Nonlinear electrical conductivity of V_2O_5 single crystals

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The electrical conductivity of V_2O_5 was studied in the temperature range 200–300 K. The measured I-U characteristics in this range are S shaped, consisting of a linear, Ohmic regime at lower current densities and a nonlinear one at higher current densities. $\ln\sigma$-vs-$(10^3/T)$ curves recorded in the Ohmic regime of the corresponding I-U characteristics show a temperature depended activation of the conductivity. In the negative-differential-resistance (NDR) region of the I-U characteristics, periodic, quasiperiodic, and chaotic oscillations were occasionally observed. A considerable increase of the sample temperature was registered in the NDR region of the I-U curves. It is shown that current filamentation can well explain qualitatively and quantitatively the form of the I-U curves. A purely thermal process can account both for the NDR region and for the temperature elevation in this region.

I. INTRODUCTION

Vanadium pentoxide (V_2O_5) is an n-type semiconductor[1,2] with a direct energy gap[3,4] [E_g(300 K)=2.19–2.36 eV]. It has a structure of space-group symmetry D_{2h}^{13} ($Pmnm$).[5,6] This material shows an easy cleavage normal to the b crystallographic axis. In other reports[7,8] the behavior of the electrical conductivity of V_2O_5 is attributed to the presence of localized states below the conduction band. Therefore the dependence of the electrical conductivity on ambient temperature is similar to that frequently observed in many amorphous materials.[9]

The current-voltage (I-U) characteristics of V_2O_5 exhibit switching and negative differential resistance (NDR).[10] Similar results have been observed in VO_2 single crystals.[11] Such effects are usually considered to have a thermal origin.[11] The formation of a current filament is among the principal considerations for the interpretation of NDR. However, such phenomena in bulk single crystals of V_2O_5 have not been extensively investigated, and detailed data concerning current filamentation and the origin of the NDR region have not yet been reported.

In the present work we report on the Ohmic conductivity of V_2O_5 single crystals as well as on the filamentary conductivity in the post-breakdown region of the I-U characteristics

II. EXPERIMENT AND RESULTS

Single crystals of V_2O_5 were grown by heating finely powdered high-purity V (nominally 99.9%) in an oxygene atmosphere (pressure 100 Torr) for 50 h at 480 °C. After this procedure single crystals were obtained with a ratio [V]/[O] corresponding to that of the V_2O_5 oxide.

Measurements of the electrical conductivity were carried out on V_2O_5 single crystals with typical dimensions $\sim 10\times1\times1$ mm^3. The four-contact method and measurements on samples with different electrode distances proved that copper paste forms Ohmic contacts of low resistivity with this material. A four-contact geometry was used in our experiments. Measurements were performed on the a-c plane of V_2O_5 crystals, and current was controlled by a Keithley 225 constant-current source. The voltage drop on the voltage electrodes was measured by a Keithley 610A electrometer.

Current-voltage (I-U) characteristics were measured in the ambient temperature range 200–300 K. Ambient temperature will be denoted in the following as T_0.

As shown in Fig. 1, I-U curves consist of two regions: the Ohmic one at lower current densities and a nonlinear one at higher current densities. Furthermore, the NDR region is more pronounced in the characteristics measured at low ambient temperatures, while at 300 K this region almost disappears. With decreasing ambient temperature the critical voltage (V_{th}) at which the slope dI/dU first becomes negative shifts to higher voltage values (first inset in Fig. 1), while the corresponding current I_{th} shifts to lower current values. In the NDR region the voltage keeps decreasing with increasing current. We observe the same behavior of the I-U characteristics also for ambient temperatures below 200

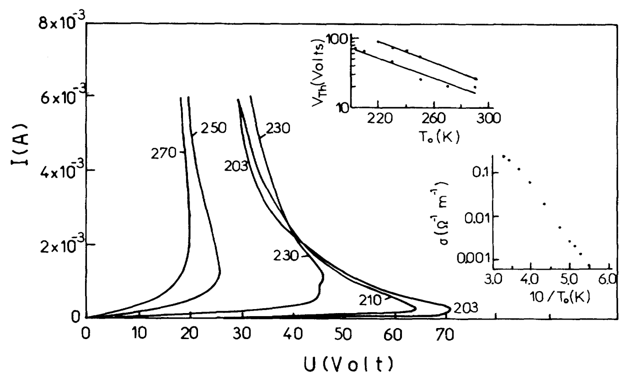

FIG. 1. I-U curves measured on V_2O_5 single crystals at various temperatures. In the first inset is shown the dependence of the threshold voltage on ambient temperature, as measured on two V_2O_5 samples. In the second inset is displayed the Ohmic conductivity of V_2O_5 crystals vs the reciprocal ambient temperature.

