Orientation-dependent strain effects on the metal-insulator transitions in (V_{0.99}Cr_{0.01})₂O₃/Al₂O₃ thin films

G. D. Zhang,^{1,2} L. Hu¹,^{2,*} M. Zhu,² R. H. Wei¹,² R. R. Zhang,³ W. H. Song,² X. B. Zhu,^{2,†} and Y. P. Sun^{2,3,4,‡}

¹Institutes of Physical Science and Information Technology, Anhui University, Hefei 230601, China

²Key Laboratory of Materials Physics, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, China

³High Magnetic Field Laboratory, HFIPS, Chinese Academy of Sciences, Hefei 230031, China

⁴Collaborative Innovation Center of Advanced Microstructures, Nanjing 210093, China

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 V_2O_3 is an archetypical Mott material which exhibits Cr doping and/or temperature-induced paramagnetic metal to paramagnetic insulator/antiferromagnetic insulator (PM-PI/AFI) transitions. However, the strain effects on the metal-insulator transition (MIT) in thin films and the mechanisms behind them are not yet fully understood. In this study, we investigate the strain effects on the MIT in $(V_{0.99}Cr_{0.01})_2O_3$ (VC1) thin films growing on c-plane (001), r-plane (012), and a-plane (110) Al₂O₃ substrates. The strains can be tuned in a wide range over 1% in VC1/Al₂O₃ thin films by changing the substrate temperature. Remarkably, the influence of strain on the MIT differs dramatically from (001)-oriented and non-(001)-oriented VC1/Al₂O₃ thin films. The PM-PI transition can be effectively modulated by strain tuning in the (001) VC1/Al₂O₃ thin films accompanied by gradual transformation from the PM/PI phase into the AFI phase upon cooling. On the contrary, both (012) and (110) VC1/Al₂O₃ thin films exhibit sharp PM-AFI transitions irrespective of the strain states. The orientation-dependent strain effects on the MIT in the VC1/Al₂O₃ thin films could be explained by the trigonal distortion within electronic correlation scenario. The trigonal distortion of $V(Cr)O_6$ octahedra along (within) the c axis (ab plane) in the (001) VC1/Al₂O₃ thin films can be directly modulated by the strains. However, the trigonal distortion in the (012) and (110) VC1/Al₂O₃ thin films would hardly be affected due to the deviation of the film orientation from the c axis. This explanation is experimentally confirmed by Raman spectra as a sensitive probe of the trigonal distortion in VC1 thin films. These results highlight the importance of trigonal distortion to understand the MIT in the V₂O₃ compound.

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I. INTRODUCTION

The metal-insulator transition (MIT) has attracted widespread attention in many condensed-matter systems because external stimuli can trigger the transition from an insulating to metallic phase or vice versa, which renders these materials to have particular interest for many device applications [1,2]. The V₂O₃ compound is an archetypical correlated oxide which exhibits different types of MITs driven by temperature, chemical doping, and hydrostatic pressure [3-5]. In ambient conditions, V_2O_3 is a paramagnetic metal (PM) and is stable in the corundum structure. Upon cooling, the PM phase evolves into an antiferromagnetic insulating (AFI) phase ($T_C \sim 160$ K) with a sudden jump in resistivity by seven orders of magnitude accompanied by a corundumto-monoclinic structural phase transition (SPT) [3,6,7]. Ti doping and/or application of hydrostatic pressure can gradually destabilize the low-temperature AFI phase and, consequently, lower T_C [4,8]. Alternately, Cr doping in $(V_{1-x}Cr_x)_2O_3$ gives rise to different features [3,9,10]. For x > 0.018, the PM phase in V₂O₃ disappears and changes into a paramagnetic insulating (PI) phase via the Cr doping with an unchanged corundum structure, which has generally served as a textbook version of the Mott-Hubbard transition [11,12]. By contrast, the Cr doping stabilizes the low-temperature AFI phase, and a PI-AFI transition takes place upon cooling [9]. For 0.005 < x < 0.018, the high-temperature PI phase in $(V_{1-x}Cr_x)_2O_3$ would evolve into the PM phase by slightly decreasing the temperature and would eventually transform into the AFI phase with further cooling [10]. The application of hydrostatic pressure on $(V_{1-x}Cr_x)_2O_3$ can also destabilize the PI/AFI phases and drive them back into the PM phase [3,9]. In this regard, it is usually recognized that the Cr doping plays the same role as "negative pressure" during the PM-PI transition. However, high-resolution x-ray absorption spectroscopy at the V pre-K edge has revealed that the PM phase reached under pressure differs from that obtained by changing doping or temperature [13,14].

