Two-dimensional current percolation in nanocrystalline vanadium dioxide films

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Simultaneous measurements of the transmittance and the resistance were carried out on 20-nm-thick VO_2 wires during the semiconductor-to-metal transition (SMT). They reveal an offset between the effective electrical and optical switching temperatures. This shift is due to current percolation through a network of nanometer-scale grains of different sizes undergoing a SMT at distinct temperatures. An effective-medium approximation can model this behavior and proves to be an indirect method to calculate the surface coverage of the films. *© 2006 American Institute of Physics*.
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Bulk vanadium dioxide undergoes a structural phase transition from a monoclinic semiconductor to a tetragonal metal near 68 °C.[1,2] This structural transition is accompanied by abrupt changes in the optical and electrical properties of the oxide. VO_2 has been the object of widespread interest as a component of electronic and photonic devices because the critical temperature T_c of this semiconductor-to-metal transition (SMT) can be adjusted from 20 to 70 °C by doping or stress.[3,4] Many of these potentially useful features are preserved in nanocrystalline VO_2. However, a unique aspect of the nanocrystals is that the width of the hysteresis loop traced out by the SMT increases as grain size is reduced.[5,6] Indeed, optical hysteresis loops with widths as large as 50 °C have been observed for isolated VO_2 nanoparticles.[7,8]

For nanoparticles in electrical contact with one another, the hysteresis loop in conductivity also widens with reduction in the size of the crystalline domains. In particular, it leads to a temperature window within which a nanostructured film is partially semiconducting and partially metallic because contiguous VO_2 nanoparticles undergo the phase transition independently.[9] Indeed, for the transition to be effective electrically, a continuous path through grains in the same state needs to exist. In a nanostructured thin film, the electrical switching behavior is therefore determined by a percolation process.

This letter presents simultaneous optical and electrical measurements of the SMT in a two-dimensional (2D) nanostructured VO_2 film and shows that there is an offset between the effective optical and electrical switching temperatures. This shift arises because the hysteresis in optical transmissivity is determined by the relative fraction of nanoparticles in the semiconducting state, while the hysteresis in electrical resistivity is governed by the evolution of a continuous percolation path. The behavior of the resistance is modeled well by a 2D effective medium calculation, which also yields an estimate of the spatial coverage of the films.

The VO_2 wires for the experiment were fabricated by depositing a layer of vanadium oxide with an equivalent thickness of 20 nm through a 1.0×0.1 cm mask onto an amorphous alumina substrate (optically polished, rms roughness less than 5 nm) using pulsed laser ablation. A vanadium target was sputtered in a 10 mTorr O_2 atmosphere by a KrF excimer laser (248 nm, 25 Hz) at a fluence of ~ 4 J/cm^2. A subsequent annealing step at 450 °C in oxygen (250 mTorr) for 45 min produced the correct stoichiometry, as determined by Rutherford backscattering to an accuracy of $\sim 2\%$.[10] The amount of material deposited was optimized to achieve small grain size and sufficient continuity along the film to obtain a wide electrical hysteresis loop. The resulting film comprises a 2D random network of contiguous VO_2 nanoparticles having a mean diameter of approximately 50 nm (Fig. 1).

After aluminum contacts were deposited at the ends of a wire by thermal evaporation, the sample was fixed on a Peltier thermoelectric heater/cooler stage with a 3-mm-diam hole in its center to facilitate simultaneous electrical and optical measurements. An infrared detector located opposite the film monitored the transmission of a 1.3 μm laser through the wire while the resistance along the wire was measured between the aluminum contacts (Fig. 2).

Figures 3(a) and 3(b) show the transmittance and resistance hysteresis loops measured for this sample. They are ~ 20 °C wide and the asymmetry between the heating and cooling branches is due to the relatively broad size distribution.[5] The reduction of the grain size has also diminished the resistance jump from the five orders of magnitude observed in the highest-quality bulk VO_2. Indeed, the properties of nanocrystalline vanadium dioxide can deviate from those of bulk material because of the reduced amount of

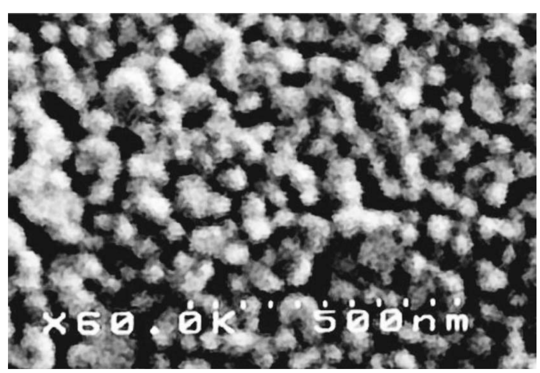

FIG. 1. Scanning electron micrograph of the sample; the amount of deposited material was adjusted to obtain both small grain size and contiguity.

