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Thickness dependence of the electronic properties in V_2O_3 thin films

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High quality vanadium sesquioxide V_2O_3 films (170–1100 Å) were grown using the pulsed laser deposition technique on (0001)-oriented sapphire substrates, and the effects of film thickness on the lattice strain and electronic properties were examined. X-ray diffraction indicates that there is an in-plane compressive lattice parameter (a), close to −3.5% with respect to the substrate and an out-of-plane tensile lattice parameter (c). The thin film samples display metallic character between 2 and 300 K, and no metal-to-insulator transition is observed. At low temperature, the V_2O_3 films behave as a strongly correlated metal, and the resistivity (ρ) follows the equation $\rho=\rho_0+AT^2$, where A is the transport coefficient in a Fermi liquid. Typical values of A have been calculated to be 0.14 $\mu\Omega$ cm K^{-2}, which is in agreement with the coefficient reported for V_2O_3 single crystals under high pressure. Moreover, a strong temperature dependence of the Hall resistance confirms the electronic correlations of these V_2O_3 thin film samples. *© 2007 American Institute of Physics.* [DOI: 10.1063/1.2824465]

First discovered by Foex in 1946,[1] vanadium sesquioxide V_2O_3 has received a great deal of attention, both by theoreticians as well as experimentalists. Indeed, it has been recognized previously that a pressure-induced metal-to-insulator transition (MIT) for V_2O_3 is driven by electron correlation,[2] establishing V_2O_3 as a prototypical strongly correlated electron system. As a result, numerous studies on the effect of composition or external parameters on the transport properties of V_2O_3 have been reported.[3–5] Particular attention has also been paid to the phase transitions of V_2O_3: in the pressure-temperature plane, two phase transitions are reported, either when applying a hydrostatic pressure or a chemical pressure [see, for example, $(V_{1-x}M_x)_2O_3$ with M=Cr, Ti, …].[3,4] For example, a system that is close to all phase boundaries is $(V_{0.985}Cr_{0.015})_2O_3$ at 200 K.[6] When the temperature is decreased, this paramagnetic metal undergoes a first order phase transition from a corundum structure with rhombohedral symmetry ($R\bar{3}c$ space group, with a=4.951 Å and c=14.003 Å) to an antiferromagnetic insulator with monoclinic structure ($I2/a$).[7] When the temperature or the Cr content is increased, a paramagnetic metal-to-paramagnetic insulator transition takes place.[6] While the former transition bears strong similarities with many usual magnetic transitions, the latter one corresponds to the famous Mott transition. Qualitatively, this Mott transition is well described by the Hubbard model: increasing the Cr content results in increasing the ratio U/W (U being the strength of the Coulomb interaction and W the bandwidth), in which case the quasiparticle residue decreases and eventually vanishes at the MIT.[8] Furthermore, when considering the optical conductivity, the optical weight at low energy is transferred to energies of order U.[9] When the system is close to the Mott point, thermal fluctuations destabilize the coherence of the Fermi liquid (FL), and an increase in temperature results into a MIT.[10–12] Several orbitals are involved at the Fermi energy and, however, a quantitative description of V_2O_3 needs to build on a more involved theory, such as the one pioneered by Held *et al.*[13]

Despite the extensive studies on polycrystalline powder and single crystal V_2O_3 samples,[14–17] there have been few reports on thin film samples. Schuler *et al.* addressed the influence of the synthesis conditions upon the classical metal-to-insulator transition and the growth modes of the films.[18] The relation between the transition temperatures and the lattice parameters have also been reported.[19–21] There is little knowledge, however, on the thickness dependence of the properties of the V_2O_3 thin films. In addition, phase transitions can have exciting applications in emerging nanoelectronic devices such as bolometers or sensors.[22] Moreover, it is required for such applications to have V_2O_3 thin films, the properties of which are clearly mastered up to a low thickness.

In this letter, we examine a series of epitaxial V_2O_3 thin films, including their lattice parameters, roughness, and Hall resistance, in order to investigate their transport properties as a function of thickness. Samples of V_2O_3 thin films, of which the thickness ranged from 170 to 1100 Å, were grown on (0001)-oriented Al_2O_3 substrates (rhombohedral with the parameters a=4.758 Å and c=12.991 Å) from a V_2O_5 target by the pulsed laser deposition technique.[19] The substrate heater was kept at a constant temperature ranging from 600 to 650 °C. A background of argon pressure around 0.02 mbar was applied inside the chamber. At the end of the deposition, the film was cooled down to room temperature at a rate of 10 K min^{-1} under a 0.02 mbar argon pressure. The film thickness was determined, to an uncertainty below two V_2O_3 unit cells, by a mechanical stylus measuring system (Dektak ^{3}ST). The structure of the films was examined by x-ray diffraction (XRD) (with the Cu $K\alpha_1$ radiation, λ=1.540 56 Å) using a Seifert 3000P diffractometer for the out-of-plane measurements and a Philips X'Pert for the in-plane measurements. In-plane a lattice parameters were ex-