Epitaxial strains in the $(V_{1-x}Cr_x)_2O_3$ thin films represent another powerful and versatile tool to tune the MIT [15–30]. Strains with different signs, magnitudes, and types can be readily introduced in the $(V_{1-x}Cr_x)_2O_3$ thin film by virtue of the mismatch of the lattice parameters and/or thermal expansion coefficients (TECs) between $(V_{1-x}Cr_x)_2O_3$ and the substrates. For instance, epitaxial growth of V_2O_3 thin films on *c*-plane (001) Al₂O₃ and (0001) LiTaO₃ substrates results in compressive and tensile strains due to different

^{*}huling@issp.ac.cn

[†]xbzhu@issp.ac.cn

^{*}ypsun@issp.ac.cn

lattice mismatches, respectively [16]. The PM phase is stabilized down to 2 K in the film on Al₂O₃, whereas T_C is increased by 20 K from the bulk value in the film on LiTaO₃. The strain tuning over a wide range in the V_2O_3 and $(V_{0.0985}Cr_{0.015})_2O_3$ thin films grown on (001) Al₂O₃ was realized by inserting and varying the Fe content in the buffer layers of $(Cr_{1-v}Fe_v)_2O_3/Cr_2O_3$ [29]. The phase transition between the PM and PI phases can be induced by strain engineering in both the pure and Cr-doped V₂O₃ films. Tensile strains have also been observed in the (001) V_2O_3/Al_2O_3 thin films, which go beyond the lattice mismatch and arise from the TEC mismatch in the *a*-axis direction, which is larger in V_2O_3 than in Al_2O_3 [15,19,23,29–32]. Interestingly, the PI phase and consequent PM-PI transition can be induced by the tensile strain in the (001) V_2O_3/Al_2O_3 thin films. Besides isotropic strain, anisotropic strain can be produced in the V_2O_3 thin films when they are growing on non-(001)oriented Al₂O₃ substrates [19,20,23,26]. However, reports of the impact of anisotropic strain on the MIT in these thin films are varied. Allimi et al. demonstrated that V₂O₃ thin films grown on *a*-plane (110) Al₂O₃ shows an insulator-toinsulator transition at T = 186 K, in striking contrast to the films grown on (001) Al₂O₃ with a MIT at T = 180 K, which are attributed to different levels of strain and commensurate changes in the film morphology [19,20]. Sakai et al. reported that V_2O_3 thin films grown on *r*-plane (012) Al₂O₃ exhibit sharper PM-AFI transitions than films on (001) Al₂O₃, which is explained by the viewpoint of intrinsic a- and caxis evolution through the MIT/SPT [23]. Kalcheim et al. demonstrated that V_2O_3 thin films grown on (110), (100), and (012) Al₂O₃ exhibit very sharp PM-AFI transitions, reminiscent of the MIT in single crystals, even though the produced anisotropic strains are comparable to and/or exceed the monoclinic distortion [26,28]. Theoretically, Wickramaratne et al. used first-principles calculations to identify that T_C is sensitive to changes in the V-V bond lengths induced by equibiaxial and uniaxial compressive and tensile strain [25].

