THERMAL MECHANISM OF THE SWITCHING EFFECT IN OXIDIZED VANADIUM

B. A. Tallerchik, E. I. Terukov,
and F. A. Chudnovskii

UDC 537.311.33

Experimental data characterizing the switching phenomenon in oxidized vanadium are presented. In order to explain the switching phenomenon thermal models of the "critical temperature" and "thermistory" types are introduced.

Thermal instability is often the cause of breakdown in dielectrics and semiconductors subject to the influence of an electric field.

At the instant at which the Joule power evolved in the sample under the influence of an electric current exceeds the rate of heat dissipation (transfer to the ambient), an avalanche-like rise in temperature occurs. The unlimited rise in current associated with the exponential fall in the resistance of the dielectric or semiconductor resulting from the rise in temperature leads to the breakdown of the material. If the breakdown is reversible, it may be put to practical use.

For example, in the case of thermistors breakdown leads to the development of an S-shaped volt–ampere characteristic, such as that illustrated in Fig. 1; this is called the "thermistor" effect [1, 2].

In the recent years many materials with an S-shaped volt–ampere characteristic have been found. These materials are used for making so-called "switching" cells or elements, and the reversible-breakdown phenomenon is called the "switching effect" [3]. In many such elements (which have found practical service in computing technology and microelectronics) the cause of the switching phenomenon is the "thermistor effect."

Switching elements composed of vanadium dioxide VO_2 [4] are of particular interest. This material undergoes a phase transiton at 70°C, changing from the semiconducting (below 70°) to the metallic state (above 70°), accompanied by a sharp jump in resistance (up to five orders of magnitude) [5].

The existence of a jump in resistance at 70°C is due to the specific character of the switching properties in VO_2 elements. In these elements the Joule power only heats the sample to the phase-transition temperature. There is thus no superheating in VO_2 (superheating is very substantial in materials having no such phase transition), and this has the effect that VO_2 elements exhibit better switching characteristics and have a longer service life than those made of other materials. The model describing this effect is called the "critical temperature" model [6, 7].

Among the large number of different kinds of materials exhibiting the switching effect, one of the latest proposed is vanadium foil preliminarily subjected to air oxidation [8]. Elements based on this kind of foil are particularly simple to make and may act as both switching elements and inductances in microelectronic circuits [9].

A mechanism was proposed in the latter paper for the switching effect in this material. According to Yu and Fisher [9], all the observed switching laws may be explained as being due to the "thermistor effect." Our own investigations disagree with Yu and Fisher [8, 9] as regards both the experimental data and their possible interpretation. We ourselves studied the switching effect in vanadium foil subjected to air oxidation at 480°C. The samples were square in shape, cut from vanadium foil 25 μ thick.

A. F. Ioffe Physicotechnical Institute, Academy of Sciences of the USSR, Leningrad. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 28, No. 2, pp. 257-262, February, 1975. Original article submitted May 8, 1974.

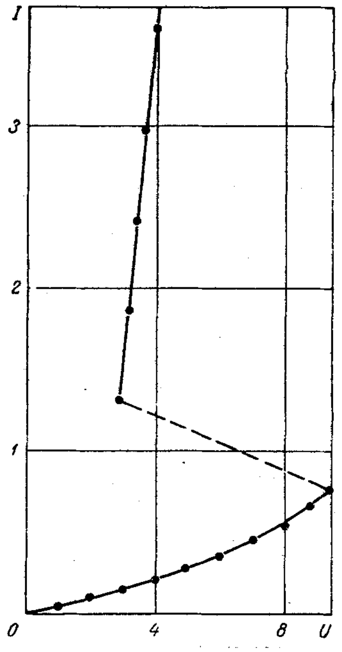

Fig. 1. Volt–ampere characteristic of oxidized vanadium foil. I, in mA; U, in V.

A typical volt–ampere characteristic of a sample possessing the switching effect is presented in Fig. 1. In recording the volt–ampere characteristic of used sprung copper contacts with a contact area of 1 mm^2. The resistance of samples made in this way varied from several ohms to tens of kiloohms, depending on the oxidation period. Depending on the resistance of the samples, the switching voltage varied from one to several tens of volts.

The dependence of the switching voltage U_S on the resistance of the layer R at room temperature was of the $U_S \sim \sqrt{R}$ type. We see from Fig. 2, that divergences from this relationship develop at low resistances. It should be noted that in samples prepared in this way the switching effect only began from a certain limiting resistance, of the order of tens of ohms; below this no switching effect occurred.