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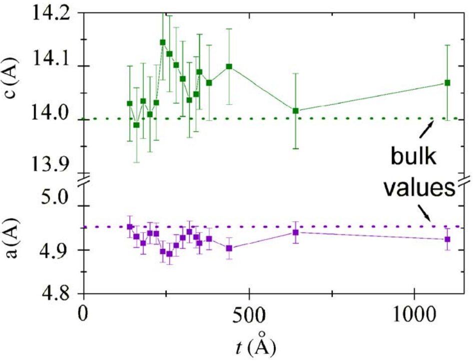

FIG. 1. (Color online) Thickness dependence of the *a* and *c* lattice parameters.

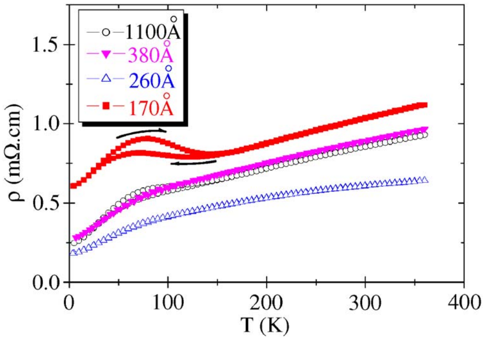

FIG. 2. (Color online) Temperature dependence of the longitudinal resistivity of several V_2O_3 thin films.

tracted from (104), (116), and (113) asymmetric reflections. The resistivities of the samples were measured in four-probe configuration using a physical property measurement system. For Hall effect measurements, a Van der Pauw configuration was used. For each temperature value, the transverse resistance is measured with an applied magnetic field (H) varying from −7 up to +7 T. The Hall resistance R_H is calculated from the transverse resistance (R_{xy}) using the formula $R_H=(tR_{xy})/H$.

As it is known that the nonstoichiometry can drastically influence the electric properties of V_2O_3,[15] an x-ray photoelectron spectroscopy study was carried out. It shows that the oxidation state of vanadium can be estimated around +3, confirming that the films stoichiometry is close to V_2O_3.[19] Here Θ-2Θ scan XRD measurements reveal that only the peaks corresponding to the $00l$ reflections (where $l=6$, 12, …) are present, which indicates that the c axis of the films is perpendicular to the plane of the substrate. Moreover, Φ scans, recorded around the (104) reflection, show three peaks separated by 120° from each other, indicating that the films have a threefold symmetry and are grown epitaxialy, with respect to the substrate. These results are in agreement with the rhombohedral symmetry observed in the bulk V_2O_3. This symmetry and the $R\bar{3}c$ space group are further confirmed by electron diffraction pattern analyses. The high quality of the films was also attested by the low value of the rocking curve close to (0.20°) measured around the (006) reflection of the film.

Figure 1 displays the evolution of the lattice parameters (c) and (a), characteristic of the $R\bar{3}c$ structure, as a function of the thickness t. The out-of-plane lattice parameter (c) is slightly larger than the bulk values by $(0.45\pm0.1)\%$, while the in-plane (a) is smaller by $(-0.55\pm0.1)\%$, confirming a biaxial compression in the (ab) plane, estimated to be $(-3.5\pm0.5)\%$ with respect to the substrate [the stress values are calculated from the mean values (c) and (a) obtained from the thickness dependence in Fig. 1]. This suggests an anisotropic strain similar to previous reports.[20] Surprisingly, the lattice parameters are almost independent of t, indicating that the films are fully strained in the whole thickness range. The surface morphology was also studied by atomic force microscopy (AFM) with a scan area of 3×3 μm^2. Topography of the V_2O_3 samples reveals that the roughness increases when the thickness increases. For example, a typical surface roughness (rms) of 4.5 Å was observed for the thinnest film (170 Å), while a thicker sample (700 Å) has a rms value of 11 Å. This may indicate that the growth mode is mixed: a layer by layer (two-dimensional mode) on the (ab) plane at the initial step of the growth and an island coalescence (three-dimensional mode) along the c axis when the thickness increases. To summarize, the structural and microstructural analyses confirm that the films crystallize in the $R\bar{3}c$ structure, as in bulk, despite a large in-plane compressive strain.

