Hysteresis in the electronic transport of $V_2O_3$ thin films: non-exponential kinetics and range scale of phase coexistence.

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The thermal hysteresis of the electronic transport properties were studied for $V_2O_3$ thin films. The temporal evolution of the resistance shows the out-of-equilibrium nature of this hysteresis with a very slow relaxation. Partial cycles reveal not only a behavior consistent with phase coexistence, but also the presence of spinodal temperatures which are largely separated. The temperature spreading of phase coexistence is consistent with the bulk phase diagram in the pressure-temperature plane, confirming that the film is effectively under an effective pressure induced by the substrate.

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INTRODUCTION

The physical properties of $V_2O_3$, cited as a prototype of strongly correlated systems, have been extensively studied especially for its spectacular metal-to-insulator (M-I) transition. Experimental evidences of a strong pressure dependence of physical properties have been accumulated. Consequently, the phase diagram in the pressure-temperature (P,T) plane was established. A lot of work has been devoted to the M-I Mott transition which can be observed when $V_2O_3$ is subjected to a chemical pressure by Chromium substitution. Such a negative pressure can be approached in thin films when growing $V_2O_3$ under tensile stress on LiTaO$_3$ substrate. The other M-I transition is associated to a change from a rhombohedral symmetry to a monoclinic symmetry and occurs at $T \approx 160K$ under atmospheric pressure. This structural transition leads to an increase of the unit-cell volume with range going from 1% to about 3.5%. This transition has a strong first order character, and a 10 K thermal hysteresis is often reported. When a hydrostatic (or uniaxial) pressure is applied, the transition temperature decreases, and above a critical pressure of roughly 26 KBars the metallic state is completely stabilized down to the lowest temperature. As a consequence, this strong pressure-dependence of the M-I transition is a motivation for thin film studies since large effective pressure can be expected by substrate-induced strains. Recently, thin films of $V_2O_3$ were grown on sapphire substrates, using pulsed laser deposition technique.

EXPERIMENTAL

Briefly, a series of $V_2O_3$ thin films, with various thicknesses ($t$), was epitaxially deposited on (0001)-sapphire substrate using the pulsed laser deposition technique. Details of the growth can be found elsewhere. Usually, thin films are under an effective pressure below a critical thickness, where the substrate causes the film to grow with uniform elastic strain. In the case of a large mismatch between film and substrate in-plane lattice parameters, the strain is quickly released in the film, leading to the so-called misfit dislocation regime. No critical thickness is then observed down to the ultra-thin film limit. It is the case here where the lattice mismatch between $V_2O_3$ and sapphire is about 4 %, as confirmed by X-ray diffraction. The tendency is even to recover the bulk parameters at low thicknesses.

The electronic resistivity ($\rho$) is measured using the four probe geometry in a commercial PPMS (Physical Properties Measurement System). The resistivity was estimated with the thin rectangular slice approximation: $\rho = R\pi/ln2LR_1(W/L)$, where $R$ is the resistance, $W$ the width, $L$ the length and $R_1(W/L)$ is the correction due to the finite size. A microbridge, whose preparation is described in 14, from a 11 nm thick film with a size of $100 \times 300 \mu m^2$ was also measured. The detailed analysis of partial cycles and of resistance relaxation were performed in this microbridge. For large current, the voltage-current characteristics show non linear behavior, as sometimes observed in samples with phase separation. However, we limit our study well inside the ohmic regime which is within the range $I = 1-500 \mu A$. We also...
checked that the relaxation of the resistance was uncorrelated with the temperature-dependence of the resistivity and that Joule heating can be avoided. The results presented hereafter were measured for a typical current of 1\,\mu\text{A}.

**FIRST-ORDER TRANSITION IN V\textsubscript{2}O\textsubscript{3} THIN FILMS**

Recently, we have shown a strong thickness-dependence in the properties of the V\textsubscript{2}O\textsubscript{3} thin films \cite{12}. In particular, we have observed that the M-I transition can be tuned by changing the thickness of the films from 2\,nm (±1\,nm) up to 300\,nm (±5\,nm). For example, the M-I transition is observed for ultrathin samples (\(t \leq 10\,\text{nm}\)) with lattice parameters close to the bulk values, whereas thicker samples (\(t \geq 22\,\text{nm}\)) present a quasi-metallic behavior down to low temperatures. For intermediate thicknesses, the situation is more complex: the films exhibit an intermediate behavior with a clear maximum in the \(R(T)\). All samples present an thermal hysteresis \(\Delta T\) in the range 20\,K-150\,K, but the magnitude of the hysteresis is maximum for the intermediate thicknesses. These various behaviors are illustrated in figure 1 where \(R(T)\) curves are plotted for three typical thicknesses.