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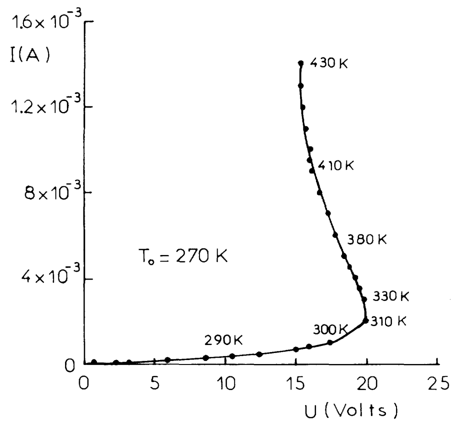

FIG. 2. Temperature values of T as measured on a typical I-U curve.

K. Maximum current was kept below 15 mA in order to avoid irreversible heat damages of the sample. After the first run, obtained with increasing current values, we measured the same I-U with decreasing current values. This measurement was in good agreement with the initial one. An I-U obtained with decreasing current values followed a hysterisis loop only after large currents had passed through the sample.

The temperature of the samples was monitored at every point of the I-U characteristic. This was succeeded using thermocouples in thermal contact with the samples. Electrical contact was avoided by applying an appropriate paste. Sample temperature will in the following be denoted as T. It was established that there is a considerable increase of the sample temperature above ambient temperature in the post-breakdown region. Threshold always occurs at $\sim$300 K. Figure 2 shows temperature values T as monitored on a typical I-U curve [see also Figs. 4(a) and 4(b)].

The $\ln\sigma$-vs-$(10^3/T_0)$ plot of V_2O_5 as measured in the Ohmic part of the corresponding I-U characteristics is shown in the second inset of Fig. 1. This curve shows that the dependence of the Ohmic conductivity of this material on temperature in the range 200–270 K follows an exponential law, leading to an activation energy $\Delta E = 0.246$ eV. At higher temperatures this dependence becomes weaker and yields an activation energy of 0.164 eV. These results are in very good agreement with values previously reported in the literature.[7,8]

III. INTERPRETATION AND DISCUSSION

A. Ohmic region

Vanadium pentoxide is generally considered as a low-mobility semiconductor.[12] Models proposed to explain the conductivity mechanisms apply Mott's theory,[7,8] assuming that vanadium pentoxide is a quasiamorphous semiconductor. In this case the Fermi level is pinned at localized states existing in the energy gap. At intermediate temperatures ($200 < T_0 < 270$ K), hopping conduction of carriers is expected, leading to a thermally activated exponential law. Theory predicts[7,13] that at these temperatures drift mobility changes as

$$\mu \sim T_0^{3/2} \exp(-E_a/k_B T_0) \ . \tag{1}$$

This law holds well for V_2O_5, and E_a was found[7] to be 0.16 eV. Since

$$\sigma = ne\mu \ , \tag{2}$$

conductivity should change with temperature according to the relation[14]

$$\sigma \sim T_0^{-3/2} \exp[-(\Delta + E)/k_B T_0] \ , \tag{3}$$

where Δ is the coupling energy of the carriers with the localized levels; the literature[7,13] estimates Δ by statistical calculations to be $\Delta = 0.10-0.12$ eV. Therefore the activation energy of the conductivity is expected to be

$$\Delta E_1 = \Delta + E_a = 0.10 + 0.16 = 0.26 \text{ eV} \ ,$$

in good agreement with the experimentally found value $\Delta E_1 = 0.264$ eV.

At higher temperatures ($T_0 > 270$ K), almost all electrons in V_2O_5 are free.[7,13] Conductivity therefore follows the mobility law, given by Eq. (1). Indeed, measurements above 270 K, shown in the second inset of Fig. 1, produce a slope much lower than the previous one, leading to an activation energy $\Delta E_2 = 0.16$ eV.

B. Nonlinear conductivity

The significant elevation of the sample temperature in the NDR region, together with the shift of the threshold voltage (V_{th}) to higher values with decreasing ambient temperature, clearly hints that an electrothermal process is dominantly responsible for the NDR region of the I-U characteristics.

In this case the heat-balance equation must hold well. Requiring radially independent solutions of the steady state $[(dT/dt) = 0]$, the following relation is obtained:[15]

$$-8\kappa/d^2(T - T_0) + \sigma(T,E)E^2 = 0 \ , \tag{4}$$

where κ is the thermal-conductivity coefficient, d the distance between the electrodes, σ the electrical conductivity, and E the electric-field strength.

