

Electroforming and Switching in Oxides of Transition Metals: The Role of Metal–Insulator Transition in the Switching Mechanism

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Electroforming and switching effects in sandwich structures based on anodic films of transition metal oxides (V, Nb, Ti, Fe, Ta, W, Zr, Hf, Mo) have been studied. After being electroformed, some materials exhibited current-controlled negative resistance with S-shaped V – I characteristics. For V, Fe, Ti, and Nb oxides, the temperature dependences of the threshold voltage have been measured. As the temperature increased, V_{th} decreased to zero at a critical temperature T_0 , which depended on the film material. Comparison of the T_0 values with the temperatures of metal–insulator phase transition for some compounds ($T_i = 120$ K for Fe_3O_4 , 340 K for VO_2 , ~500 K for Ti_2O_3 , and 1070 K for NbO_2) showed that switching was related to the transition in the applied electric field. Channels consisting of the above-mentioned lower oxides were formed in the initial anodic films during the electroforming. The possibility of formation of these oxides with a metal–insulator transition was confirmed by thermodynamic calculations. © 1996 Academic Press, Inc.

1. INTRODUCTION

The switching effect with current-controlled negative resistance was originally found and investigated in chalcogenide semiconductors (1). Voltage–current curves of some chalcogenide-based thin-film sandwich structures after electrical forming are S-shaped. Similar phenomena have also been observed in oxides, mainly those of transition metals. Threshold switching (without any memory effects) with an S-type V – I curve has been observed in metal–oxide–metal (MOM) structures with Nb_2O_5 (2, 3), NbO_2 (4, 5), TiO_2 (3, 6), VO_2 (7), Ta_2O_5 (3), and Fe oxide (8). The oxide films were prepared by different methods: thermal oxidation of the metals (Nb, Ta, Ti, Fe) (3, 5, 6, 8), anodic oxidation (V, Nb, Ta, Ti) (2, 3, 7), and deposition of niobium dioxide onto NbO substrates (4).

At present there is no consensus on the description of the switching phenomenon. Numerous theoretical explanations of this effect in chalcogenides, oxide glasses, and transition metal oxides fall within two groups according to the mechanism assumed: either electrothermal or electronic (1).

In this paper we report the results on electroforming and switching in MOM structures with thin-film oxides of transition metals—V, Ti, Nb, Fe, Ta, W, Mo, Zr, Hf. All oxide films were obtained by the same technique, namely by anodic oxidation of corresponding metals. Our main concern was to investigate the temperature dependence of the threshold parameters, because these data are required in order to understand the switching mechanism.

2. EXPERIMENTAL

The sandwich devices under study were fabricated by oxidation of the metal substrates: both polished foils and vacuum-deposited layers. Al or Au electrodes were evaporated onto the surfaces of oxide films to complete the MOM structure. The spring-loaded point contacts (gilded wire 0.5 mm in diameter, see Fig. 1a) were also used.

The oxidation was carried out electrochemically, under anodic polarization in an electrolyte. Anodic oxidation (9) permits the synthesis of high-quality homogeneous oxide films. The thickness of the films can be easily controlled by the anodizing voltage. Anodization was carried out under both galvanostatic and voltstatic conditions. Ta, Nb, W, Zr, and Hf were anodized in 0.1 N aqueous solutions of phosphoric and sulfuric acids (9), while for oxidation of vanadium and molybdenum the electrolyte was made up from 22 g of benzoic acid (C_6H_5COOH) plus 40 ml of the saturated aqueous solution of $Na_2B_4O_7$ per liter of acetone (10). Fe, Ti, and several Nb samples were anodized in a $KNO_3 + NaNO_3$ eutectic melt at 570–620 K. The thickness, d , of anodic oxide films (AOF) was estimated using the anodizing voltage V_a in combination with capacitance or optical measurements (9).

The voltage–current characteristics of initial structures and those obtained during and after electroforming were investigated using the ac oscillographic method or a dc recorder. The temperature dependence of the switching parameters was measured in the range from 77 to 600 K in liquid nitrogen (or its vapor) and in air.

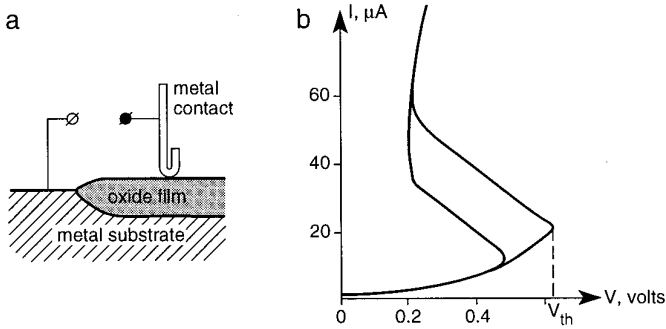


FIG. 1. Sandwich structure (a) and V - I curve (b) of the structure with anodic oxide film on vanadium. Oxide film thickness $d = 120$ nm, $T = 295$ K.

