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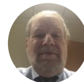

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Relaxation dynamics of the metal-semiconductor transition in VO_2 thin films

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The temperature dependent metal-insulator transition in VO_2 films displays substantial hysteresis. This is usually attributed to supercooling or superheating in the grains. In the hysteretic region at fixed temperature there is a relaxation of the resistance toward a presumed equilibrium value. We have made careful measurements of this relaxation, and find that it proceeds with a logarithmic dependence on time. If the transformation is thermally activated in individual grains, the log(t) behavior can be explained either by a wide distribution of activation energies U among grains or a dependence of U on the phase of adjacent grains. © *2010 American Institute of Physics*.
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When the metal-insulator (MI) transition of VO_2 is monitored as a function of temperature, it generally displays a substantial hysteresis and transition width (see Fig. 1). This is most pronounced in polycrystalline thin films. The transition width is probably related to variations in the grains; for example, it has been argued[1,2] that the transition temperature in a grain is a function of the density of oxygen defects which in turn depend on the grain size. The hysteresis is usually ascribed to the martensitic nature of the structural transition, where several atoms in a unit cell must move simultaneously to reach a phase of lower free energy.[1] This allows substantial supercooling and superheating. A number of works[3–5] have explored the details of hysteresis in the $R(T)$ curves with the assumption that these curves are well defined. It can easily be experimentally verified, however, that a hysteresis loop is not unique but depends on the rate at which temperature is varied. This suggests that there is a relaxation toward some equilibrium value at all points on the hysteresis loop. The best way to explore this relaxation is to sit at a fixed temperature and observe changes in resistance over time. In this note we describe measurements of this relaxation process.

VO_2 thin films were deposited by reactive sputtering from a vanadium target by the reactive ion beam bias target deposition using an $(Ar+O_2)$ gas mixture and the detailed growth conditions can be found elsewhere.[6] The film thickness, determined by x-ray reflectivity, was $\sim$100 nm. Atomic force microscopy (AFM) was used to characterize the surface morphology. X-ray diffraction (XRD) was used to determine the phase composition/texture of the VO_2 films and all the measurements were performed at room temperature. Figure 2(a) shows XRD spectra of 2θ scan for the VO_2 film deposited on (0001) sapphire substrate. The only film peak observed was the (020) monoclinic VO_2 peak indicating single phase monoclinic VO_2. The full width of half maximum of 0.19° was measured for the (020) monoclinic VO_2. The absence of other diffraction peaks from monoclinic VO_2 implied that the film was highly textured grown on c-plane sapphire with $(010)_{m\text{-}VO_2} \| (0001)_{Al_2O_3}$. The in-plane texture of the film was determined by azimuthal (φ) scans of $(2204)_{Al_2O_3}$ and $(110)_{m\text{-}VO_2}$, respectively. As shown in Fig. 2(b), six $(110)_{m\text{-}VO_2}$ peaks were observed thanks to three equivalent variants that were separated by 120°. In addition, $(110)_{m\text{-}VO_2}$ was rotated 30° from $(2204)_{Al_2O_3}$. The forming of three variants was likely due to the very large lattice mismatch between VO_2 and sapphire and was consistent with the previous reported on the texture of VO_2 films grown on c-plane sapphire.[7] Figure 2(c) is an AFM image of VO_2 film surface over an area of 1 μm^2. There were no pin holes or nano cracks observed thus the influence of these defects on the transport properties can be ruled out. The test devices were fabricated using a one-step mask photolithographic process. The top contact was a 300 nm Au/20 nm Ti deposited by electron beam evaporation. The contact pads had a width of 250 μm and were separated by a gap of 10 μm. Contact to the pads was made via Al wire bonds.

