CRITICAL THERMISTORS BASED ON V_nO_{2n-1} (n = 3-6)

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New types of critical thermistors are proposed, based on V_3O_5, V_4O_7, V_5O_9, and V_6O_{11}. It is shown that they can be prepared from Magnelli-phase single crystals, which do not decompose during the phase change. Volt—ampere characteristics and switching voltage—temperature curves were obtained.

Thermally sensitive semiconductor resistors are widely used in various branches of technology. Among these, a special position is occupied by critesistors, i.e., thermistors which show a jump in resistance at some critical temperature T_c. Below T_c, their resistance is high and varies exponentially with temperature, while above T_c it is metallic in nature. The sharp change in resistivity at T_c is due to a metal—semiconductor phase change, such as is exhibited by certain transition and rare earth metal oxides and chalcogenides. Vanadium oxides show this behavior most clearly. Several types of critesistors based on V_2O_3 and VO_2 have been manufactured and used in a variety of equipment [1, 2]. Type ST8 polycrystalline thermistors based on V_2O_3 are fabricated by ceramic sintering techniques. Their resistance changes by more than three orders of magnitude in the vicinity of 140°K. The same procedure is used in fabricating type ST9 thermistors, based on VO_2, which have a two-order resistance jump at about 340°K. Although widely used in technology, these thermistors have a number of basic disadvantages. In particular, a resistance jump by a factor of 100-1000 is clearly insufficient for many automatic control systems. A steeper change would also be desirable. Single VO_2 crystals show eight orders [4]. Their polycrystalline counterparts have jumps which are several orders smaller.

The production of V_2O_3- and VO_2-based thermistors in sintered polycrystalline form is justified not only on a technological basis, but by the fact that single crystals of these compounds develop cracks as a result of repeated switching between the semiconducting and metallic states. This changes their electrical

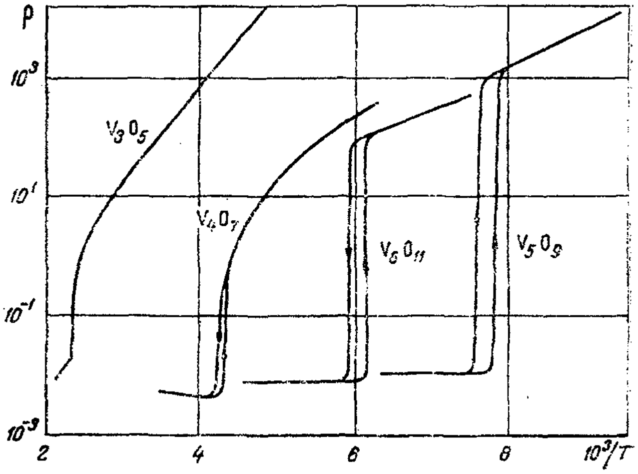

Fig. 1. Resistivity vs temperature for single crystals of vanadium oxide ρ, Ω · cm; $10^3/T$, °K^{-1}.

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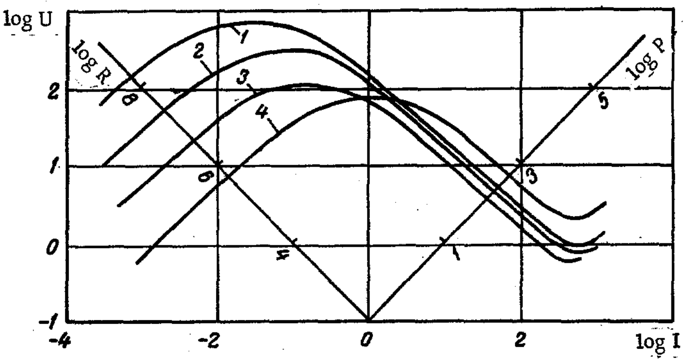