As mentioned above, the MIT in the V₂O₃ compounds get entangled with the SPT and magnetic transition. From a microscopic point of view, it is fundamental to understand how the different degrees of freedom like the charge, lattice, orbital, and spin interact and which one is predominant in determining the MIT. The crystal lattice can be readily accessed by the strain in thin film, which facilitates the understanding of multiple interactions as well as the MIT. The strains in V_2O_3 thin films are usually quantified to be equivalent to positive or negative hydrostatic pressure by calculating the change in the lattice parameter or volume and are discussed within the V_2O_3 bulk phase diagram [15,17–22]. However, there is an essential difference between the hydrostatic pressure in bulk materials and strain in thin films from the viewpoint of the crystal structure since the hydrostatic pressure is isotropically compressive, whereas the epitaxial strain imparted by an underlying substrate constrains the inplane lattice parameters and the out-of-plane lattice parameter responses to the in-plane epitaxial strain controlled by the Poisson effect [25]. Therefore, the strain effects on the MIT in V₂O₃ thin films are not yet fully understood. In addition, previous studies have also indicated that Cr-doping-induced local structural distortion/disorder accounts for the PM-PI transition in $(V_{1-x}Cr_x)_2O_3$ [33–35]. $(V_{1-x}Cr_x)_2O_3$ (0.005 < x < 0.018) thin films provide an ideal platform to investigate the strain effects on the PM-PI/AFI transition in the presence of Cr-doping-induced local structural distortion/disorder and to distinguish the predominant factor in controlling the MIT [10].

In this study, we investigate the strain effects on the MIT in $(V_{0.99}Cr_{0.01})_2O_3$ (VC1) thin films grown on (001), (012), and (110) Al_2O_3 substrates. The strain tuning in a wide range over 1% can be achieved in VC1/Al₂O₃ thin films by changing the substrate temperature T_S during film growth. It is found that the strain effects on the MIT of VC1/Al₂O₃ thin films strongly depend on the substrate orientations. A PM-PI transition with a large resistivity change of \sim 37 500% at 300 K can been effectively induced by strain engineering in the (001) VC1/Al₂O₃ thin films. The PI/PM phase gradually transforms into the AFI phase upon cooling. On the contrary, the (012) and (110) VC1/Al₂O₃ thin films exhibit sharp PM-AFI transitions irrespective of the strain states. The orientation-dependent strain effects on the MIT in VC1/Al₂O₃ thin films can be explained by the trigonal distortion within the electronic correlation scenario. The strains in the (001) VC1/Al₂O₃ thin films would directly modulate the trigonal distortion of VO_6 octahedra along (within) the c axis (ab plane). However, the trigonal distortion in the (012) and (110) VC1/Al₂O₃ thin films would hardly be affected due to the deviation of the film's orientation from the c axis. This explanation is experimentally verified by Raman spectra as a sensitive probe of the trigonal distortion in VC1 thin films. These results clearly indicate the importance of trigonal distortion to understand the MIT in the V₂O₃ compound.

II. EXPERIMENT DETAILS

VC1 thin films were deposited on *c*-plane (001), *r*-plane (012), and a-plane (110) Al₂O₃ substrates by pulsed laser deposition. A VC1 ceramic target was ablated by a KrF excimer laser with an energy density of 2 J/cm² and a repetition rate of 5 Hz. The distance between the target and the substrate was 5 cm. During growth, T_S was controlled in the range of 673–873 K for the (001) and (110) $VC1/Al_2O_3$ thin films and 773–973 K for the (012) VC1/Al₂O₃ thin films, respectively. The films were grown and cooled down to room temperature in a high vacuum of 10^{-3} Pa. The thicknesses of the films were maintained at \sim 120 nm. The structural properties of the VC1 thin films were characterized by x-ray diffraction (XRD) using Cu $K\alpha$ radiation at room temperature. Electrical transport properties were measured on a physics property measurement system using the standard four-probe method. The Raman spectra were measured by a Horiba Jobin YvonT64000 Micro-Raman instrument with a torus 532 laser $(\lambda = 532 \text{ nm})$ as an excitation source in the backscattering geometry. A back-illuminated charge-coupled device cooled by liquid nitrogen was used to detect the scattered light.