The longitudinal resistivity (ρ) of V_2O_3 films is plotted in Fig. 2 as a function of temperature. In contrast to bulk samples, none of the investigated films exhibit a strong temperature-dependent resistivity. This is especially valid for $t>220$ Å, in which case the resistivity increases continuously with temperature as in a metal. Nevertheless, some hysteresis is observed, though strongly suppressed with respect to the bulk. The relative positions of the resistivity curves are not significant of a thickness dependence. It mostly results from the residual resistivity ρ_0, which depends on extrinsic factors such as scattering at the grain boundaries. As can be seen in Table I, the values of ρ_0 vary even under similar growth conditions. Thus, we can conjecture that the above found stress in the (ab) plane results into a larger bandwidth and hinders the paramagnetic metal-to-antiferromagnetic insulator transition. In contrast, for thinner films ($t<220$ Å), the films are metallic with a weak increase of the resistivity near 150 K. Its origin might be a reminder of the structural transition.

As shown in Fig. 3, resistivity data for all films follow a law in $\rho=\rho_0+AT^2$ in the temperature range from 2 K up to a

TABLE I. Thickness t, residual resistivity ρ_0, Fermi liquid transport coefficient A, temperature T_d, carriers number n, and Hall mobility μ_H for three films.

t (Å)	ρ_0 (mΩ cm)	A (10^{-5} mΩ cm K^{-2})	T_d (K)	$n_{300\ K}$ (cm^{-3})	$\mu_{H(300\ K)}$ [cm^2 $(V\ s)^{-1}$]
1100	0.24	19.6	18.7	4.5 ± 0.210^{22}	0.16 ± 0.05
380	0.27	14.0	17.5	4.4 ± 0.410^{22}	0.15 ± 0.06
260	0.19	10.2	15.8	4.9 ± 0.510^{22}	0.21 ± 0.10

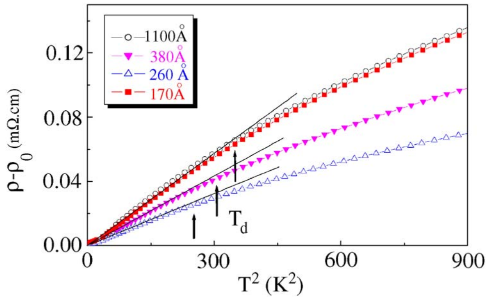

FIG. 3. (Color online) Resistivity vs T^2 in the low temperature region. The T_d temperature is also indicated.

characteristic temperature T_d. Here, ρ_0 represents the (film dependent) residual resistivity and A the transport coefficient in a Fermi liquid. This behavior, which differs from simple metals that exhibit T^3 or T^5 behavior, is seldom observed over such a temperature range, except for a few strongly correlated electron system, such as $Ca_3Co_4O_9$.[23] Table I summarizes the values ρ_0, A, and T_d for a series of films. The average value of A is close to $0.14\ \mu\Omega\,\mathrm{cm\,K^{-2}}$ across the whole thickness range, indicating that the A coefficient is not *significantly* thickness dependent. Moreover, it should be noted that such values are similar to those measured for single crystal V_2O_3 samples subjected to high pressures (26–52 kbars).[17] The high A values involve the existence of strong electronic correlations in our metallic thin films. The product $A(T_d)^2/a$ is about two orders of magnitude lower than h/e^2, indicating that the FL behavior does not extend up to the effective Fermi temperature. Instead, an additional scattering channel opens up at $T > T_d$, which might be provided by spin fluctuations. To better quantify the temperature range where this scattering channel is relevant, we performed Hall effect measurements in the temperature range of 2–300 K. Figure 4 shows the resulting Hall resistance (R_H) for a series of films. The positive slope of the Hall resistance implies holelike charge carriers, as inferred by McWhan and Remeika.[14] Moreover, while the Hall resistance would be nearly temperature independent in a regular metal, here, it exhibits a strong temperature dependence, especially for $T < 200$ K. In particular, the strain involved in our films has little influence on the location of the maximum of R_H, as it is located at a temperature very close to the one reported for metallic bulk samples.[24] Nevertheless, this temperature slightly increases as the thickness decreases. A similar result has been observed in the aforementioned single crystals with an increase in pressure, indicating that the decrease of the thickness is consistent with an increase of the pressure. At room temperature, in the temperature-independent regime, the values of the carrier number (n) and Hall mobility (μ_H) can also be extracted from the Hall resistance value (see Table I). For the thicker film (1100 Å), they are calculated to be $n=4.5\pm0.210^{22}\ \mathrm{cm^{-3}}$ and $\mu_H=0.16\pm0.05\ \mathrm{cm^2\,V^{-1}\,s^{-1}}$, which are consistent with the ones observed in V_2O_3 single crystals.[14] Note that R_H looses its temperature dependence above ~200 K, which indicates that above this temperature, the correlation length of the fluctuations that scatter the electrons becomes of the order of the lattice parameter. Consequently, in this regime, the resistivity is expected to be T linear, which is indeed observed for most of the films.