Fig. 2. Magnelli-phase thermistor characteristics, measured in still air. 1) V_4O_7, 77°K, 2) V_5O_9, 77°K, 3) V_6O_{11}, 77°K, 4) V_3O_5, 207°K. U in volts, P in mV, I in mA, R in Ω.

characteristics markedly. Single V_2O_3 crystals are particularly prone to cracking, and break down after several tens of switchings. The nature of this cracking is still unclear. We believe that a possible cause is twin formation on going from metal to semiconductor. This is related to monoclinic deformation occurring in the phase transition, as a result of the displacement of vanadium atoms along one of the three basic hexagonal axes b_H. This deformation is equally probable along each of the three directions, and twinning is a result of this threefold degeneracy [5]. Twinning in VO_2 is caused by the arbitrary pairing of vanadium atoms along the monoclinic axis a_M in the metal — semiconductor transition [6]. High stresses occur at the twin boundaries, because of the strong deformation anisotropy, and cause single-crystal cracking. This is especially pronounced in V_2O_3, in which the unit-cell volume changes by 3% during the phase transition [4].

In addition to V_2O_3 and VO_2, vanadium forms a series of intermediate oxides, in which the vanadium ion is trivalent and quadrivalent. These oxides were first prepared by Magnelli and are called Magnelli phases. The general formula for these compounds is V_nO_{2n-1}, where n = 3-9. Most of them have a metal — semiconductor phase transition. Table 1 indicates phase-transition temperatures and resistivity jumps for these compounds [7]. As seen from the table, vanadium oxides cover the temperature range from 70 to 420°K. This makes possible the development of new types of critesistors with various critical temperatures. We have undertaken to develop such devices.

Fabrication Technique

Magnelli-phase single crystals were grown in a closed volume, using the gas-transport reaction method with $TeCl_4$ as the carrier [7]. This method was selected because of its simplicity and the quality of crystals produced.

The initial charge was prepared from a mixture of V_2O_3 and V_2O_5 powders, in the proper ratio to yield the desired oxide. After careful mixing, the charge was heated in a sealed ampoule for 2 days at 600°C, followed by 5-6 days at 900°C. It was then ready for the transport process.

The transport reaction was performed in optical quartz ampoules with inner diameter 14-17 mm, wall thickness 2-2.5 mm, and length 150-190 mm. Approximately 2 g of powder was placed in the bottom of the ampoule. Since $TeCl_4$ is very hygroscopic, it was added to the ampoule in a vacuum. Transport took place over a period of 10-30 h in an oven with a temperature gradient. The source zone was at 1040°C and the crystallization zone was at 920°C. After completion of the process, the ampoule was opened and washed with hot HCl. The crystals were then washed with hot and cold water and dried.

TABLE 1. Phase-Transition Characteristics in Vanadium Oxides

Compound	V_2O_3	V_3O_5	V_4O_7	V_5O_9	V_6O_{11}	V_7O_{13}	V_8O_{15}	VO_2
Phase-transition temperature, °K	150	420	244	129	174	—	70	340
Resistivity jump	10^8	10^2	10^3	10^6	10^4	—	10^1	10^5