We considered a value of thermal conductivity, $\kappa = 0.02 \text{ W cm}^{-1} \text{K}^{-1}$ (see also in Ref. 16 values of κ for three different vanadium oxides). By the use of Eq. (4), we derived the values of electrical conductivity, σ, in the nonlinear region of the I-U characteristic. The values were found to be almost identical for all ambient temperatures and followed an exponential law of the form

$$\sigma = \sigma_0 \exp(-E_a/k_B T) \ ,$$

where $E_a \sim 0.19$ eV. Such curves are shown in Fig. 3 for different ambient temperatures.

The activation energy E_a is practically the same before (0.16 eV) and after (0.19 eV) the threshold.

In case that a thermal process is indeed responsible for our results, the temperature distribution at the various points of the I-U curve should be given by[17]

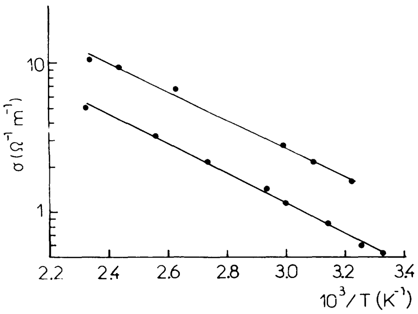

FIG. 3. Conductivity vs sample temperature in the nonlinear part of the I-U curves, as calculated from Eq. (4), at two different ambient temperatures.

$$T = T_0 \Delta E\{\Delta E + k_B T_0[\ln(R/R_{\rm th}) - 1]\}^{-1} , \quad (5)$$

where ΔE is the activation energy of the conductivity in the nonlinear region (0.19 eV), R the static resistance at every point of the I-U curve, and $R_{\rm th}$ the static resistance at $V_{\rm th}$. The use of the above equation resulted in satisfactory fittings of the temperature distribution, as shown in Fig. 4 for two different ambient temperatures.

Using the values of Fig. 3 of the post-threshold conductivity, we calculated the effective cross section of the sample in the NDR region from the equation

$$S = (1/\sigma)(I/V)d . \quad (6)$$

We found that the effective cross section S of the sample was strongly dependent on current values. S grows with I, and at high values of I it tends to reach a value corresponding to the total cross section A of the sample ($A = 3\times10^{-7}$ m^2). This behavior is strongly reminiscent of the dependence of the filament cross section on current values in the cases when the NDR region is produced by the formation of a current filament.[18,15] The filament is a high-conductivity channel of elevated temperature.

Application of the same procedure for other ambient temperatures produces practically a similar dependence of the filament cross section on current values.

The above result lends credibility to the assumption that a highly conductive channel with finite width is formed in the prethreshold region, causing the drop of the sample resistance.

If the above consideration is valid, then it suggests the spatial phase separation of the sample into two different conducting states. In this case a simple phenomenological model, introduced by Peinke *et al.*,[18] can be used to describe quantitatively our results. Two different conductivities are attributed to the two phases. The filament pattern corresponds to a parallel connection of two resistors R_1 and R_2. We define $r_i = \rho_i d/A$ $(i=1,2)$ and $\delta = r_2/r_1 = \rho_2/\rho_1$, where ρ_1 and ρ_2 are the resistivities of the two phases. Then a current-controlled I-U curve can be obtained using the equation[18]

$$V(I) = R_1R_2/(R_1+R_2) = r_2/[\delta + x(1-\delta)] , \quad (7)$$

where $x = S/A$ and S is the filament cross section. To solve (7) we use the values of the prethreshold conductivi-

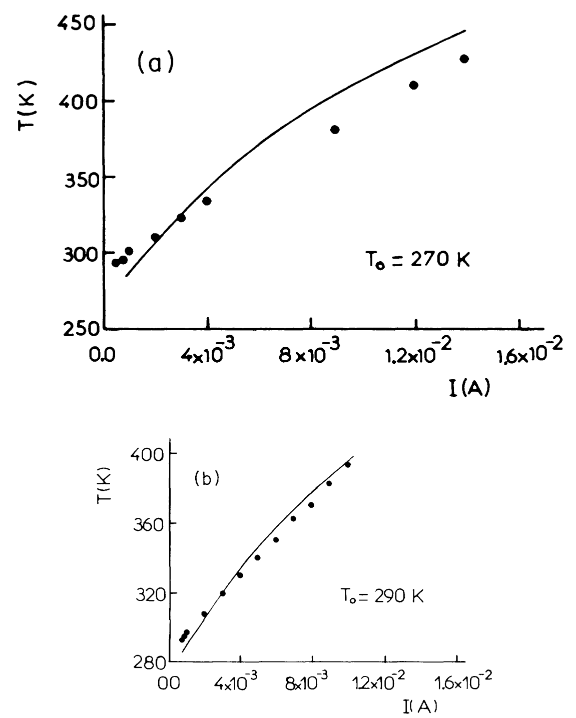

FIG. 4. Sample temperature vs current values (solid circles) for ambient temperatures (a) $T_0 = 270$ K and (b) $T_0 = 290$ K. Solid lines represent theoretical fitting obtained by the use of Eq. (5).