3. RESULTS

3.1. Electroforming and V - I Characteristics

The voltage-current characteristics of the initial structures are nonlinear and slightly asymmetric. The resistance at zero bias, measured with the point contact, is in the range 10^7 – 10^8 Ω for the vanadium anodic oxide, which is the most highly conductive material.

When the amplitude of the applied voltage reaches the forming voltage V_f , a sharp and irreversible increase in conductivity is observed and the $I(V)$ curve becomes S-shaped. With increasing current, the voltage-current curve may change until the parameters of the switching structure are finally stabilized. The process outlined above is qualitatively similar to the electroforming of the switching devices based on amorphous semiconductors (1). The forming voltage depends on the temperature (V_f increases upon cooling) and film thickness. The thicker the film, the higher the required V_f . The value of V_f correlates to that of V_a because d is proportional to V_a (9). A similar correlation is characteristic of the AOF breakdown: the breakdown voltage is also of the order of V_a .

Thus, the first stage of the forming does not differ from the conventional electrical breakdown of oxide films. However, if the postbreakdown current is limited, this results in the formation of a switching channel rather than a breakdown channel. The latter would be expected to have metallic-like conductivity and no negative resistance (NR) in the V - I characteristic. It is quite evident that the phase composition of this switching channel must differ from the material of the initial oxide film, because the channel conductivity exceeds that of an unformed structure by several orders of magnitude.

Forming does not always result in an S-type curve. In some instances a transition of the structure to a high-conductivity state (~ 100 Ω) with ohmic behavior takes place; i.e., in this case breakdown rather than forming occurs. Breakdown is more probable in Ta_2O_5 , WO_3 , HfO_2 , and

MoO_3 films, while in the V- and Nb-based structures, it is the electroforming that results in the S-shaped $I(V)$ curves in most cases. The anodic films on Ti and Fe hold an intermediate position. Switching has not been observed in Zr oxide films. Electroforming of W-, Fe-, and Hf-based structures was carried out at 77 K, because at room-temperature breakdown took place and no switching effects were observed. The characteristic feature of switching in Ta, Mo, Hf, and, to a lesser extent, in W oxide films, is the instability of parameters and the gradual disappearance of the S-type NR under the influence of current flow and thermal cycling.

The voltage-current curve for electroformed vanadium-AOF-metal structure is shown in Fig. 1b. The parameters of the structures (threshold voltage V_{th} and current I_{th} , resistances of OFF and ON states) may vary by up to an order of magnitude from point to point for the same specimen. Such a wide range of variation of the V_{th} and R_{off} values, as well as the absence of correlation between these switching parameters and the parameters of the sandwich structures (the electrode material and area, the film thickness), leads to the conclusion that resistance and threshold parameters are mainly determined by the forming process. Conditions of the forming process cannot be unified in principle, because the first stage of forming is linked to breakdown, which is statistical in nature. As a result, the diameter and phase composition of the channel (and, consequently, its effective specific conductivity) vary with position in the sample. This accounts for the scatter in the parameters and for the seeming absence of their thickness dependence.

Similar behavior has been observed for the other materials. On average, for $d \approx 100$ nm, a typical value of V_{th} is 1–5 V; i.e., the threshold field is $(1\text{--}5) \times 10^5$ V/cm at room temperature. The greatest differences between these oxides are observed when the temperature dependences of their threshold parameters, such as V_{th} , are measured.

3.2. Temperature Dependence of the Threshold Voltage

Figure 2 shows $V_{th}(T)$ curves for the sandwich structures based on iron, vanadium, titanium, and niobium. For Ta_2O_5 , WO_3 , HfO_2 , and MoO_3 , no reproducible results were obtained because of instabilities in their voltage-current curves with temperature. As the temperature increased, V_{th} decreased, tending to zero at some finite temperature T_0 . This is best exhibited by the vanadium and titanium oxide structures. The values of T_0 vary considerably for different oxides, but they are nearly identical for different structures of the same oxide.