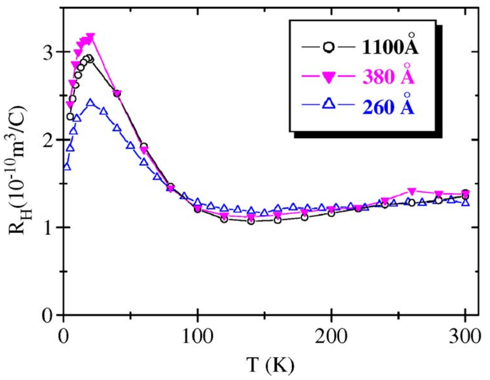

FIG. 4. (Color online) Temperature dependence of the Hall resistance of several V_2O_3 thin films.

In summary, high quality epitaxial V_2O_3 thin films were grown, with thickness ranging from 170 to 1100 Å by pulsed laser deposition on sapphire substrate ($0001\text{-}Al_2O_3$). Using multiple of characterization techniques, we confirm that the films have the same rhombohedral structure ($R\bar{3}c$ space group) as in the bulk despite the substrate-induced strains. The thickness dependence of the electronic properties shows the suppression of the classical metal-to-insulator transition with a metal-like behavior. At low temperature, the dependence of the resistivity as a function of T^2 was measured to be that of a strong correlated metal, and it was confirmed by temperature dependence of the Hall resistance.

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[1] M. Foex, C. R. Acad. Sci. III **223**, 1126 (1946).
[2] N. F. Mott, Proc. Phys. Soc., London, Sect. A **62**, 416 (1949).
[3] D. B. McWhan, A. Menth, J. P. Remeika, W. F. Brinkman, and T. M. Rice, Phys. Rev. B **7**, 1920 (1973).
[4] M. Yethiraj, J. Solid State Chem. **88**, 53 (1990).
[5] P. Limelette, A. Georges, D. Jérome, P. Wzietek, P. Metcalf, and J. M. Honig, Science **302**, 89 (2003).
[6] H. Kuwamoto, J. M. Honig, and J. Appel, Phys. Rev. B **22**, 2626 (1980).
[7] P. Dernier and M. Marezio, Phys. Rev. B **2**, 3771 (1970).
[8] W. F. Brinckman and T. M. Rice, Phys. Rev. B **2**, 4302 (1970).
[9] G. A. Thomas, D. H. Rapkine, S. A. Carter, A. J. Millis, T. F. Rosenbaum, P. Metcalf, and J. M. Honig, Phys. Rev. Lett. **73**, 1529 (1994).
[10] J. Spałek, A. Datta, and J. M. Honig, Phys. Rev. Lett. **59**, 728 (1987).
[11] A. Georges, G. Kotliar, W. Krauth, and M. J. Rozenberg, Rev. Mod. Phys. **68**, 13 (1996).
[12] R. Frésard and G. Kotliar, Phys. Rev. B **56**, 12 909 (1997).
[13] K. Held, G. Keller, V. Eyert, D. Vollhardt, and V. I. Anisimov, Phys. Rev. Lett. **86**, 5345 (2001).
[14] D. B. McWhan and J. P. Remeika, Phys. Rev. B **2**, 3734 (1970).
[15] Y. Ueda, K. Kosuge, and S. Kachi, J. Solid State Chem. **31**, 171 (1980).
[16] S. A. Shivashankar and J. M. Honig, Phys. Rev. B **28**, 5695 (1983).
[17] D. B. McWhan and T. M. Rice, Phys. Rev. Lett. **22**, 887 (1969).
[18] H. Schuler, S. Klimm, G. Weissmann, C. Renner, and S. Horn, Thin Solid Films **299**, 119 (1997).
[19] S. Autier-Laurent, B. Mercey, D. Chippaux, P. Limelette, and Ch. Simon, Phys. Rev. B **74**, 195109 (2006).
[20] S. Yonezawa, Y. Muraoka, Y. Ueda, and Z. Hiroi, Solid State Commun. **129**, 245 (2004).
[21] Q. Luo, Q. Guo, and E. G. Wang, Appl. Phys. Lett. **84**, 2337 (2004).
[22] L. Mechin, J.-M. Routoure, B. Guillet, F. Yang, S. Flament, D. Robbes, and R. A. Chakalov, Appl. Phys. Lett. **87**, 204103 (2005).
[23] P. Limelette, V. Hardy, P. Auban-Senzier, D. Jérome, D. Flahaut, S. Hébert, R. Frésard, Ch. Simon, J. Noudem, and A. Maignan, Phys. Rev. B **71**, 233108 (2005).
[24] S. A. Carter, T. F. Rosenbaum, P. Metcalf, J. M. Honig, and J. Spałek, Phys. Rev. B **48**, 16841 (1993).