On the Field-Induced Insulator- Metal Transition in VO_2 Films

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1. Introduction

First-order metal-insulator phase transitions (MIT) in crystalline materials have been known for many years [**1**] and correspond to a transformation between states with a dielectric (semiconductor) and a metallic types of conductivity. These transitions occur under the influence of certain external parameters, such as temperature and pressure, as well as with varying material composition. Materials exhibiting these phenomena include many transition metal oxides of which over 40 are known to possess MIT [**2,3**].

Among the best-known MIT materials are vanadium oxides. Being able to combine with oxygen in 2-, 3-, 4-, and 5-valent states, vanadium forms a series of oxides of which at least 8 exhibit MIT [**4**]. Phase transition in V_2O_3 occurs at a critical temperature T_C = 150K and in VO_2 at T_C = 340K, with the electrical conductivity changing by up to 10 and 5 orders of magnitude, respectively. The MIT in vanadium oxides is also accompanied by a discontinuous variation of other than electrical properties, such as optical, magnetic, etc. Vanadium dioxide, VO_2, is of particular interest for technology because its transition occurs near room temperature and furthermore its T_C is tunable in a wide range by doping with impurities such as tungsten. A recent review of vanadium oxide electronics [**5**] exhaustively cites the relevant literature. Another recent review [**6**] has a somewhat different focus and perspective.

Despite numerous attempts, no commercially viable application of VO_2 has been found so far. One known application, in infrared-vision systems, employs a closely-related but non-transitioning non-stoichiometric VO_X rather than VO_2. The reason for choosing VO_X over VO_2 had to do with a difficulty of dealing with the hysteretic nature of a transition in VO_2. A recently proposed VO_2 sensor for infrared-vision systems utilizes a spectacular bolometric effect that is of non-hysteretic nature [**7**], even though it is within the hysteretic loop of the transition. This proposal has not found commercial use either.

The dramatic difference in the electronic spectrum on the metallic and the dielectric side of the transition opens the possibility for *switching* applications triggered by an external electric field applied to a thin transitioning film in a gated structure. Since the field penetrates very differently into the dielectric and the

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metallic phase, the field energy in the two phases is different.[1] As a result, application of an external electric field shifts the critical temperature of the transition [**8-21**].

We had estimated [**14**] such a shift δT_C for a transistor-like structure with a thin VO_2 film sandwiched between two metallic plates insulated from the film by dielectric layers, cf. Fig. 1. One of these plates is the ground plane and to the other a gate voltage V is applied, resulting in

$$\delta T_C = -\frac{(C_M - C_D)V^2}{2(S_M - S_D)} \tag{1}$$

where S_M and S_D denote the entropy densities and C_M and C_D the electrostatic capacitances per unit area of the film in the metallic and the dielectric phase, respectively. In this estimate it is assumed that the entire film undergoes the transition. As suggested in [**14**], this may be "true for a thin enough film, where the formation of in-plane transition boundary is energetically unfavorable". The negative sign in Eq. (1) implies that application of a gate voltage drives the system into its metallic state.[2] For an applied voltage V = 1V in an exemplary gated structure, we found $\delta T_C \approx -1$K. This is a substantial shift but it is hardly adequate for switching applications.

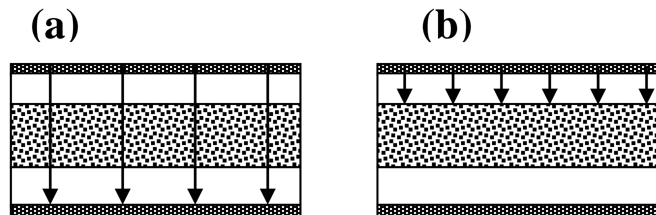

Figure 1. Schematic diagram of an experimental arrangement. Grounded vanadium oxide film is sandwiched between two insulated metallic gates. When the film is in dielectric state (a), the electric field lines penetrate through the film and terminate on the bottom metallic plate. When the film is metallic (b), the electric field lines terminate on the film surface.