III. RESULTS AND DISCUSSION

Figure 1(a) schematically shows the corundum structure of the hexagonal lattice shared by many metal oxides with the



FIG. 1. (a) Schematic diagram of the hexagonal lattice and representative crystal planes. (b) Lattice mismatches between VC1 (PM phase) and Al_2O_3 substrates with different orientations.

formula A_2O_3 and representative crystal planes. VC1 exhibits a temperature-induced PI \rightarrow PM transition upon cooling at around 300 K, in which both the PI and PM phases have the corundum structure but with different lattice parameters such that *a* decreases and *c* increases across the PI \rightarrow PM transition [10,31,32]. The bulk material of VC1 (Al₂O₃) at room temperature (PM phase) has lattice parameters *a* = 4.954 (4.758) Å and *c* = 14.003 (12.99) Å. As a result, isotropic and anisotropic biaxial strain due to lattice mismatch can be produced in VC1 thin films when they are grown on Al₂O₃ substrates with different orientations [as shown in Fig. 1(b)].

Using the methodology of lattice mismatch, the strains in thin films can be usually be tuned by choosing suitable substrates with different lattice parameters for epitaxial growth [36]. However, this strategy for strain tuning in V_2O_3 thin films is hindered by the limited substrates for epitaxial growth [17-23]. Furthermore, the strains in the V₂O₃ thin films derived from the lattice mismatch can persist only in very thin layers because the elastic strain energy would accumulate and become energetically unfavorable with increasing film thickness. As a result, the epitaxial strain would gradually relax and release the elastic strain energy when the film thickness is larger than the critical thickness that leads to pseudomorphic growth [21,22,37]. Consequently, strain tuning using the film thickness would additionally introduce enhanced surface and interface contributions in ultrathin films and complicate the understanding of the MIT [37–39]. In addition to the film thickness, T_S is another important parameter during film growth and subsequent cooling processes [30,40-44]. A higher T_S could promote strain relaxation because there would be more thermal energy to overcome the kinetic barrier [40-42]. After deposition, the thin films follow the TEC of the substrates in the cooling process from T_S to room temperatures, which affects the strain states [43,44]. The film thickness and T_S can be viewed as utilizing thermodynamic and kinetic factors to modulate strain relaxation during film growth, respectively.

Figure 2 shows the XRD pattern for the (001) VC1/Al₂O₃ thin films with different T_S . VC1 thin films are highly oriented along the (00*l*) direction without secondary phases. The azimuthal ϕ scans along (104) reflections reveal threefold symmetry for both films and substrates, which is consistent with the corundum structure and indicates epitaxial growth of VC1 thin films (see the Supplemental Material, Fig. S1 [45]).



FIG. 2. XRD patterns of the (001) VC1/Al₂O₃ thin films with different T_s around (a) (00*l*) and (b) (104) diffraction peaks. The inset shows the rocking curve around the (006) peak for the VC1 thin films.

The high quality of VC1 thin films is also confirmed by the rocking curve measurements (ω scan) with a full width at half maximum of 0.04° – 0.11° [as shown in the inset of Fig. 2(a)]. The out-of-plane lattice parameters *c* of VC1 thin films can be extracted from the (00*l*) diffraction peaks using the Bragg equation. Afterwards, the in-plane lattice parameters *a* are determined by the (104) diffraction peaks [as shown in Fig. 2(b)].

Given the in-plane lattice mismatch of 4.1%, it is expected that the (001) VC1/Al₂O₃ thin films will experience in-plane compressive strain without considering other strain contributions. Figure 3 depicts the change in *a* and *c* of VC1 thin films with T_S . The value of *a* (*c*) monotonously increases (decreases) with the increase of T_S , resulting in the evolution of in-plane strain states from compressive to tensile by increasing T_S , which goes beyond the lattice mismatch. It is well known that VC1 exhibits a PI phase with the corundum structure at high temperature, whose TEC along the *a* axis $(8.8 \times 10^{-6} \text{ K}^{-1})$ is slightly larger than that of Al₂O₃



FIG. 3. The change in *a* and *c* values of (001) VC1/Al₂O₃ thin films with T_S . The inset shows the relationship between ϵ_{zz} and ϵ_{xx} , which gives rise to a Poisson ratio v of ~0.36.