The M-I transition in V\textsubscript{2}O\textsubscript{3} single crystals occurs with strong first order characteristics \cite{17}. Generally, the hysteresis of a first order phase transition results from the possibility of supercooling (superheating) metastable states \cite{18}. The hysteresis observed in our films could indicate such a first order transition, but its width is surprisingly large (\(\Delta T \approx 130\,\text{K}\) compared to 10\,K for the bulk samples). The broadening of the hysteresis seems to be specific to the thin film form, and may originate from several factors as described below. The first factor is that the decreasing of the system dimensions (or system thickness) can induce a finite size effect, which can lead to the so-called "rounding field" \cite{19}. As a consequence, the width of the first order transition is strongly dependent on the thickness, and \(\Delta T_c \propto t^{-1}\). This has been indeed used to explain the thermal broadening of the M-I transition in VO\textsubscript{2} films \cite{20}. In our V\textsubscript{2}O\textsubscript{3} samples, we do not observe any significant thickness-dependence of the thermal hysteresis width as seen in figure 2. The second possibility is that the growth generates quenched disorder, which can modify a first order transition to a continuous one. Actually, this has been shown for a dimensionality \(D = 2\) on the basis of general grounds \cite{21}. For \(D = 3\), the quenched disorder can also smooth the transition even if this latter still retains first order characteristics. To understand the role of such disorder upon the width \(\Delta T\) of the hysteresis, our samples were annealed under argon atmosphere, since such thermal treatment is usually used to order a sample (as in manganites \cite{22}). It is unlikely that the quenched disorder (cationic or oxygen disorder) plays a strong role in our films because, even if the residual resistivity slightly changed by about 10\,\%, the shape of the \(R(T)\) and the width \(\Delta T\) of the hysteresis remain unchanged after thermal treatment.

Finally, a third source of heterogeneity in our films can be the clamping of the unit cell that can induce (likely heterogeneous) strains \cite{23}. Using a two-parallel resistor model, we explained that the peculiar shapes of the
can be correlated on the (P,T) phase diagram. We will now focus on the nature of the thermal resistance hysteresis and show how it can be correlated on the (P,T) phase diagram.

**TIME-DEPENDENT EFFECTS AND NON EXPONENTIAL KINETICS**

To understand the nature of the hysteresis, we have measured on a microbridge of 11 nm thick film the time-dependence of resistance. A slow relaxation can be observed for 20 K ≤ T ≤ 150 K (Fig. 3). The sign of the relaxation depends on whether the metastable state is stabilized after heating or cooling the sample.

To fit the time-dependence resistance (R(t)), different functional forms can be proposed: exponential, stretched exponential or logarithmic time dependence. Here, the relaxation is clearly non-exponential. The simplest explanation of such non-exponential kinetics, which is ubiquitous in disordered systems, is that the relaxation can be intrinsically exponential in different domains, but that the relaxation time is not unique at the sample scale. This is in agreement with the idea that different domains with different critical temperatures are present in the sample. For non-interacting domains, a large statistical averaging of exponential relaxation times leads to the stretched exponential in the form R(t) ∝ exp(±t/τ0)β (where τ0 is a relaxation time and β < 1 the relaxation exponent) [24]. If the acquisition time is moderate (typically of the order of one hour), such a stretched exponential provides a good fitting of the data. The non-exponential time dependence obtained (β ≈ 0.2) confirms a non Debye relaxation, and indicates that the distribution function of characteristics times is rather flat. The second case to describe the data leads to a logarithm relaxation of the form R(t) ∝ ln(t + τ0). In order to distinguish between the two fits, very long relaxation times (t ≈ 1 Day) were performed, and the resulting curves are presented in figure 4. The plots show that the relaxation is even more slower than expected from the stretched exponential. The plot clearly evidences a logarithmic-dependence of the resistivity as a function of time, whereas the stretched exponential is not satisfactory for long periods (unless we do not add a second stretched exponential somewhat arbitrarily to fit the data).

Logarithm relaxation is usually observed in complex and strongly interacting materials [24]. For example, it is observed in glasses, whether they are structural, magnetic or electronic, and this relaxation corresponds to the ageing of the system. To check the hypothesis of glassy properties in our sample, we tried to observe spe-
pecific properties of glassy states such as memory and rejuvenation. Note that in the case of a glassy state, a memory effect is usually seen after a negative temperature cycling, because the spent time at the low temperature does not influence on the ageing of the system. Here, a negative temperature cycling during the relaxation \((80 \text{ K} \rightarrow 75 \text{ K} \rightarrow 80 \text{ K})\) stops the resistance relaxation and then helps the system to reach its equilibrium. Since we do not observe genuine glassy characteristics, the slow kinetics are not due to the fact that the system always explores metastable states. The relaxation is rather due to the nucleation of M-I domains with a large number of transition temperatures into a M matrix (when cooling the sample). This broad distribution of transition temperatures is the reason for the large number of relaxation times inferred by the logarithmic relaxation. This relaxation is very slow, showing that the kinetics are extremely constraint. We think that this is due to the long range strain effect induced by the substrate because of the clamping of the unit cell at the bulk transition temperature. This kind of relaxation is similar to the kinetics of phase transformations subjected to pressure.