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[1]To our knowledge, the possibility of such an effect was first suggested by Valiev et al. [**8**]: "The influence of the electric field [...] may be connected with the difference in energy of the electric field $F^2/8\pi$ in the metal and in the semiconductor, a difference that manifests itself in expulsion of the field from the metal".

[2]Because of the wrong sign in an equation leading to (1), the opposite conclusion was erroneously stated in Ref. [**14**].

The electrostatic effect (1) is based on thermodynamics and is independent of a physical origin of the metal insulator transition. However, this mechanism is rather weak, as it allows shifting T_C by at most several degrees. A much stronger effect, albeit model-dependent, is introduced in the next Section and will form the basis for our subsequent discussion. Here we wish to stress that the idea of inducing insulator-to-metal transition in a thin vanadium oxide film by applying an external electric field is a sound idea. The effect surely exists!

Nevertheless, despite multiple reports that observe such an effect and the sound theoretical reasons for its existence (see [**8-21**] and literature cited in the reviews [**5, 6**]), the status of this problem is unsatisfactory and we offer our reflections on the reason why. We believe that for a sufficiently large applied field the transition indeed occurs, but it is confined to an infinitesimal sliver at the surface of the sample. In its “insulator” phase, the VO_2 sample is, in fact, a semiconductor with a relatively narrow bandgap and a rather high conductivity at temperatures of the experiment. As a result, the field-induced transition is never observed in a gated bulk sample. The transition has been reported only in double-gated films, but even there the effect is rather small because most of the film remains semiconducting and shunts the emergent metallic sliver.

We discuss the conditions under which the transition can be induced in the entire film, rather than its top sliver. We show that this favorable situation can be realized when the film is sufficiently thin, so that the energy cost of converting the entire film into the metallic phase (which is “thermodynamically wrong” in the part of the film away from the surface) is smaller than the would-be cost of creating a domain boundary between the two phases. At this time, we cannot predict how thin the film should be for the proposed stabilization of the entire-film transition by the domain boundary energy, but we discuss the physical quantities that should be determined to make this prediction.

Finally, we discuss the need for the ground plane, which does not sit well with the technological reality that the best and thinnest VO_2 films are grown on insulating monocrystalline sapphire substrates. In large transistor-like structures with gate lengths of a micron and longer, the ground plane appears indispensible, for otherwise the field configuration would be accommodated with tiny domain boundaries across the film. The phase boundary must be comparable to the film area for its energy to count. Whether or not this can be accomplished with deep submicron gate lengths is an open question.

2. Electron concentration induced transition

There is no definitive theory of the metal-insulator transition in vanadium oxides. Possible mechanisms under discussion are the electron-phonon or Peierls mechanism and electron correlation mechanism of Mott-Hubbard type [**1**, **22-23**]. Ultrafast experiments [**24-27**] where the transition is excited by femtosecond optical pulses support the electron correlation model, at least in VO_2. Nowadays, this seems to be the prevalent view of most practitioners [**5**, **6**, **28**].

The correlation model naturally leads to the assumption that the transition is controlled by the concentration of mobile carriers. This implies a model of the transition triggered by the total electron concentration in the dielectric phase, irrespective of whether it results from doping, thermal excitation, photo excitation

– or is induced by an applied electrostatic field. We are interested, of course, in the latter case. In an intrinsic semiconductor in the absence of an applied field, the chemical potential μ is approximately in the middle of the dielectric gap E_G. As the field F is applied, μ moves toward one of the allowed bands and the concentration of electrons (or holes) in the vicinity of the surface increases. At some critical concentration we can expect a transition to the metallic state.

Although there is yet no quantitative theory to describe such a transition, the very existence of induced concentration effect should be regarded as likely. The critical carrier concentration may be estimated to be of the order of the thermal carrier concentration that arises in the dielectric phase at the transition temperature T_C due to the thermal excitation across the gap. That concentration is of the order 10^{18} cm^{-3} and should be easily achievable by field-effect. The induced-carrier effect is much "stronger" than the electrostatic field energy effect and should work in a wide range of temperatures. The expected "strong" effect is very attractive for switching applications [**14**].