FIG. 4. Temperature-dependent resistivity of the (001) VC1/ Al₂O₃ thin films under different strain states. The inset shows the room-temperature resistivity as a function of $\epsilon_{[001]}$.

 $(7.3 \times 10^{-6} \text{ K}^{-1})$ [3,46,47]. In this case, the strain that evolves during the growth and subsequent cooling processes would dominantly arise from the lattice mismatch between VC1 and Al₂O₃, whereas the TEC mismatch plays a minor role in the cooling process [43,44]. It is worth noting that T_S can be utilized as a clean and convenient parameter to tune the strain states in VC1 thin films. The underlying origin is the fact that T_{S} modulates the degree of strain relaxation during film growth since T_S provides the thermal energy for kinetic strain relaxation [40-42]. The degree of strain relaxation directly determines the strain state after cooling to room temperature (see the Supplemental Material, Fig. S2). At room temperature, the a value of the VC1 bulk is referred to that in the PM phase (a = 4.954 Å). Growth of VC1 thin films on Al₂O₃ substrates occurs at T_S well above the PM-PI transition, during which the films adopt the high-temperature corundum structure. After deposition, VC1 thin films are cooled from T_S to room temperature by following the TEC of Al₂O₃ substrates. As a result, the *a* values of $VC1/Al_2O_3$ thin films can exceed the bulk value of the PM phase at high T_S with enhanced strain relaxation. Furthermore, the in-plane compressive (tensile) strain usually accompanies out-of-plane tensile (compressive) strain, which is described by the Poisson effect. The ratio of the out-of-plane strain ϵ_{zz} to the in-plane strain ϵ_{xx} and ϵ_{yy} is denoted as the Poisson ratio, $\upsilon = -\epsilon_{zz}/(\epsilon_{xx} + \epsilon_{yy})$. As shown in the inset of Fig. 3, the value of v is fitted to be ~ 0.36 , which is close to the theoretical calculation result [25].

Figure 4 shows temperature-dependent resistivity of the (001) VC1/Al₂O₃ thin films. It is found that the strains can dramatically alter the electrical properties as well as the MIT. For a VC1 thin film with $\epsilon_{[001]} = 1.02\%$, the PM-AFI transition is strongly suppressed with the increase of resistivity by a factor of ~1.5 across the transition (see the Supplemental Material, Fig. S3). The PM-AFI transition gradually recovers with decreasing $\epsilon_{[001]}$ to 0.06% and -0.28%, accompanied by the increase in resistivity of the PM phase by several times. The PM phase evolves into the PI phase with further



FIG. 5. Temperature-dependent resistivity of the (110) VC1/ Al_2O_3 thin films (dashed and dotted lines) and (012) VC1/ Al_2O_3 thin films (solid lines) under different strain states.

decreasing $\epsilon_{[001]}$ to -0.54% and -0.69%, while the lowtemperature AFI phase remains with the increase in resistivity by several orders of magnitude. As shown in the inset of Fig. 4, the PM-PI transition can clearly be seen with a resistivity change at 300 K up to \sim 37 500%. In addition, the temperature-induced PM-PI transition in the VC1 single crystal is absent in the thin films, which would result from the clamp effect of substrates constraining the lattice variation during heating and cooling that is robustly coupled with the transition [23,29]. It is also evidenced that the PM-PI transition in $(V_{1-x}Cr_x)_2O_3$ would dominantly arise from the variation of the crystal lattice rather than the simultaneous introduction of local structural distortion or disorder around Cr dopants. As discussed below, the PM-PI transition can be understood as an orbital-selective MIT driven by the variation of trigonal distortion [48–50].