The temperature dependence of the resistance of low-resistivity oxidized vanadium foil exhibited a jump in resistance at 50-70°C (characteristic of the VO_2 metal-semiconductor phase transition), as well

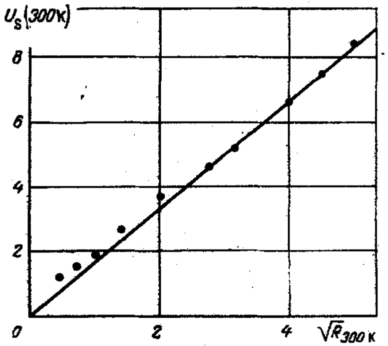

Fig. 2

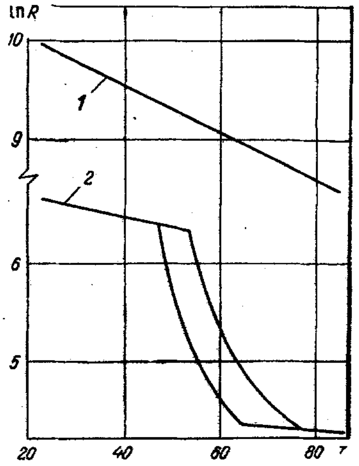

Fig. 3

Fig. 2. Switching voltage as a function of the square root of sample resistance at room temperature $(R_{300}) \cdot (U_S$, V; R, kΩ; $\sqrt{R_{300K}}$, $(k\Omega^{1/2})$. Continuous line, calculation; points, experimental.

Fig. 3. Temperature dependence of the resistance of high-resistivity (curve 1) and low-resistivity (curve 2) samples (T, °C). Conductivity activation energies 0.2 and 0.09 eV for curves 1 and 2, respectively.

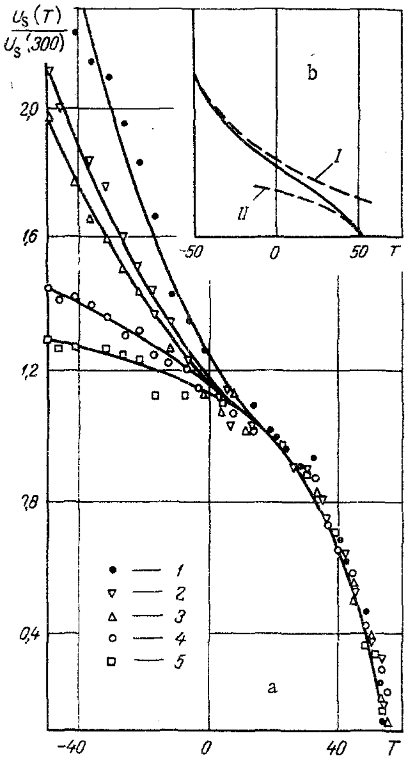

Fig. 4. Temperature dependence of the switching voltage (1, resistance of the 26-kΩ sample, 2) 16, 3) 13, 4) 500, 5) 200) (a), and temperature dependence of the switching voltage borrowed from [7] (I) $U_s \sim T_0 \exp(E/2kT_0)$; II) $U_s \sim (T_k - T_0)^{1/2}$). T in °C.

as temperature hysteresis (Fig. 3) [5]. At temperatures below 50°C the temperature dependence of the low-resistivity samples bore an exponential character.

For high-resistivity samples the temperature dependence of the resistance had an exponential character over the whole temperature range studied, and no hysteresis appeared (Fig. 3).

The activation energy of the samples studied was markedly dependent on the time of oxidation. For nominal resistances between tens of ohms and tens of kiloohms, the activation energy rose from 0.09 to 0.2 eV. The thickness of the oxide layers meanwhile varied from $(3.0 \pm 1)\ \mu$ for low-resistivity samples to $(5.0 \pm 1)\ \mu$ for those of the high-resistivity type.

We recorded the switching voltage as a function of the ambient temperature for oxidized vandium foil with various nominal resistances. The experimental data are presented in Fig. 4a. We see from Fig. 4a that above room temperature the relationship between the switching voltage and the ambient temperature is of the same character in both low- and high-resistivity samples. The temperature at which the switching effect vanishes completely is ~60°C. We note that this is close to the phase-transition temperature of VO_2.

Below room temperature the relationship between the switching voltage and the ambient temperature constitutes a family of curves, with the sample resistance acting as a parameter.

Discussion of the Experimental Results. The foregoing experimental results may be explained within the framework of the two thermal models proposed for describing the switching properties of VO_2 in [6, 7], the "critical temperature" effect being operative above room temperature and the "thermistor model" below.

1. As already indicated, the "critical temperature" model assumes that, as a result of the heating of the sample by the Joule thermal energy, the phase-transition temperature of VO_2 (~70°C) is reached, and the sample resistance changes very sharply. For this model the switching voltage is

$$U_s^2 = \frac{\alpha (T_k - T_0)}{\sigma_0} \exp\left(\frac{\Delta E}{kT}\right). \tag{1}$$

2. In the "thermistor model" [10], it is considered that, under the action of Joule heat, the temperature of the material increases in such a way that, owing to the exponential character of the electrical conductivity, the resistance of the sample falls sharply and the volt – ampere characteristic becomes S-shaped. The temperature dependence of the switching voltage is then

$$U_s^2 = \alpha \frac{kT_0^2}{\sigma_0 \Delta E} \exp\left(\frac{\Delta E}{kT_0} - 1\right). \tag{2}$$

The temperature dependence of the VO_2 switching voltage actually observed may readily be explained by these two mechanisms, the "thermistor model" being operative below room temperature and the "critical temperature" model above, as in Fig. 4b.