In some cases, when a certain value $T = T^*$ is achieved, the region with $dU/dI < 0$ in the $I(V)$ curve vanishes, though the ON and OFF states are separated by an inflection point which marks the V_{th} value. The only exception

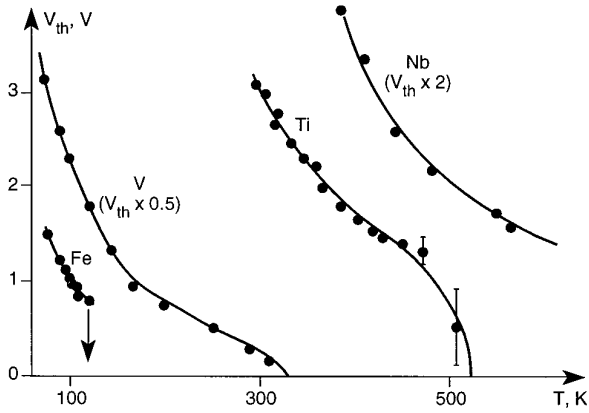


FIG. 2. Threshold voltage for the MOM structures on the basis of different oxides as a function of ambient temperature. The thicknesses of anodic oxide films are: on Fe, 45 nm, on V, 180 nm, on Ti, 200 nm, and on Nb, 60 nm. The structures with point contacts were used, except that a deposited Al top electrode was used in the case of the vanadium oxide sample.

is the behavior of the Fe-based structures, for which (after T^* has been achieved at $V_{th} \neq 0$) the $I(V)$ curve is still nonlinear, yet without any peculiarities. This value of T^* is marked by an arrow in the figure. For the Nb– Nb_2O_5 –metal structures, it was impossible to measure the $V_{th}(T)$ relationship over the whole temperature range, because heating above 300°C induced processes related to diffusion and changes in the channel phase composition, leading to degradation of the switching structure. Nevertheless, it is evident from Fig. 2 that for the niobium oxide, T_0 exceeds 600 K.

3.3. Discussion

3.3.1. Thermodynamics of the electroforming process. We consider the process of electroforming in detail. The initial AOF represents, as a rule, the highest oxide of the metal (e.g., Nb_2O_5 in the case of niobium). However, lower oxides always exist near the AOF–metal interface in the form of transition layers or as separate inclusions. This can be explained in terms of thermodynamics. Consider the reaction



The change of the Gibbs (isobaric) potential for this reaction is

$$\Delta G_r = \nu_2 \Delta G_2^\circ - \nu_1 \Delta G_1^\circ, \quad [2]$$

where ΔG_1° and ΔG_2° are the standard isobaric potentials of formation, and ν_1 and ν_2 are the numbers of moles of oxides which take part in the reaction. For Reaction

[1] the subscripts 1 and 2 in Eq. [2] are related to Nb_2O_5 and to NbO_2 ; $\Delta G_r = -171$ kJ/mole. Since $\Delta G_r < 0$, Reaction [1] proceeds spontaneously; consequently, NbO_2 is always present at the Nb– Nb_2O_5 interface. Similar calculations for NbO as the reaction product yield $\Delta G_r = -45$ kJ/mole.

Many transition metals exhibit multiple oxidation states and form a number of oxides. Obviously, the lower oxide to be formed is mainly that with the minimum ΔG_r . Figure 3 demonstrates the variation of $\Delta G_r(x)$ for Fe_2O_3 , Nb_2O_5 , V_2O_5 , and TiO_2 in reactions similar to [1], where x is the stoichiometric index of oxygen. ΔG_r values were calculated using Eq. [2]; the data on ΔG° for the calculations were taken from Refs. (11, 12). The minima in these curves correspond to Fe_3O_4 , NbO_2 , VO_2 , and Ti_2O_3 ; therefore, these oxides form as intermediate layers between the metal substrate and the corresponding oxide of highest valence. Real systems are far from being a plane-parallel structure with two oxide layers; hence, the suggested approach is rather oversimplified. Nevertheless, the above considerations show that formation of those oxides is thermodynamically reasonable; whether it is kinetically possible can only be judged from experiment. For example, in AOF on vanadium the vanadium dioxide layer may be rather thick (10),