As shown in Fig. 1, the lattice mismatches between VC1 and Al_2O_3 are isotropic in the *c*-plane and anisotropic in the *r*- and *a*-planes. Furthermore, the TECs along [001] and $\overline{111}$] of VC1 in the PI phase (Al₂O₃) are $3.5(8.1) \times 10^{-6} \text{ K}^{-1}$ and 5.0 (7.9) \times 10⁻⁶ K⁻¹, respectively [3,46,47]. In this case, the VC1 thin films will experience anisotropic strain due to anisotropic lattice mismatch and/or TEC mismatch when growing on (012) and (110) Al₂O₃ substrates (see the Supplemental Material, Fig. S4). Similarly, T_S can also be used to tune the strain states (see the Supplemental Material, Fig. S5). Despite this, the anisotropic strains have a minor impact on the MIT of (012) and (110) VC1/Al₂O₃ thin films, which is shown below. Accordingly, the out-of-plane strains due to the Poisson effect are used to quantify the strain states for simplicity. Figure 5 depicts the temperature-dependent resistivity of the (012) and (110) VC1/Al₂O₃ thin films under different strain states. The most prominent feature is that both (012) and (110) VC1/Al₂O₃ thin films exhibit sharp PM-AFI transitions with a resistivity change of more than 10^5 irrespective of the strain states. This result is distinct from that of the (001)VC1/Al₂O₃ thin films, which can provide an essential clue



FIG. 6. Schematic diagrams of (a) (001), (012), and (110) planes and (d) trigonal distortion in the VC1.

to uncover the mechanism underlying the PM-AFI transition. First, the selective sensitivity of the PM-AFI transition to the substrate orientations as well as strain states in VC1 thin films clearly indicates that the structural factor for controlling the transition will act within the *ab* plane and along the *c* axis as in the case of the (001) VC1/Al₂O₃ thin films, whereas it weakens substantially when deviating from the *ab* plane (*c* axis) as in the case of the (012) and (110) VC1/Al₂O₃ thin films. Second, the anisotropic strains in the (012) and (110) VC1/Al₂O₃ thin films cannot suppress the PM-AFI transition and merely lead to the variation of T_C within ~40 K, which is consistent with the result for V₂O₃ thin films due to the strain-modulated energy scales compared to the transition [26].

In this regard, it is valuable to recall the corundum structure of VC1, which builds from the $V(Cr)O_6$ octahedra by edge sharing within the *ab* plane and face sharing along the *c* axis (as shown in Fig. 6). The trigonal distortion of the $V(Cr)O_6$ octahedra denoted as the compression (elongation) or elongation (compression) within the *ab* plane (along the threefold symmetry c axis) gives rise to the deviation from ideal cubic symmetry. The introduction of a trigonal crystal field D_{trg} by the trigonal distortion tends to split the t_{2g} orbital into a_{1g} and e_{o}^{π} orbitals [5]. Quantitatively, the D_{trg} value defines the energy scale of the a_{1g} orbital with respect to the e_g^{π} orbital, and it is higher for $D_{trg} > 0$ and lower for $D_{trg} < 0$ [48]. As a result, the a_{1g} orbital occupation will decrease (increase) with the increase (decrease) of the D_{trg} value, acting as an "external field" in the t_{2g} orbital sector [49,50]. A small trigonal distortion ($D_{\rm trg} \approx 0.3 \, {\rm eV}$) occurs spontaneously in the PM phase of the V_2O_3 bulk [12,13]. The trigonal distortion, or, equivalently, the D_{trg} value, directly correlates with the lattice parameters and is quantified by the c/a ratio [51]. The isostructural PM-PI transition triggered by the Cr doping or temperature in $(V_{1-x}Cr_x)_2O_3$ is accompanied by abrupt changes in the lattice parameters, c/a ratio, and D_{trg} value, rendering it an orbital-selective MIT [3,14,48-52]. In addition, the importance of trigonal distortion for understanding the PM-PI transition does not mean that the electronic correlation can be ignored since the PI phase and PM-PI transition fail to be reproduced without electronic correlation [11,53]