**MINOR LOOPS AND PHASE COEXISTENCE**

It is now necessary to determine the region of phase coexistence and the stability limit of the metastable states, e.g. the spinodal limit. A way to confirm and to get more informations on the phase coexistence is to perform subloops in the hysteresis cycle. The reason is the following. As far as the transformation from one state to another is not complete, partial hysteretic cycles can be observed.

Typical partial cycles measured on the microbridge are shown in figure 5 and figure 6. For the cycling sequence high T→low T→high T shown in figure 5 we observe that the metastability begins at \(T \approx 150 \text{ K}\) and ends at \(T \approx 20 \text{ K}\). However, the reverse cycling sequence low T→high T→low T shown in figure 6 exhibits a quite different behavior. The three first curves are fully reversible (label 1, 2 and 3 in the figure 6) whereas the 70K-one (label 4) shows irreversibility. Since it is necessary to heat at temperature \(T \geq 70 \text{ K}\) to observe that a thermal hysteresis begins to develop, this means that phase coexistence begins at \(T \approx 70 \text{ K}\) and ends at \(T \approx 150 \text{ K}\). This asymmetry appearing for partial cycles and depending on the initial temperature indicates that below 70 K, the high resistance state is strongly favored and can be regarded as the stable state (even if some parts of the sample can be stabilized in the low resistance state by supercooling from high temperature). Thus, the analysis shows that the zone of phase coexistence extends only from 70 K to 150 K. From the \((P,T)\) bulk phase diagram of the V$_2$O$_3$, the transition line which determines the M-I transition can be described as a straight line with a slope \(\Delta T_c/\Delta P \approx -3.5\text{/Kbars}\) for \(T > 70 \text{ K}\) and a quasi-horizontal line with a slope \(\Delta T_c/\Delta P \approx -40\text{/Kbars}\) for \(T < 70 \text{ K}\). The pressure-induced at the transition has been thus calculated to be \(\Delta P_{max} \approx 27\text{ KBars}\) for a complete blocking of the transition. This value is higher than the critical pressure (26 KBars) reported in V$_2$O$_3$ single crystals by McWhan et al. and shows that a fully strained film should not exhibit any M-I transition. Since a first order transition leads to an heterogeneous state when the pressure increases at a constant volume, we assume that our film sustains a very broad and continuous effective pressure distribution (from \(P \approx 0\) to \(P \approx 27\text{ KBars}\), where each pressure is statistically equivalent). Therefore, the film should also display a very broad critical temperature distribution ranging from 0 K to 150 K. However, from the \((P,T)\) diagram, a simple estimation shows that the phases whose critical temper-
atures are in the range $0 < T_c \leq 70 \text{K}$ are statistically unfavorable. As a consequence, the temperature range where the phase coexistence occurs is going from 70 K to 150 K, in agreement with the analysis of the partial cycles. This is summarized in figure 7. Even if partial cycles were not performed for all the thicknesses investigated, the hysteresis cycles were always similar in terms of characteristic temperatures (see Fig.2). This suggests that our analysis is not thickness-dependent as far as the width of the phase coexistence is concerned. Finally, one has to note that $V_2O_3$ crystals form cracks because of fractures, which occur during the volume change at the M-I transition. This is not the case in our films. In bulk $V_2O_3$, M and I phases correspond to different structural symmetries, which transform into each other via a (local) first order transition. Some indications of the thermoelastic martensitic effect importance in the M-I transition in $V_2O_3$ have been reported using acoustic emission measurements [27]. We propose that in the particular case of $V_2O_3$ films, substrate enables a releasing of the strain by inducing a heterogeneous state, as it is the case in a martensitic scenario, where a large number of small domains increases the spread in transition temperature of each domain [28].

**CONCLUSION**

We have presented a detailed study of thermal hysteresis present in the transport properties of $V_2O_3$ thin films. Non-exponential relaxation and partial cycles are observed, showing a broad region of phase coexistence. Using partial hysteresis cycles, this zone of the phase coexistence has been precisely established. The limit of metastability corresponds well to what can be expected if the film is under an effective pressure induced by the substrate. We believe that such results will be of the general interest for the thin film physics that display metal-to-insulator transition.

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