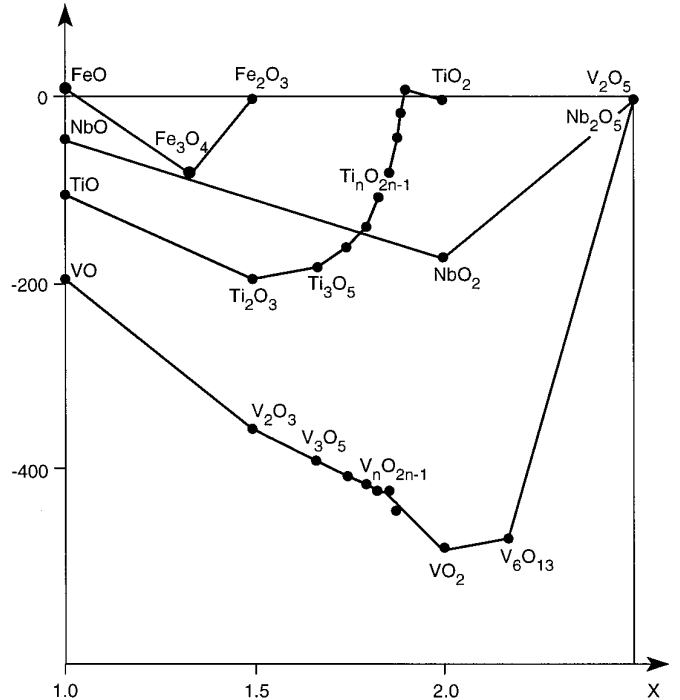


FIG. 3. Gibbs potential change ΔG_r (per 1 g-atom of metal) for the reaction of the highest oxide with metal substrate versus x , the oxygen stoichiometric index of the lower oxide, which is formed in this reaction. All ΔG° values for calculations were taken from Ref. (11) but with more precise data for VO_2 ($\Delta G^\circ = -665$ kJ/mole) and TiO_2 (rutile, $\Delta G^\circ = -888.6$ kJ/mole) (12).

and only a very thin film near the outer boundary is close to the V_2O_5 stoichiometry. The similar ordering of layers evidently exists in iron oxide. It is known that in a thermal oxide of iron, the Fe_3O_4 phase usually predominates (13). On the other hand, the AOF on Nb and Ti mainly consists of Nb_2O_5 and TiO_2 (9), and NbO_2 or Ti_2O_3 layers seem to be relatively thin.

During electroforming, current-induced heating of the film under the electrode leads to a diffusion both of metal from the substrate into the film and of oxygen from the outer layer to the inner layer. Also, the transport of metal and oxygen ions due to the applied electric field is possible. Since no external oxygen is present during electroforming (unlike during thermal or electrochemical oxidation), no reaction can take place except the reduction of the highest oxide of AOF. The reduction results in growth of the channel, consisting of the lower oxide, through the film from one electrode to another. Evidently, substances with the minimum ΔG_T value (see Fig. 3) will be predominant in the phase composition of the channel. The current increase after forming may cause further reduction of the channel material, leading to a predominance of the phases such as VO, NbO, and TiO. Many of the lowest oxides of transition metals (mono- and suboxides) exhibit metallic properties (14); the accumulation of these phases in the channel will therefore lead to an irreversible increase in conductivity, i.e., to breakdown.

3.3.2. Switching mechanism. The above compounds (VO_2 , Fe_3O_4 , Ti_2O_3 , and NbO_2) have one feature in common, namely a metal–insulator phase transition (MIT) (15, 16). The MIT phenomenon is characterized by the sharp and reversible change in the conductivity at a certain temperature T_t . For instance, vanadium dioxide at $T < 340$ K is a semiconductor; at $T = T_t = 340$ K the conductivity abruptly increases by four to five orders of magnitude; above the transition temperature VO_2 exhibits metallic properties. For NbO_2 , $T_t = 1070$ K. Ti_2O_3 undergoes a gradual transition in the range 400–600 K (15). Magnetite is a semiconductor both above and below its transition temperature (~ 120 K) (16), though its resistivity decreases on heating by two orders of magnitude at $T = T_t$. For the switching devices based on these metals, the temperatures T_0 (or T^* in Fe oxide) coincide with the corresponding values of T_t (see Fig. 2). This suggests that the switching mechanism is caused by the metal–insulator transition.

Electrical switching due to MIT has been extensively studied for vanadium dioxide. Switching in VO_2 is explained by the current-induced Joule heating of the sample up to $T = T_t$, which has been confirmed by the direct IR-radiation measurements of the switching channel temperature (17, 18). Switching has been observed in single crystals (19), planar thin-film devices (17, 18), as well as vanadate glasses (20) and V_2O_5 -gel films (21). When as-prepared samples do not consist of pure vanadium dioxide, prelimi-

nary electroforming is required, resulting in the formation of the VO_2 -containing channel (20, 21). In MOM structures of VO_2 (7), the switching effect is also caused by the MIT. For such samples the threshold voltage decreases with temperature and reaches zero at $T = T_t$. Switching elements for other transition metal oxides exhibiting MIT are expected to show similar behavior, but at different T_t 's.