Qualitatively, we assume that the transition driven by electron concentration is controlled by the position of the chemical potential μ relative to the conduction band E_C (in a homogeneous system), cf. Fig. 2. Denote by $\varphi(T)$ the critical position of μ at a given temperature T, corresponding to the transition. We regard the temperature as fixed and vary the concentration. Dielectric phase corresponds to $\mu < \varphi(T)$.

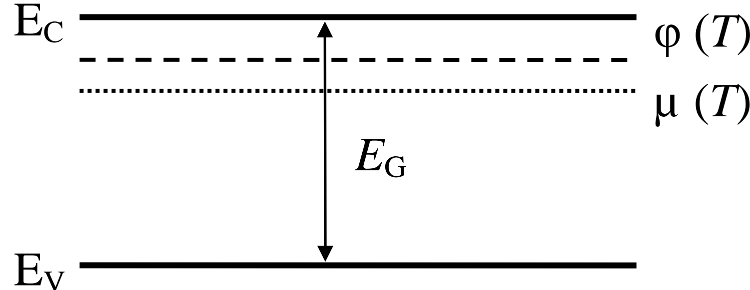

Figure 2. Schematic band diagram of vanadium oxide in its semiconductor phase. At a fixed temperature T, the position of chemical potential μ varies with the induced electron concentration. The metal-insulator transition occurs at a critical position $\mu = \varphi$

We shall continue describing the system by its dielectric diagram even when the semiconductor phase is unstable. This provides the meaning to $\mu > \varphi$ as the level of the chemical potential that would be present if the dielectric phase were stabilized externally.

For the difference ΔG in the free energy density per unit volume between the metallic and dielectric phases we assume the model illustrated in Fig. 3.

Here in this diagram the quantity Δ_D is the penalty the system pays for keeping a unit volume metallic in the region where $\mu < \varphi$, i.e. where the volume should be dielectric; similarly, Δ_M is the penalty for maintaining a dielectric unit volume in the region where it should be metallic. The sum of these quantities, $\Delta_D + \Delta_M = \Delta$, is the total discontinuity in the free energy density upon transition, but their ratio is totally unknown at this time.

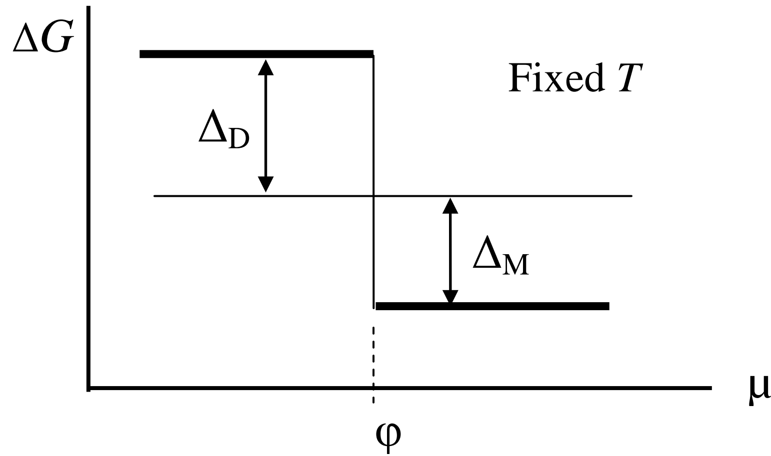

Figure 3. Difference $\Delta G = G_M - G_D$ in the free energy densities between the metallic and dielectric phases. For $\mu > \varphi$, the dielectric phase is unstable and the meaning of μ is the level the chemical potential would have if the phase were stabilized externally.