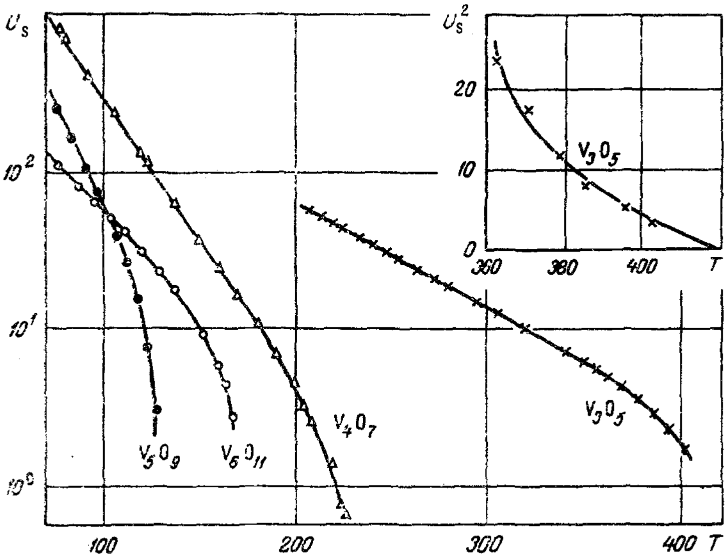

Fig. 3. Log of switching voltage vs temperature for vanadium oxide thermistors. Upper right-hand corner: U_s^2 vs T for V_3O_5-based thermistor. U_s in volts, U_s^2 in volts^2, T in °K.

Single crystals of V_3O_5, V_4O_7, V_5O_9, and V_6O_{11} were grown in this way. Their compositions were checked by x-ray analysis and by their resistance — temperature curves. The crystal forms and dimensions varied over a rather wide range. The best specimens had dimensions of $7 \times 2.5 \times 1$ mm. Some crystals grew in the form of needles 6-7 mm long and 0.01-0.02 mm^2 in cross section.

The gas-transport method can also be used to grow epitaxial vanadium oxide films. In particular, we have grown single-crystal VO_2 films with a resistivity jump of about four orders, using single TiO_2 (rutile) crystals as substrates.

Specimen Characteristics

Measurements of resistivity vs temperature were made on the crystals using the four-contact method. Colloidal-silver contact material was used. The resistivity curves are shown in Fig. 1. It can be seen from Fig. 1 that all the compounds had rather sharp resistivity jumps of several orders of magnitude. All the oxides exhibited temperature hysteresis.

This behavior makes it possible to fabricate thermistors with the following critical temperatures: V_3O_5 — 420°K, V_4O_7 — 235°K, V_6O_{11} — 169°K, and V_5O_9 — 130°K. The most perfect specimens, in the form of plates 3-6 mm long and 0.5-0.05 mm^2 in cross section, were selected for these devices. A layer of silver was applied to the ends of the specimen by firing silver paste or by sputtering in a vacuum. Flexible leads were then soldered to the silver. The resistances of these thermistors in the conducting state did not exceed 1 Ω.

We have studied the variation in temperature dependence of resistance with the number of switchings from the metallic to the semiconducting state. The change in device parameters did not exceed 20% after $3 \cdot 10^4$ switchings. The resistance in the conducting state usually increased somewhat. The specimens were examined under the microscope after each 1000 switchings. In some of the single crystals, cracks were formed which increased in size with subsequent switching. However, crack formation was a result of crystal imperfections, and occurred at the block boundaries in block crystals. These cracks did not form in perfect crystals.

The stability of single Magnelli-phase crystals against repeated transitions from metal to semiconducting phase clearly distinguishes them from V_2O_3 and VO_2 crystals, in which cracks appear on the first switching and result in breakdown after repeated switching. As indicated earlier, this cracking may be caused by twinning during the phase transition. There is no twinning in the Magnelli phases, and their single crystals do not break down in passing through the critical temperature. The stability of V_nO_{2n-1} crystals against repeated transitions through the critical point opens broad possibilities for the use of these oxides in single-crystal form, for which the resistance-jump steepness and the jump itself are considerably greater than for polycrystalline sintered material.

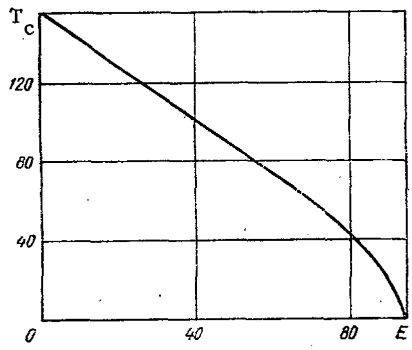

Fig. 4. Critical temperature T_c vs electric field E for V_2O_3 single crystals. E in kV/cm.