The switching effect in the WO_3 -based sandwich structures can also be explained in terms of a metal–insulator transition, which occurs in nonstoichiometric WO_{3-y} (within a very narrow interval of variable y) at T_t ranging from 160 to 280 K (22). Because of the narrow interval of “appropriate” stoichiometric compositions, the S-type $V(I)$ curve is not likely to appear in tungsten trioxide, and in most cases breakdown occurs instead. For switching structures on anodic films on W, T_0 was found to lie between 77 and 300 K, because switching occurs in liquid nitrogen and is absent at room temperature. Therefore, T_0 may turn out to be equal to T_t .

No data on MIT in molybdenum oxides are available in the literature, except for the transition in one Mo-containing compound (bronze $K_{0.3}MoO_3$, $T_t = 180$ K (15)). Further studies are required to clarify the switching effects in AOF on Mo. Also it seems reasonable to carry out switching experiments in $K_{0.3}MoO_3$. From the electrical properties of Ta and Hf oxides, the formation of metastable lower oxides during electroforming should be also possible. The properties of these oxides are practically unknown, but some metastable oxides of this type have been referred to, for example, for the Ta–O system (14). However, in MOM structures with tantalum, molybdenum, and hafnium oxides (as well as tungsten trioxide), the electrical properties of some local sections of the films may be determined by inclusions of other metals as impurities. This may also account for the problems of reproducibility in these samples.

Thus, the experimental data on the switching effect in d -metal oxide thin films can be explained in terms of a switching mechanism driven by the MIT. We believe that in all cases the electrothermal and electrochemical processes occurring during electroforming are responsible for the switching channel formation. The channel consists of material which can undergo a transition from a semiconducting state to a metallic state at a certain temperature T_t . For the V-, Ti-, Nb-, and Fe-based structures, the possibility of formation of the channels, consisting completely or partly of VO_2 , Ti_2O_3 , NbO_2 , and Fe_3O_4 , respectively, is also confirmed by thermodynamic calculations. The S-shaped voltage–current curve is conditioned by the development of an electrothermal instability in this channel. When a voltage is applied, the channel is heated to $T = T_t$ (at $V = V_{th}$) by the current and the structure undergoes a transition from a high-resistance (OFF) insulating state to a low-resistance (ON) metallic state.

In high electric fields (10^5 – 10^6 V/cm), the possible influence of electronic effects on the MIT should be taken into account. A field-induced increase in charge carrier concentration will act to screen Coulomb interactions (15), leading to the elimination of the Mott–Hubbard energy gap at $T < T_t$. Moreover, transitions of this type may be important in those materials where the usual temperature-induced MIT with a well-defined T_t does not take place; i.e., in oxides of Ta or Hf, or in chalcogenide glasses.

4. CONCLUSION

The results presented above, as well as the other data on the switching in transition metal oxides (2–8), indicate that current instabilities with the S-type NR exhibit several common features. In particular, for each of the investigated materials there is a certain fixed temperature T_0 , above which switching disappears. At $T \leq T_0$, the threshold voltage decreases as the temperature rises, tending to zero at $T = T_0$. Comparison of these temperatures with the temperatures of MIT for some compounds ($T_t = 120$ K for Fe_3O_4 , 340 K for VO_2 , ~ 500 K for Ti_2O_3 , and 1070 K for NbO_2) shows that the switching effect seems to be associated with the insulator–metal transition in an electric field. The channels, consisting of these lower oxides, are formed in anodic films initially produced during preliminary electroforming.

We emphasize that in this paper we have confined our attention strictly to S-type threshold switching in oxides of transition metals. Electrical instabilities with voltage-controlled (N-type) NR and various memory effects have also been reported by many workers both in oxides and in other materials (23). However (aside from chalcogenide semiconductors), “pure” threshold switching with an S-shaped $I(V)$ curve is characteristic of number of transition metal oxides. This is closely linked to the electronic structure of the transition metals. A set of valence states associated with the existence of an unfilled d -shell in these atoms leads to the formation of several oxide phases with different properties, ranging from metallic to insulating (14). This accounts for the ease of chemical transformations during electroforming. On the other hand, it is specifically the behavior of d -electrons in the compounds of transition metals that is responsible for the unique properties of these materials, causing strong electron–electron and electron–phonon correlations, which play an important role in the mechanism of MITs (15, 16).

To summarize, the above discussion was intended to show that with a simple electrothermal model it is possible to explain the experimental data on switching in MOM

structures based on anodic films of transition metal oxides. In this model it is assumed that the switching mechanism is connected to the MIT. For a more detailed understanding, it is important to take electron-correlation effects into account, which may contribute to the development of the insulator-to-metal transition in high electric fields.

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