3. Field-induced transition in a film

Consider a dielectric VO_2 film of thickness d in an external electric field F. To determine, what happens with the film, when part of it, a layer of thickness x, is subject to $\mu > \varphi$ (while stabilized in the dielectric phase), we must tally the penalties. The reason the layer may not transition to metal is associated with the boundary energy b between the two phases. The quantity b is per unit area and its value should be also considered unknown at this time. The value of x depends only on the electric field and increases with the field. There is a well-defined equation $x = x(F)$ that is determined by electrostatics of the accumulation layer.

Three possible configurations are illustrated in Fig. 4. In the configuration (a), the film remains dielectric, paying the penalty $x\Delta_M$.

In the configuration (b), a thin layer x_m goes metallic and screens the applied field. The remaining portion $(x - x_m)$ is no longer under metallic condition. Since the field does not penetrate beyond x_m, the film underneath has $\mu < \varphi$ and no

penalty is extracted. Except, of course, for the boundary energy b, which is the only penalty in this configuration.

We can safely assume that x_m is very small, on the order of $(\hbar/E_G)v_F$, where $v_F \approx 10^8$ cm/s is the Fermi velocity of electrons in the metallic phase, and $E_G \approx 0.5$ eV is the bandgap energy in the dielectric phase. The actual extent of x_m should be determined from the Ginzburg-Landau equation that describes the spatially inhomogeneous transition. The combination $x_m = (\hbar/E_G)v_F$ appears reasonable on dimensional consideration. It gives $x_m \approx 10$Å.

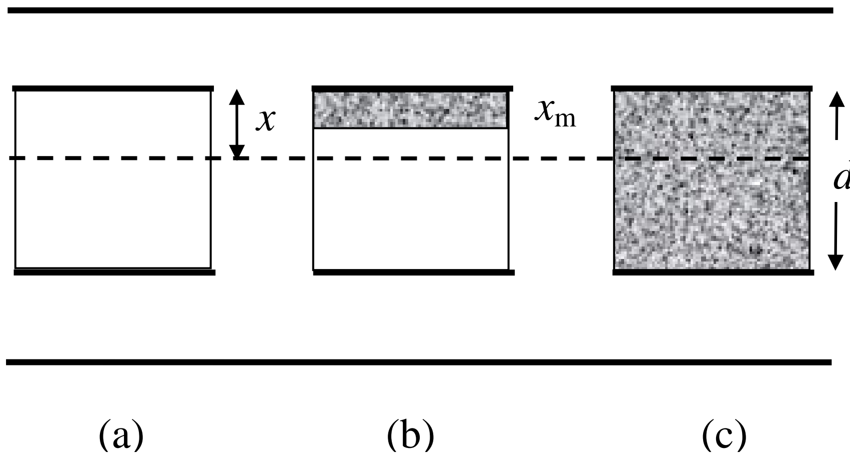

Figure 4. Possible configurations of the transitioning thin film in an external electric field. The strength of the field is characterized by the thickness x of a sublayer where $\mu > \varphi$ (while the film is stabilized in the dielectric phase). The relation $x = x(F)$ is well-defined by the electrostatics and needs not be specified analytically. (a) The entire film remains dielectric. (b) A sublayer of thickness x_m goes metallic and screens the applied field. (c) The entire film goes metallic.

In the configuration (c), the entire film goes metallic and there is no boundary penalty. However, most of the film, $(d - x)$, is in the regime $\mu < \varphi$ and hence pays the penalty for being metallic, $\Delta_D(d - x)$.

For *thick enough films*, only configurations (a) and (b) are competitive. The transition occurs in thick films at large enough fields, when $x > b/\Delta_M$. Due to the smallness of x_m, the effect of the transition is not very strong and may be hard to see in resistance measurements. The reason is that the conductivity of a thick VO_2 film in its "dielectric" phase (where the intrinsic free-carrier concentration is considerable at room temperature, $n \approx 10^{18}$ cm^{-3}) is rather high and it would not be much changed by the conversion to metal of a surface sublayer of thickness x_m.