The monoclinic structure of the AFI phase is distorted from the corundum structure by tilting the vertical V-V bond direction about 1.8° from the *c* axis, accompanied by an abrupt change in the V-V bond length in the basal plane and along the c axis and broken threefold rotational symmetry [6]. The low-symmetry crystal field in the monoclinic structure would further split the e_g^{π} orbital and modify the mixture between the a_{1g} and e_{g}^{π} orbitals, lowering the a_{1g} orbital occupation compared to that in the PM and PI phases with the corundum structure [52]. As for antiferromagnetic order in the AFI phase, the closest V-V pairs along the c axis are ferromagnetically coupled, and one (two) of the three closest V-V pairs in the basal plane is (are) aligned ferromagnetically (antiferromagnetically) [54]. Theoretical study has revealed that the low a_{1g} orbital occupation in the AFI phase contributes to the next-nearest-neighbor antiferromagnetic correlation and is responsible for the antiferromagnetic order [55]. The a_{1g} orbital occupation in the AFI phase decreases (increases) with the increase (decrease) of the D_{trg} value as well [48]. In this respect, the stabilization of the AFI phase upon Cr doping in the phase diagram might be rooted in the enhanced trigonal distortion and consequently low a_{1g} orbital occupation.

In film form, the interplay between $(V_{1-x}Cr_x)_2O_3$ and Al₂O₃ substrates can offer another effective tool for modulating the trigonal distortion. It is evident that the strain effect in the (001) $(V_{1-x}Cr_x)_2O_3/Al_2O_3$ thin films coincides with the trigonal distortion and can directly modulate the trigonal distortion over a wide range, which mimics that of Cr doping and is different from that of hydrostatic pressure in bulk materials [30]. Specifically, the in-plane (out-of-plane) tensile (compressive) strain would increase D_{trg} and decrease the a_{1g} orbital occupation, giving rise to the PM-PI transition analog to Cr doping in bulk materials [3]. In contrast, the modulation of the trigonal distortion would decrease D_{trg} and increase the a_{1g} orbital occupation in the case of in-plane (outof-plane) compressive (tensile) strain [48–50]. As a result, the PM phase becomes more delocalized, which agrees well with the experimental and theoretical results [49,56]. Meanwhile, the decrease (increase) of D_{trg} (a_{1g} orbital occupation) results in the gradual suppression of the low-temperature AFI phase [55]. In contrast, the trigonal distortion is hardly affected by the strains when the films are grown on nonoriented (001) Al₂O₃ substrates since the in-plane (out-of-plane) strain direction deviates from the *ab* plane (*c* axis). In this case, the strain would play a secondary role behind the trigonal distortion in the MIT if the trigonal distortion is the predominant factor in controlling the MIT. This deduction is consistent with the fact that the (012) and (110) VC1/Al₂O₃ thin films exhibit a sharp PM-AFI transition irrespective of the variation of the strain state. Therefore, this trigonal distortion scenario can explain our results that the MIT in the (001) $VC1/Al_2O_3$ thin films can be effectively modulated by the strains, whereas the PM-AFI transitions in the (012) and (110) VC1/Al₂O₃ thin films are insensitive to the variation of strains, fairly well.

To further verify this explanation, Raman measurements were performed to experimentally detect the variations of trigonal distortion in the VC1 thin films with the strains and substrate orientations because the Raman spectra are a sensitive probe for the trigonal distortion [56–58]. The corundum structure of VC1 has the symmetry of the $R\overline{3}C$ space group and D_{3d} point group, which results in two Raman irreducible E_g and A_{1g} modes [59]. Both the E_g and A_{1g} modes could be



FIG. 7. Room-temperature Raman spectra of the (001) VC1/Al₂O₃ thin films with different $\epsilon_{[001]}$. The red and blue dotted lines denote the E_g , A_{1g}^L , and A_{1g}^H modes in the VC1 bulk in the PM and PI phases, respectively.

affected by the trigonal distortion [57]. Specifically, the E_g mode arises from the motions of oxygen along the *c* axis and V(Cr) in the basal plane. The $A_{1g}^L(A_{1g}^H)$ mode can be described as outward (inward) motion of oxygen accompanied by the out-of-phase (in-phase) motion of the V(Cr) pairs along the *c* axis (see the Supplemental Material, Fig. S5). In particular, the motion of oxygen and V(Cr) ions in the A_{1g}^L mode would be greater than that in the A_{1g}^H mode for a given vibration energy. Therefore, the A_{1g}^L mode exhibits stronger scattering intensity and is more sensitive to the trigonal distortion than the A_{1g}^H mode [57].