The volt—ampere characteristics of these critesistors are important because they provide information concerning the resistance—power dissipation relationship in the ON state. Typical Magnelli-phase thermistor characteristics are shown in Fig. 2. A log—log scale is used, since the same curves, relative to axes at 45°, represent resistance vs power dissipated. Deviation of the volt—ampere characteristics from Ohm's law begins at a power dissipation above 1 mW. As for conventional thermistors with negative temperature coefficients of resistance, the characteristics have segments with negative differential resistance, whose occurrence is related either to the usual thermistor effect or with heating to the critical temperature T_c, depending on the ambient temperature. The question of which switching mechanism is operative at a particular temperature can be decided from the variation of switching voltage with ambient temperature. An expression for the switching voltage U_s as a function of ambient temperature T_0 can easily be obtained from the heat-balance equation, giving

$$U_s = \sqrt{HA(T_M - T_0)\exp\left(\frac{B}{T_M}\right)}, \tag{1}$$

where the thermistor temperature T_M at the maximum of the volt—ampere characteristic is

$$T_M = \frac{B}{2}\left(1 - \sqrt{1 - \frac{4T_0}{B}}\right). \tag{2}$$

Since T_M must not exceed the critical temperature T_c, i.e., $T_M \leq T_c$, then for

$$T_0 < \frac{B}{4}\left[1 - \left(1 - \frac{2T_c}{B}\right)^2\right] \tag{3}$$

the switching voltage will depend exponentially [1] on ambient temperature, as for a conventional thermistor, and for

$$T_0 > \frac{B}{4}\left[1 - \left(1 - \frac{2T_c}{B}\right)^2\right] \tag{4}$$

the relationship will be

$$U_s = \sqrt{HA\exp\left(\frac{B}{T_c}\right)}\sqrt{T_c - T_0}. \tag{5}$$

Figure 3 shows switching voltage vs ambient temperature for Magnelli-phase thermistors. It can be seen from Fig. 3 that for temperatures which differ greatly from the transition temperature T_c, the relationship is exponential, while at temperatures near T_c the switching voltage varies as $T^{1/2}$, corresponding to heating to the critical temperature. The temperatures at which the transition from one switching mechanism to the other occurs are V_3O_5 — 380°K, V_4O_7 — 190°K, V_5O_9 — 103°K, and V_6O_{11} — 115°K. These temperatures are in good agreement with the values obtained from expression (3).

In conclusion, we will discuss some possible applications of vanadium oxide critesistors. The first broad area of application is based on using the resistance jump directly. They can be used for contactless switching in heat-protection systems, in systems for temperature measurement, monitoring, and control, in systems for monitoring and controlling compressed-gas levels, etc. [1, 2]. These systems are extremely simple, reliable, and inexpensive. Their disadvantage is that the choice of critical temperatures is small, and methods of varying the critical temperature are not well-developed. Moreover, varying T_c usually results in a decrease in the resistance jump [8].

At the present time, the relay effect, i.e., varying the critical temperature by an applied electric field, is very significant. The effect of electrical field on T_c in dc operation is a result of ordinary Joule heating, as shown by the curves of Fig. 3. However, when the dissipation coefficient H is increased, or when the device is operated in the pulsed mode, the cause of switching may be different. We have made a detailed study of the effect of electric field on V_2O_3 [9]. It turns out that in this case, T_c is a linear function of the applied field down to 40°K, as shown in Fig. 4. This relationship results from the effect of the field on the electronic structure of the crystal and is a purely electronic effect. It has been reported [10] that for pulses shorter than 1 μsec in VO_2, switching from the dielectric to the metallic state cannot be explained on the basis of Joule heating. The nature of the effect of electric field on transition temperature in Magnelli phases requires additional investigation.

NOTATION

U_S, switching voltage; H, dissipation coefficient; A and B, material constants; T_M, temperature at volt—ampere characteristic maximum; T_0, ambient temperature.

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