In our experiment, we quickly change the temperature of a thin film VO_2 sample from a value well above the MI

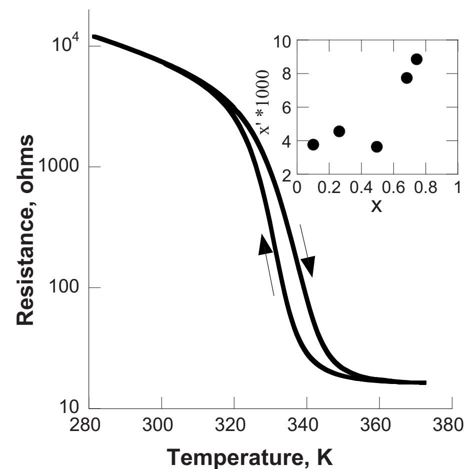

FIG. 1. The semiconductor-metal transition in a VO_2 thin film. Inset: $x' = dx/d(\ln t)$ as a function of the fraction of semiconducting grains for the data in Fig. 3. The corresponding temperatures (lowest to highest x) are 345, 340, 335, 330, and 327.5 K.

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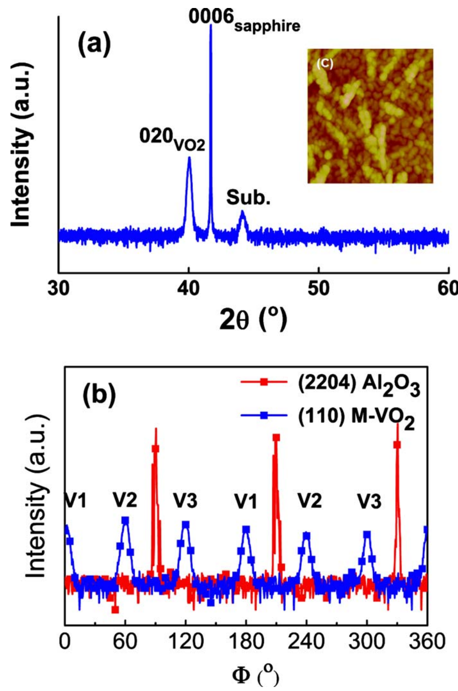

FIG. 2. (Color online) (a) XRD spectrum of vanadium oxide thin films deposited on (0001) sapphire substrate. (b) Azimuthal (φ) scans for (010) oriented VO_2 on a (0001) Al_2O_3 substrate. V1, V2, and V2 denote three equivalent variants of $(110)_{m\text{-}VO_2}$ that were separated by 120°. (c) Atomic force microscope image of VO_2 surface over 1 μm^2 area.

transition to a point within the transition. After the temperature has stabilized, we record the resistance as a function of time. The resistance is a measure of the number of crystallites that have transformed from the starting metallic phase to the semiconducting phase. Considered as a two-dimensional array of connected grains whose resistivity is either ρ_s, that of the semiconducting phase, or ρ_m, that of the metallic phase, effective medium theory[8] yields the relationship

$$x = \frac{(R - R_m) \times (R + R_s)}{2R \times (R_s - R_m)}, \quad (1)$$

where x is the fraction of semiconducting grains, R is the measured resistance, R_m is the resistance in the metallic phase, and R_s is the resistance of the semiconducting phase. Considering a transition of the form shown in Fig. 1, we can regard R_m as a constant. However, R_s varies significantly through the width of the transition and can be estimated by extrapolating from the region below the onset of the transition.

To make this measurement, we place the sample in a small home-built oven whose temperature is controlled with a diode thermometer. A second thermometer is pressed against the bottom of the chip carrier. Starting from a temperature 370 K, where the VO_2 film is fully in the metallic phase, we drop the temperature to a point in the hysteretic region. Using a Lakeshore 331 controller, it takes ~13–16 min for the temperature of the thermometer next to the sample to stabilize to within 0.1 K of the final setpoint. The approach is monotonic, without oscillations. Once the temperature has stabilized, we record the resistance with a Keithley 199 voltmeter as a function of time. Equation (1) is used to convert resistance to fraction x of semiconducting grains.

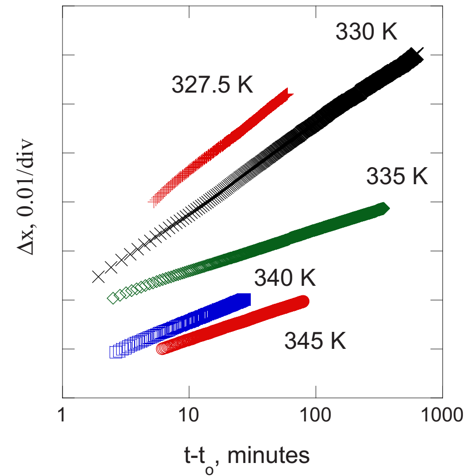

FIG. 3. (Color online) Time evolution of the calculated semiconductor fraction at various temperatures, offset for clarity. The mean value of x is 0.101, 0.262, 0.496, 0.682, 0.744 at 345, 340, 335, 330, and 327.5 K, respectively.