Figure 7 shows the room-temperature Raman spectra of (001) VC1/Al₂O₃ thin films under different strain states. It is clear that the Raman modes exhibit obvious shifts with the strains in the (001) VC1/Al₂O₃ thin films. For the VC1 thin film with $\epsilon_{[001]} = 1.02\%$, the Raman peaks at ~204, ~238, and ~504 cm⁻¹ can be assigned as the E_g , A_{1g}^L , and A_{1g}^H modes, respectively. The softening (hardening) of the E_g (A_{1g}) mode compared to the $(V_{1-x}Cr_x)_2O_3$ bulk in the PM phase results from the strain-induced modulation of the trigonal distortion and the resultant decrease (increase) of e_{a}^{π} (a_{1g}) orbital occupation [30,56]. The E_g and A_{1g} modes of the VC1 thin films in the PM phase are gradually restored to the bulk values with the decrease of $\epsilon_{[001]}$ to 0.06% and -0.28%. With further decreasing $\epsilon_{[001]}$, the VC1 thin films evolve from the PM phase into PI phase, accompanied by a notable blueshift of the A_{1g} mode due to the systematic change in elastic constants $C_{\mu\nu}$, which matches well that of $(V_{1-x}Cr_x)_2O_3$ single crystals [57,60,61]. Figure 8 depicts the room-temperature Raman spectra of the (012) and (110) VC1/Al₂O₃ thin films. It is interesting to note that the E_g and A_{1g} modes remain almost unchanged with the strain and resemble those of bulk materials in the PM phase, which correspond to the sharp PM-AFI transitions in the (012) and (110) VC1/Al₂O₃ thin films. This contrast strongly confirms that the trigonal distortion can be effectively modulated by the strains in the (001) VC1/Al₂O₃ thin films



FIG. 8. Room-temperature Raman spectra of (a) the (012) VC1/Al₂O₃ thin films and (b) (110) VC1/Al₂O₃ thin films under different strain states. The dotted lines denote the E_g , A_{1g}^L , and A_{1g}^H modes of the VC1 bulk in the PM phase.

and the strains in the (012) and (110) VC1/Al₂O₃ thin films play a negligible role in the trigonal distortion. Furthermore, these results clearly reveal the key role of trigonal distortion for understanding the MIT in $(V_{1-x}Cr_x)_2O_3$. We note that this trigonal distortion scenario is consistent with previous studies in which V₂O₃ thin films exhibit sharp PM-AFI transitions when grown on non-(001)-oriented Al₂O₃ substrates and that the PM-AFI transitions can be largely affected in the (001) V₂O₃/Al₂O₃ substrates [17,23,26–30].

IV. CONCLUSION

In conclusion, the strain effects on the MIT in the VC1/Al₂O₃ thin films were investigated. A wide range of strain tunings over 1% in (001), (012), and (110) VC1/Al₂O₃ was achieved by changing T_S . It was found that the impact of strains on the MIT of VC1/Al₂O₃ thin films strongly varies with the substrate orientations. Specifically, the PM-PI transition can be successfully induced by strain engineering in the (001) VC1/Al₂O₃ thin films with gradual evolution into the AFI phase upon cooling. In contrast, the (012) and (110) VC1/Al₂O₃ thin films exhibit sharp PM-AFI transitions that are independent of the strain states. These results can be explained by the distinct variation of trigonal distortion with the strains for different substrate orientations. In the (001) VC1/Al₂O₃ thin films, the trigonal distortion that occurs as the compression or elongation within the *ab* plane or along the c axis can be directly modulated by the strain. The trigonal

distortion in the (012) and (110) VC1/Al₂O₃ thin films is hardly affected due to the deviation of the film orientation from the *c* axis. The strain- and orientation-dependent trigonal distortion is further confirmed by the Raman spectra. The orientation-dependent strain effects on the MIT highlight the importance of trigonal distortion to understand the MIT in the V₂O₃ compound.

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