer plays the...
role of an insulator that prevents the electrical contact between the piezoelectric transducer and the V$_2$O$_3$ sample, still we pasted another thin mica layer larger than the V$_2$O$_3$ sample on the top electrode to ensure the insulation [h in Fig. 1(iii)]. After the glue is dried, a drop of ethanol was added onto the tape. Thanks to the porous structure of the removable-type Scotch tape, the liquid can penetrate to the back side of the tape, where it selectively dissolves the glue of the tape without affecting the cyanoacrylate glue [Fig. 1(iv)]. Thus, the tape can be removed [Fig. 1(v)], leaving the V$_2$O$_3$ film on the piezoelectric disk [Fig. 1(vi)].

C. Electrical and mechanical properties measurement

$V_p$ dependence of $R_{V_2O_3}$ ($V_{V_2O_3}-V_p$) in the stacked samples was measured in air at RT. For the four-probe resistance measurement, a constant current was provided by a dc power source (Yokogawa, 7651) and the voltage on the film was recorded by a data logger (Graphitec, GL820). Sinusoidal bias was generated by a function/arbitrary waveform generator (Agilent, 33250A) and provided to the piezoelectric disk after 200-times amplified by a high voltage power amplifier (TREK, PA05039) to achieve the amplitude of 200 V at maximum. The current for resistance measurement was 50 μA ($V_{V_2O_3}$) and 1 mA (TiN). The frequency of $V_p$ was 0.1 Hz. In the case of memory effect measurement, the bias was provided to the disk by a dc high-voltage source (Keithley, 2410).

The piezoelectric coefficient $d_{33}$ of the element (of the same product number but a different chip from samples in the main experiments) was measured as a function of bias by using a laser Doppler vibrometer (Polytec, OFV-552 and OFV-3001). A small wave (of an amplitude of 10 V and a frequency of 1 kHz) was superposed over a large wave (of 250 V and 0.1 Hz), and then the response was collected through a lock-in amplifier. Out-of-plane strain as a function of $V_p$ was obtained by multiplying $d_{33}$ by $V_p$. The in-plane strain of the piezoelectric element was measured with a strain gauge (Tokyo Measuring Instruments Lab., CFLA-1-350-17) pasted on it with cyanoacrylate glue. Each resistance value of the gauge was then monotonically as $V_p$ increases, indicating the strain-induced modification of the electric property of the film. At a certain $V_p$ value, the shape of $R_{V_2O_3}$-$V_p$ curves transforms from monotonous to butterfly-type, which contains a sudden drop of the resistance during the increase of bias. The transformation from monotonous path could explain the coexistence of the component of low resistivity and that of low $c/a$ found in the RSM. In a region of $V_p$ value $\leq$ 90 V (corresponding to the electric field $\leq$ 4.5 kV/cm), $R_{V_2O_3}$ increases monotonically as $V_p$ increases, indicating the strain-induced modification of the electric property of the film. At a certain $V_p$ value, the shape of $R_{V_2O_3}$-$V_p$ curves transforms from monotonous to butterfly-type, which contains a sudden drop of the resistance during the increase of bias. The transformation from monotonous

III. RESULTS AND DISCUSSION

XRD analysis of the obtained V$_2$O$_3$ films on the mica substrates revealed that the films were out-of-plane oriented along its $c$-axis [Fig. 2(a)] and in-plane oriented in sixfold symmetry [Fig. 2(b)], suggesting the epitaxial growth of the films. The $c$-axis lattice parameter of a V$_2$O$_3$ layer was found from the $2θ$-ω profile to be 13.97 Å, indicating slight out-of-plane compressive strain. RSM around V$_2$O$_3$ (1 0 10) reflections from a V$_2$O$_3$/muscovite mica sample (a) $2θ$-ω scan profile (b) $ω$-scan profiles around the mica (102) peak (top) and the V$_2$O$_3$ (1 0 10) peak (bottom). (c) A RSM image around the mica (108) and the V$_2$O$_3$ (1 0 10) reflections. Two white lines represent c/a ratios of 2.79 and 2.815. Triangle and square symbols, corresponding to (a, c) of (5.1 Å, 13.9 Å) and (4.9 Å, 14.9 Å), respectively, represent centers of two typical components.