Figure 3 shows the evolution of x with time, at several temperatures. In all cases it increases with the form

$$x = x_1 + x' \ln(t - t_0). \quad (2)$$

The fitted value of t_0 is roughly the time at which the sample temperature has stabilized. If there were was a single energy barrier U that must be surmounted for the grains to switch to the semiconducting phase we would expect a dependence $x = x_0 + [x(0) - x_0]\exp(-t/\tau)$ where x_0 is the equilibrium value and $\tau \sim \exp(U/kT)$. This form, which has the same number of fitting parameters as in Eq. (2), always gives a much poorer fit.

After cycling to the metallic state our samples generally do not return to the starting 300 K resistance until at least a day has elapsed. This may be due to a persistence of metallic domains, as has been proposed in other works.[4,9] The possibility of such regions means that the film is not in a well-defined state in the heating portion of the resistance transition. We have found that resistance relaxation measurements on the heating portion of the hysteretic curve often display anomalies in $R(t)$; abrupt changes in slope or jumps in resistance. These may be a consequence of the poorly defined initial conditions or manifestations of avalanche behavior.[10] We thus concentrate on the cooling portion, where the behavior is more consistent.

It is important to demonstrate that the evolution in resistance we observe in our measurements does not represent some sort of permanent change in the film structure. To avoid this, we have tried to minimize the number of thermal cycles performed during the course of our measurements. The change in resistance characteristics above and below the MI transition during this period was less than 3%. Studies of the effect of thermal cycling[11,12] have generally showed that the $R(T)$ characteristic changed only slightly after numerous thermal cycles in our range of interest. Yin *et al.*[11] found that there was no change even after cycling to 450 K.

The observed $\log(t)$ dependence is unusual but not unique; similar behavior is seen in stress relaxation following plastic deformation,[13] decay of a trapped field in a type II superconductor,[14] and some magnetic materials.[15] In Ref. 16, a logarithmic relaxation of the resistance was observed in a very thin V_2O_3 film. The MI transition was far from "nor-

mal," with nonmonotonic (dR/dT) and a very broad transition (140 K). Indeed, the explanation offered for the $\log(t)$ response was based on idiosyncrasies of this film, supposed to consist of mesoscopic domains with widely varying transition temperatures. It is unlikely that this describes our film, and a more general explanation should be sought.

Two general approaches have been used to explain a logarithmic decay.[13] In the first, we suppose that there is in fact a distribution of activation energies U, leading to a distribution of decay times τ. In a given grain the probability of switching has the form $[1-\exp(-t/\tau)]$. Since each grain has a different activation energy, the net number of grains to have switched is a sum of probabilities with different values of t/τ. It turns out that if the activation energies have a uniform distribution the sum accurately approximates a $\ln(t)$ dependence. Of course, a perfectly uniform distribution is unlikely over a wide range of energies. Numerical calculations show that in order to display a $\ln(t)$ dependence over more than two decades of time (as we see in our data taken over a long period) there must be a uniform distribution of activation energies up to at least $8kT$. If $n(U)$ is the fraction of grains with activation energy less than U, then we expect the coefficient x' in Eq. (2) is approximately $kT(dn/dU)$.

A second approach is based on a single energy barrier that increases linearly with the fraction of grains that have switched. The stress in a given grain is no doubt affected by the structural phase of adjacent grains; this in turn could affect the activation energy in the grain of interest. The mean activation energy would thus be modified by the fraction x of grains that have switched; $U=U_0+\lambda x$. This is the model generally used to account for flux creep in hard superconductors.[14] It is shown[13,17] that with positive λ the thermal activation response is logarithmic in time, with the coefficient $x'=kT/\lambda$ [see Eq. (2)]. It should be noted that Ramirez *et al.*[4] fit the hysteresis loop in a VO_2 film using a negative value of λ, which would rule out this explanation entirely.