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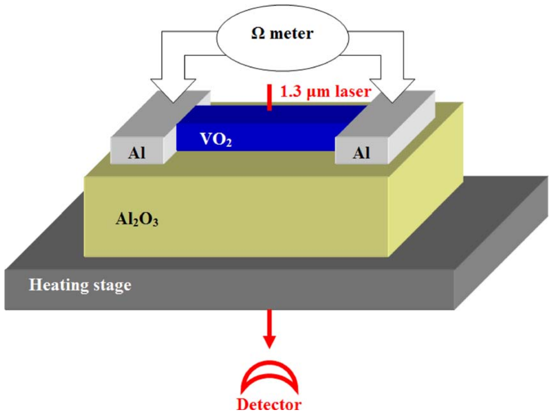

FIG. 2. (Color online) Schematic of the structure allowing simultaneous optical and electrical characterization. The VO_2 wire is deposited on amorphous Al_2O_3 and is terminated by Al contacts.

nucleating centers,[7] the large number of grain boundaries and the presence of oxygen vacancies (most likely at the surface).[11] The activation energy deduced from the exponential behavior of the resistance in the semiconducting phase is approximately 0.36 eV, in good agreement with previous reports.[12,13]

To first approximation, the optical transmittance depends linearly on the volume fraction of the metallic phase and the drop on the heating branch indicates that the nanocrystals start to switch at ~54 °C. The measured resistance also begins to deviate from semiconducting behavior around 54 °C. However, between 54 and 60 °C, this deviation is small compared to the total jump. Significant change in resistance begins only at approximately 60 °C. This offset constitutes the difference between the electrical and optical signatures of the SMT.

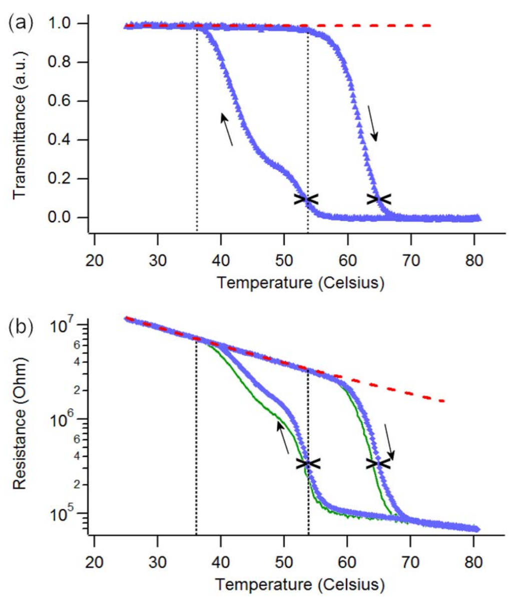

FIG. 3. (Color online) Transmittance (a) and resistance (b) curves measured simultaneously as a function of temperature. The dashed lines show the extrapolation of the film properties in the semiconducting phase. The dotted lines mark the beginning of the transition for the heating branch and the end of the transition for the cooling branch (these temperatures correspond to a 5% deviation from the transmittance at room temperature). Crosses indicate the percolation thresholds (90% of the VO_2 is metallic). The full line in (b) is the reconstructed hysteresis deduced from Eq. (3) using $\kappa=0.52$, γ_m was extracted from the transmittance.

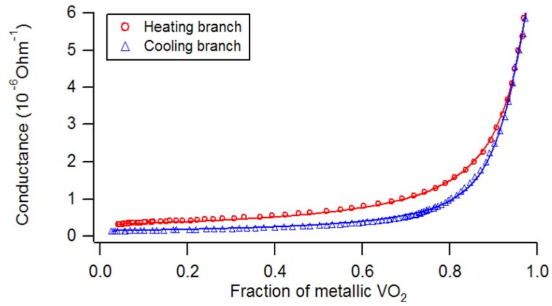

FIG. 4. (Color online) Dependence of the conductance on the fraction of VO_2 that is metallic; this fraction is calculated from the transmittance curve [Fig. 3(a)] and is then substituted for temperature in the resistance data [Fig. 3(b)]. The continuous curves are obtained using the effective medium approximation.

These two regimes of strong and weak dependence of resistance on temperature occur during both the heating and the cooling processes; this behavior is emphasized in Fig. 4 where the conductance is plotted as a function of the metallic fraction of VO_2. Electric current is sensitive to the specific location of the metallic grains along the path between electrodes. If only a small fraction of particles has turned metallic, a continuous low-resistance path does not exist and the total resistance is not greatly affected. This explains the nearly constant regime in Fig. 4. As the temperature increases, conducting paths form and the resistance change is greater. The formation of the first metallic path corresponds to a threshold temperature. Current percolation is thus the origin of the behavior of the resistance in the sample. An effective medium approximation (EMA) can be used to model this nonlinear evolution.