Figure 3(a) shows the results of $R_{V_2O_3}$-$V_p$ properties in a ~50 nm-thick V$_2$O$_3$ film, where $V_p$ was swept sinusoidally with various amplitudes ($V_p$ value) from 50 to 200 V. The resistance value at zero bias ($R_00$) at a current of 200 μA, which corresponds to a resistivity of the order of $10^{-4}$ Ω cm, suggests the existence of a metallic phase of the V$_2$O$_3$ film at RT. The formation of a filament-like conductive

FIG. 2. XRD results from a V$_2$O$_3$/muscovite mica sample. (a) $2θ$-ω profile. (b) $ω$-scan profiles around the mica (102) peak (top) and the V$_2$O$_3$ (1 0 10) peak (bottom). (c) A RSM image around the mica (108) and the V$_2$O$_3$ (1 0 10) reflections. Two white lines represent c/a ratios of 2.79 and 2.815. Triangle and square symbols, corresponding to (a, c) of (5.1 Å, 13.9 Å) and (4.9 Å, 14.9 Å), respectively, represent centers of two typical components.
to butterfly-type occurred gradually between 90 and 100 V of amplitude [see inset of Fig. 3(a)]. With a $V_p$ amp of 200 V, the maximum resistance and the minimum resistance during the cycling (276.8 and 157.0 $\Omega$, respectively) give the peak-to-peak resistance change ($\Delta R$) of 119.8 $\Omega$, reaching 60% of $R_0$ (199.0 $\Omega$). Naturally, when the $R_{V_2O_3} - V_p$ curves are of butterfly-type, the peak of resistance appears twice in a cycle of $V_p$, suggesting a possibility to utilize the present system as a frequency doubler that can be switched on/off by the voltage (Fig. 4). We performed a control experiment on another sample with the same structure but with a $\sim$100-nm-thick TiN$_x$ layer instead of V$_2$O$_3$. The result is shown in Fig. 3(b), with the monotonous or the butterfly-type curves quite similar to those in the V$_2$O$_3$ sample, suggesting a common driving force for the resistance change in both V$_2$O$_3$ and TiN$_x$. Nevertheless, only a feeble resistance change ratio $\Delta R/R_0$ of 0.7% was observed on the TiN$_x$ layer. The hundred times-higher relative variation of resistance in V$_2$O$_3$ indicates an anomalously high strain dependence of resistivity.

The observed $R_{V_2O_3} - V_p$ behaviors, the monotonous increase with a hysteresis for small $V_p$ amp and the butterfly-type curves for large $V_p$ amp, are similar to the usual minor and major loop deformation curves of piezoelectric materials. Figures 5(a) and 5(b) show out-of-plane strain ($\epsilon_{\text{out}}$) and in-plane strain ($\epsilon_{\text{in}}$), respectively, of the piezoelectric element as functions of $V_p$. The butterfly piezoelectric cycle is observed when the electric field is large enough to induce the polarization reversal. A smaller $\epsilon_{\text{out}}$ than the expected one for pristine PZT (0.25% p-p in present result against 0.4% p-p in pristine one)$^{21,22}$ is probably due to restriction by the bottom electrode plate. As the piezoelectric disk expands in the out-of-plane direction, there is a correlated in-plane contraction, i.e., the piezoelectric disk exerts an in-plane compressive strain on the V$_2$O$_3$ film, which in turn results in the elongation of the c-axis and the shrinkage of the a-axis and thus an increase of the V$_2$O$_3$ c/a ratio. Conversely, the out-of-plane deformation of the piezo disk vanishes at the coercive field, as well as the in-plane compressive strain exerted on V$_2$O$_3$, leading to a decrease of the V$_2$O$_3$ c/a ratio. This strongly suggests that the change of $R_{V_2O_3}$ is induced by the deformation of the piezoelectric disk, as the insulating (metallic) phase of V$_2$O$_3$ is accompanied by a low (high) c/a ratio.

To evaluate the out-of-plane piezo-driven strain of the mica layer, we performed XRD 2$\theta$–$\omega$ scans applying various $V_p$. $V_p$ of $-200$ V was applied prior to the measurement, followed by the measurement with $V_p$ changed as $0 \rightarrow +100 \rightarrow 0 \rightarrow -200$ V, expecting negative poling throughout the measurement. We observed the apparent shift of the mica (005) diffraction peak,
depending on the history of \( V_p \) [Fig. 6(a)]. As shown in Fig. 6(b), \( \varepsilon_{\text{out}} \) of the mica layer displays a normal tendency, shrinking under a positive bias (+100 V) and retaining a part of deformation (0 V) compared to the initial zero-bias state. Nevertheless, \( \varepsilon_{\text{out}} \) in the mica layer at +100 V \((-4.5 \times 10^{-5}\)\) was as small as one-tenth of \( \varepsilon_{\text{in}} \) in the piezoelectric layer \( [4 \times 10^{-4}; \text{Fig. 5(b)}] \). This suggests that the transfer of the piezoelectric base in-plane deformation toward the mica layer is incomplete, probably due to some elastic deformation of the glue in-between. We attempted to estimate the deformation of the glue in-between. We attempted to estimate the gauge factor (\( \gamma \)) of the V\(_2\)O\(_3\) film by using the above results, assuming that \( \varepsilon_{\text{in}} \) is identical between the mica layer and the V\(_2\)O\(_3\) film deposited on it. Under 2d isotropic stress applied in-plane, \( \varepsilon_{\text{in}} \) and \( \varepsilon_{\text{out}} \) are related as \( \varepsilon_{\text{in}} = (-1/2) \varepsilon_{\text{out}} \), where \( y \) is Poisson’s ratio, 0.25 for mica.\(^{25}\) \( \Delta R / R_0 \) of \( \sim 30\% \) [Fig. 3(a)] and \( \varepsilon_{\text{out}} \) (mica) of \( \sim 4.5 \times 10^{-5} \) [Fig. 6(b)] for \( 0 \leq V_p \leq +100 \) V give a \( \gamma \), defined as \( \Delta R / R_0 / \varepsilon_{\text{in}} \) of the V\(_2\)O\(_3\) layer of \( 3.3 \times 10^3 \). This value is outstanding compared to \( y \) of general metal thin films in a range of \( 10^0 \) to \( 10^{-1}\).\(^{23,24}\) The only explanation for the huge \( \gamma \) of the V\(_2\)O\(_3\) layer should be the piezo-actuated evolution of \( c/a \) ratios, which drove the material towards insulating phase, even though the initial \( c/a \) ratios have been scattered in a wide range. The present mechanism is expected to offer even more significant resistivity change, if the in-plane deformation of a pristine piezoelectric base could be 100% transferred to the V\(_2\)O\(_3\) layer (in which case \( \varepsilon_{\text{in}} \) of V\(_2\)O\(_3\) would be about 15 times larger than the present experiment). Further study should be focused on improving the strength of displacement in the piezoelectric layer and the stress transfer efficiency between piezoelectric and V\(_2\)O\(_3\) layers.