In summary, we have observed that the relaxation of the resistance in a VO_2 film toward its equilibrium value proceeds as the logarithm of time at a fixed temperature in the hysteretic region. From our measurements we can extract a parameter $x'=dx/d(\ln t)$ relevant to two following competing explanations of this effect: either the density of activation barriers dn/dU where there is a wide distribution of barrier heights or λ, the parameter characterizing the dependence of barrier height on x. This is plotted in the inset of Fig. 1 as a function of x. There is a clear trend, although the data taken at 335 K give an outlying point.

The $R(T)$ characteristics of VO_2 films vary widely, depending on deposition method. This reflects variations in grain size, impurity concentration, etc. We believe that an analysis of the time dependence of resistance relaxation could shed light on some of these variations. It was shown in Ref. 5 that the nucleation sites within grains are quite certainly extrinsic and could involve simple vacancies, wall dislocations, untransformed regions, etc. The details of the activation barriers will accordingly vary substantially between films. Likewise the interaction with adjacent grains could depend on grain orientations and the nature of the nucleation sites. It would be of some interest to compare values of x' for films prepared by the numerous methods that have been reported.

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[1] V. A. Klimov, I. O. Timofeeva, S. D. Khanin, E. B. Shadrin, A. V. Ilinski, and F. Silva-Andrade, Tech. Phys. **47**, 1134 (2002).
[2] J. Narayan and V. M. Bhosle, J. Appl. Phys. **100**, 103524 (2006).
[3] L. A. L. de Almeida, G. S. Deep, A. M. N. Lima, and H. Neff, Opt. Eng. **41**, 2582 (2002).
[4] J. G. Ramirez, A. Sharoni, Y. Dubi, M. E. Gómez, and I. K. Schuller, Phys. Rev. B **79**, 235110 (2009).
[5] R. Lopez, T. E. Haynes, L. A. Boatner, L. C. Feldman, and R. F. Haglund, Jr., Phys. Rev. B **65**, 224113 (2002).
[6] K. G. West, J. W. Lu, J. Yu, D. Kirkwood, W. Chen, Y. H. Pei, J. Claassen, and S. A. Wolf, J. Vac. Sci. Technol. A **26**, 133 (2008).
[7] Z. P. Wu, S. Yamamoto, A. Miyashita, Z. J. Zhang, K. Narumi, and H. Naramoto, J. Phys.: Condens. Matter **10**, L765 (1998); S. Lysenko, V. Vikhnin, F. Fernandez, A. Rua, and H. Liu, Phys. Rev. B **75**, 075109 (2007).
[8] J. Rozen, R. Lopez, R. F. Haglund, and L. C. Feldman, Appl. Phys. Lett. **88**, 081902 (2006).
[9] D. J. Hilton, R. P. Prasankumar, S. Fourmaux, A. Cavalleri, D. Brassard, M. A. El Khakani, J. C. Kieffer, A. J. Taylor, and R. D. Averitt, Phys. Rev. Lett. **99**, 226401 (2007); **100**, 019906(E) (2008).
[10] A. Sharoni, J. G. Ramirez, and I. K. Schuller, Phys. Rev. Lett. **101**, 026404 (2008).
[11] W. Yin, K. G. West, J. W. Lu, Y. Pei, S. A. Wolf, P. Reinke, and Y. Sun, J. Appl. Phys. **105**, 114322 (2009).
[12] C. Ko and S. Ramanathan, J. Appl. Phys. **104**, 086105 (2008).
[13] F. R. N. Nabarro Mater. Sci. Eng., A **309**, 227 (2001).
[14] Y. B. Kim, C. F. Hempstead, and A. R. Strnad, Phys. Rev. Lett. **9**, 306 (1962).
[15] S. Chikazumi and S. H. Charap, *Physics of Magnetism* (Robert E. Krieger, Malabar, 1978), Chap. 15.
[16] C. Grygiel, A. Pautrat, W. Prellier, and B. Mercey, EPL **84**, 47003 (2008).
[17] P. W. Anderson, Phys. Rev. Lett. **9**, 309 (1962).