Bruggeman's symmetrical effective medium theory has been used to describe the dependence of the dielectric constant of VO_2 films on temperature[14,15] and to model the electrical hysteresis[16] when the metallic phase and the semiconducting phase coexist. This theory treats a particle in an inhomogeneous material as a domain embedded in a medium with an effective conductivity σ_e. For inclusions in a two-dimensional system, the volume fraction δ_i and the conductivity σ_i of each component satisfy[17]

$$\sum \delta_i \frac{\sigma_i - \sigma_e}{\sigma_i + \sigma_e} = 0. \tag{1}$$

In the present case, vanadium dioxide has segregated on the surface of the substrate and voids of zero conductivity must be included to model the film as a 2D medium. This leads to

$$-\delta_a + \delta_m \frac{\sigma_m - \sigma_e}{\sigma_m + \sigma_e} + \delta_s \frac{\sigma_s - \sigma_e}{\sigma_s + \sigma_e} = 0, \tag{2}$$

where a is noted for air, m for VO_2 in the metallic phase and s for VO_2 in the semiconducting phase. Equation (2) can be divided by the coverage of the film $\kappa = 1 - \delta_a = \delta_m + \delta_s$, which simplifies to

$$\frac{\kappa - 1}{\kappa} + \gamma_m \frac{\sigma_m - \sigma_e}{\sigma_m + \sigma_e} + (1 - \gamma_m) \frac{\sigma_s - \sigma_e}{\sigma_s + \sigma_e} = 0. \tag{3}$$

In this representation, the effective conductivity can be written as a function of γ_m, the fraction of VO_2 that is metallic. The value of σ_e in the high temperature phase ($\gamma_m = 1$) and in the low temperature phase ($\gamma_m = 0$) can be extracted from electrical measurements. This leads to σ_m and σ_s since

$$\sigma_m = \frac{\sigma_e(\gamma_m = 1)}{2\kappa - 1} \quad \sigma_s = \frac{\sigma_e(\gamma_m = 0)}{2\kappa - 1}. \tag{4}$$

The expression deduced from Eq. (3) for the effective conductance is used to fit the experimental data, defining σ_m and σ_s as constant parameters. The resulting curves successfully model the behavior of the measured conductance (Fig. 4). The total vanadium dioxide coverage deduced from the calculations is found to be 52% on the heating branch and 55% on the cooling branch, in good agreement with the values extracted from the scanning electron micrographs $(50\% < \kappa < 60\%)$. Similarly, Eq. (3) can be used to reconstruct the electrical hysteresis [Fig. 3(b)].

The value for the coverage deduced from the data does not depend on the relative change in conductivity, but is instead related to the minimum fraction of material required to form a single metallic path between the electrodes. In the EMA, this threshold ϕ_c is 50% of the surface. From the measurements in Fig. 4, this implies that nearly 90% of the VO_2 has to be in a metallic state to create a continuous conducting path; the corresponding threshold temperatures for the heating and the cooling branch are indicated in Fig. 3. The 2D EMA is in good agreement with percolation theory[18,19] in which ϕ_c is approximately 45%. In three dimensions, the value of ϕ_c has been measured at 16%.[18] Therefore, for films comprising more than one layer of grains, the fraction of metallic material required to reach the threshold is smaller, so that the apparent shift between the optical and electrical branches of the hysteresis should be greatly reduced.

The percolation effects reported here should be expected in any nanocrystalline VO_2 film in which the grains switch independently and will affect the electrical as well as the thermal transport properties. However, as the grain size increases and the film becomes more uniform and more three dimensional, the transition will occur within a smaller temperature range. There is thus a trade-off between the amplitude of the changes in the properties of the material and the width of the temperature window in which the film is in an intermediate state. Also, the value of ϕ_c is not universal if the distance between the electrodes is reduced to a length scale at which the distributions of the nanocrystals are not statistically equivalent. Therefore, the dimensions of reproducible devices are strongly constrained, unless the size and arrangements of the nanoparticles are controlled lithographically to make the percolation threshold deterministic.

In summary, this work has shown that current percolation leads to an intermediate state in which the film is partially opaque but still semiconducting. An effective medium model successfully reproduces this behavior and can be used to extract the spatial coverage of the films. Percolation should be taken into account in the design of any vanadium dioxide based electronic element in order to reach the desired characteristics. The offset between the effective electrical and optical switching temperatures opens the possibility of designing tristate optoelectronic devices.

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