The critical field F_c for the transition in thick films is defined by the electrostatic relation $x_c = x(F_c)$ with a finite thickness of penetration x_c. For thick films the critical field penetration thickness is given by

$$x_C = \frac{b}{\Delta_{\mathrm{M}}} \; . \tag{2}$$

In the opposite limit of *thin films*,

$$d\,\Delta_{\mathrm{D}} < \quad b \; , \tag{3}$$

the configuration (c) becomes competitive, $\Delta_D(d - x) < x\Delta_M$, and the entire film undergoes transition. This happens at large enough fields, $x > d\,\Delta_D/(\Delta_D + \Delta_M)$, and the critical field now corresponds to

$$x_C = \frac{d\,\Delta_{\mathrm{D}}}{\Delta_{\mathrm{M}} + \Delta_{\mathrm{D}}} \; . \tag{4}$$

Equation (4) together with the electrostatic relation $x_c = x(F_c)$ determines the critical field for driving the transition in a thin film.

Note that in light of (3) the thin-film critical field (4) is *smaller* than the corresponding field (2) for thick films.

4. Need for ground plane

The above estimates necessarily assume a double-gated structure, cf. Figs. 1 and 4. In this case the domain boundary is *planar* and the boundary energy *per unit area* may compete on equal footing with the phase energy densities corresponding to different configurations. However, best thin films of VO_2 are produced on insulating crystalline substrates, such as sapphire. In these structures a meaningful ground plane is hard to organize. The ground plane is “meaningful” if it attracts most of the field lines emanating from the gate electrode; therefore it must be positioned close to the film, much closer than the source-drain spacing. Otherwise, instead of the configurations of Fig. 4, the electric field lines would terminate on the source and drain contacts and the domain walls would be “vertical” (across the film). Vertical walls may also tangibly contribute to the energy balance; thus, they possess enough energy to stabilize non-hysteretic branches in temperature excursions within the hysteresis loop of the metal-insulator transition in thin VO_2 films [7]. However, for long gates (e.g., of order a micron or longer) the vertical-wall area would be negligible compared to the area of the film and the boundary energy would hence not be significant.

The situation may be more favorable for deep submicron gates. It seems reasonable that for short enough gates the vertical wall energy may be sufficient to stabilize the transition in the entire film. Philosophically, however, the short-gate quest seems to undermine perhaps the main advantage of the three-terminal switch

based on a metal-insulator transition: namely that its speed is independent of the gate length. As discussed earlier [**14**], unlike field-effect transistors, the speed of such a switch is not limited by carrier drift time under the gate.

Therefore, we believe the main research effort would be best deployed in the development of a viable technology for the deposition of a high-quality thin VO_2 film on a substrate that could be fashioned into providing a *meaningful insulated ground plane*.

5. Conclusion

First-order metal insulator phase transitions in thin VO_2 films can be controlled by an applied electric field. The effect can be used for the implementation of useful devices such as a three terminal ultra-fast switch. For the successful development of such a switch it is imperative that the thin film be double-gated and moreover be thin enough to transition as a whole, rather than separating into two planar domains, the metallic and the semiconducting. We have argued that in thin enough films, the entire-film transition can be stabilized by the domain boundary energy.

It would be very worthwhile to develop a quantitative theory that microscopically describes the spatially inhomogeneous first-order transition. Such a theory should be able to provide an estimate for the key quantities required to assess the needed film thickness. First and foremost, this is the domain boundary energy b, about which we presently know next to nothing, quantitatively. Another parameter one would like to know, is the breakdown of the free-energy discontinuity upon transition, $\Delta = \Delta_D + \Delta_M$, into its components describing the "penalties" on the metallic and the dielectric sides of the transition. While the Δ itself can be estimated from the transition latent heat data (about 1 kcal/mol [**1**]), nothing is known about its breakdown into Δ_D and Δ_M. Still another interesting (and unknown at this time) quantity is the thickness x_m of a metallic sliver that forms on the surface bulk (or thick-film) VO_2 in response to an applied electric field. Smallness of this quantity that we have estimated as $x_m = (\hbar/E_G)v_F \approx 10Å$, should account for the unsatisfactory status of the problem today.

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