3. The experimental results obtained in the present investigation may readily be explained on the basis of these two models on allowing for the change in conductivity activation energy which occurs during the oxidation of the foil.

Above room temperature we have $U_s \sim (T_k - T_0)^{1/2}$ for every one of the samples studied, this being a characteristic relationship for the "critical temperature" model, as in Eq. (1) (compare Figs. 4a and 4b). Moreover, for this model we have $U_s \sim \sqrt{R}$, as in Eq. (1). In Fig. 2 the continuous line illustrates our calculated relationship between U_s and $\sqrt{R}$. We see that only in the low-resistance range is there any deviation from this relationship, and this may be attributed to the small thickness of the layer on the low-resistivity samples. It is well known that in thin samples contact phenomena may play an appreciable role, and that as a result of this the switching characteristics deviate from those predicted by purely thermal laws [11].

The behavior of the air-oxidized vanadium foil may be explained by the presence of VO_2 in the oxidized layer, in addition to other oxides. This is confirmed by analysis based on x-ray diffraction. The VO_2 phase, in fact, appears in both high- and low-resistivity samples. Apparently, the VO_2 phase plays a leading part in the switching properties of such foils above room temperature in both high- and low-resistivity samples, although in the high-resistivity samples the electrical properties of the phase fail to appear at low voltages (no temperature hysteresis), in agreement with the results presented in [8].

Below room temperature the behavior of the high- and low-resistivity samples differs considerably. For the high-resistivity samples $U_S \sim \exp(\Delta E/2kT_0)$. This behavior is described by the ordinary thermistor model, as in Eq. (2). The behavior of the low-resistivity samples, on the other hand, may be explained within the framework of the "critical temperature" model, after allowing for the changes taking place in the conductivity activation energy. The fall in activation energy in the low-resistivity samples, in fact, shifts the temperature T_{01} of the transition from the "thermistor model" to the "critical temperature" model in the low-temperature direction. Actually, if we remember that for $T_k = 330°K$ and $T_0 = 300°K$ the exponential terms in Eqs. (1) and (2) are approximately equal, we obtain the following equation for the temperature of the transition from the "thermistor model" to the "critical temperature" model:

$$\frac{kT_{01}^2}{\Delta E} \cong T_k - T_{01}. \qquad (3)$$

If in Eq. (3) we substitute the experimental value of the activation energy for the low-resistivity samples, E = 0.09 eV, we obtain $T_{01} = 246°K$. This indicates that the "critical temperature" model holds reasonably well for low-resistivity samples, even below room temperature. For a more accurate quantitative analysis we must also allow for the thickness of the layer.

We may thus draw the following conclusions:

1. In an oxidized vanadium foil having a resistance of tens or hundreds of ohms the temperature dependence of the switcing voltage may be qualitatively described in a very satisfactory manner (over the whole temperature range studied) within the framework of the "critical temperature" model, after allowing for the changes taking place in the activation energy of electrical conduction. In samples having a resistance of the order of tens of kilohms, the "critical temperature" model holds above room temperature and the "thermistor model" below.

2. The switching properties of the oxidized vanadium foil may be explained by the presence of a VO_2 phase in the oxide layer; this is supported by x-ray diffraction analysis and electrical measurements.

NOTATION

U_S	is the switching voltage, V;
R	is the resistance of oxide layer, Ω;
α	is the thermal conductivity, W/m·°K;
T_k, T_0, T_{01}	are the critical temperature, temperature of the surroundings (ambient) and transition temperature from one model to the other, °K;
σ_0	is the electrical conductivity as $T \to \infty$, $\Omega^{-1} \cdot m^{-1}$;
ΔE	is the conductivity activation energy, eV;
k	is the Boltzmann's constant, $W/m^2 \cdot deg^4$.

LITERATURE CITED

1. A. G. Shashkov, Thermoresistors and Their Application [in Russian], Énergiya, Moscow (1967).
2. I. Duchene, Microelectronics, 4, 37 (1972).
3. S. R. Ovshinsky, Phys. Rev. Lett., 21, 1450 (1968).
4. K. Van Stensel, F. Van de Burg, and C. Kooy, Phil. Res. Rep., 22 (170) (1968).
5. W. Paul, Mat. Res. Bull., 5, 691 (1970).
6. C. N. Berglund, IEEE Trans. on Electron. Devices, ED-16, No. 5, 432 (1964).
7. J. C. Duchene, M. M. Terraillon, M. Pailly, and G. B. Adam, IEEE Trans. on Electron. Devices, ED-18, No. 12, 1151 (1971).

8. R. I. Yu and P. D. Fisher, IEEE Trans. on Electron. Devices, ED-18, No. 10, 975 (1971).
9. R. I. Yu and P. D. Fisher, Appl. Phys. Lett., 19, No. 5, 158 (1971).
10. H. Fritzche and S. R. Ovshinsky, J. of Noncryst. Solids, 4, No. 2, 464 (1970).
11. B. T. Kolomiets, É. A. Lebedev, and K. D. Tsédin, Fiz. Tekh. Poluprov., 5, No. 8, 1568 (1971).