Finally, we mention the memory effect of the present sample. As one can see in the hysteretic minor loops in Fig. 3(a), \( R_{V_2O_3} \) can take different values at zero bias (\( V_p = 0 \)), depending on the history of \( V_p \). Figure 7(a) shows \( V_p \) and \( R_{V_2O_3} \) as the functions of time, in which \( V_p \) was manually controlled. We find that \( R_{V_2O_3} \) at zero bias (which we define as "memory resistance") retained at various values after various \( V_p \) ("set voltage"), suggesting its function as a multi-level resistive random access memory (ReRAM) or a memristor. Retention of the memory resistance for a long period as 7000 s was also confirmed [Fig. 7(a)]. Figure 7(b) shows the relationship between the set voltage and the memory resistance, showing that the memory resistance is a monotonous function of the set voltage as far as the piezoelectric layer retains the negative poling. The memory resistance in Fig. 7(b) ranged from 210.0 to 235.2 \( \Omega \), i.e., it varied for 12% with respect to its minimum value. The origin of this feeble memory effect is most likely, the hysteresis in deformation of the piezoelectric disk. On the other hand, the PI–PM phase transition is known to be of the first order, and thus the evolution of the resistance according to the hydrostatic pressure contains a hysteresis region.\(^{25}\) Therefore, one can expect a strain-induced non-volatile resistance switching between PM and PI phases (=a memory effect) on a V\(_2\)O\(_3\)-based material with a huge resistance change of three orders of magnitude.

**Fig. 6.** (a) \( 2\theta-\omega \) profiles around the mica (005) reflection in a V\(_2\)O\(_3\) film/thin mica layer/piezoelectric element stacked sample with application of \( V_p \) as \( 0 \rightarrow +100 \rightarrow 0 \rightarrow -200 \) V. The piezoelectric layer was negatively poled prior to the measurement. Intensity is normalized. Triangles indicate the center of peaks deduced from fitting with a pseudo-Voigt function. (b) Evolution of out-of-plane strain, calculated from the XRD peak position in (a), of the mica layer along the change of \( V_p \).
The piezo-actuated evolution of the mica layer, detected by a biased XRD technique, allowed one to roughly estimate a huge gauge factor of this V2O3 film.\(^2\) Advantageously, the memory effect based on the PM–P1 phase transition in V2O3 is expected to work at the whole temperature region of this boundary, from 180 K to 390 K,\(^2\) well covering the required operating temperatures of both commercial and industrial devices.

### IV. CONCLUSIONS

We grew epitaxial (0001)-oriented V2O3 thin films by a PLD technique on muscovite mica substrates and then transferred a peeled-off V2O3 film onto a commercial ceramic PZT-based piezoelectric element. The \(R_{V2O3,0} - V_p\) property on this sample showed butterfly-type curves that reflected the deformation of the piezoelectric disk. The 60% peak-to-peak change of \(R_{V2O3}\), and the \(c/a\) ratio of the mica layer, detected by a biased XRD technique, allowed one to roughly estimate a huge gauge factor of this V2O3 film to be about \(3 \times 10^3\), ascribed to the piezo-actuated evolution of the piezoelectric disk was observed in the \(R_{V2O3,0} - V_p\) properties. The bilayer of piezoresistive and piezoelectric materials offers a possibility of piezoelectrically-driven switching and memory devices with simple structures.

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![FIG. 7](image-url)