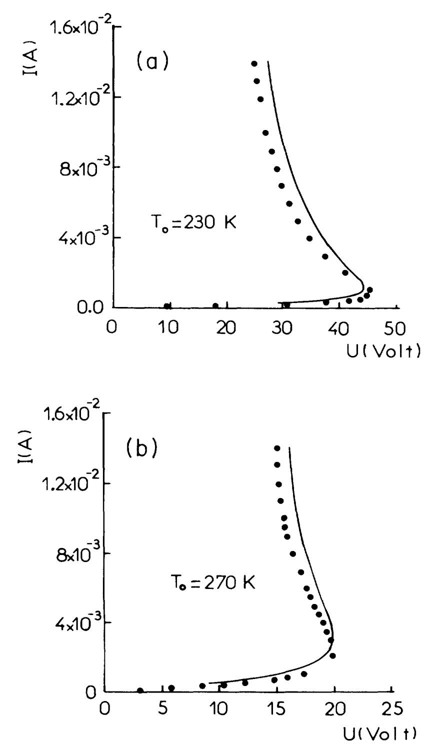

FIG. 5. Reproduction of the experimental I-U (solid circles) with Eq. (7) (solid lines), for (a) $T_0 = 230$ K and (b) $T_0 = 270$ K.

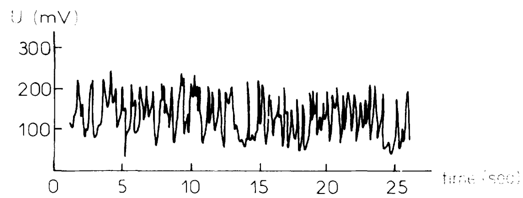

FIG. 6. Chaotic oscillations, as registered on the NDR region of the I-U characteristics.

ty (second inset in Fig. 1) for phase 1 and the values of post-threshold conductivity (Fig. 3) for phase 2, as well as the values of the filament cross section S found by Eq. (6). Thus we succeed in a satisfactory reproduction of the experimental I-U through Eq. (7). This result is shown in Fig. 5 for two different temperatures.

C. Voltage oscillations

The NDR region in the S-shaped I-U characteristics of V_2O_5 gives rise to spontaneous oscillations. At certain current values these oscillations are chaotic in form. Their upper and lower amplitude limits and mean repetition rate depend on current density and temperature. Figure 6 shows a typical example of such chaotic oscillations. At current values above 10 mA, the crystals may undergo a self-oscillating state and produce periodic oscillations, the amplitude and frequency of which are clearly current and temperature dependent. Such oscillations, like the chaotic ones, are considered to be sample limited (see also Ref. 19). If a capacitor is connected in parallel to the V_2O_5 crystals, a very stable periodic oscillation is registered for all current values on the NDR region (Fig. 7). The frequency of such wave forms is controlled by the current bias of the system, and the oscillations are considered to be circuit induced.

The character of the voltage oscillations in a system exhibiting a nonlinear I-U characteristic can be correlated to the movement of the high-conductivity filament or/and to the appearance of more than one filament in

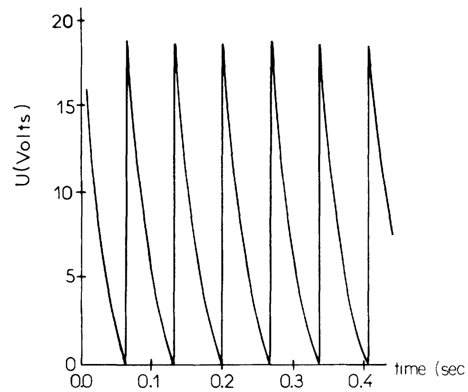

FIG. 7. Circuit-induced oscillations obtained with a capacitor parallel to the sample ($C = 1\ \mu F$).

the specimen. Support for this assumption provides the direct observation of such procedures, mentioned in Ref. 20.

Work in this field is still in progress.

IV. CONCLUSION

The nonlinear electrical behavior of the V_2O_5 compound is principally electrothermal in origin, a conclusion well supported by the fact that our experimental data have all the features for such an interpretation.

This is due to the formation of a high-current-density filament, in which the elevated current density results in an increased power dissipation, leading to joule heating.

As the temperature increases, conductivity also increases because of the semiconducting character of the compound. This feed path is monitored by the filament cross section.

The spatial dynamic character of the filament is reflected in the increase of its cross section, while the temporal dynamic character is expressed by voltage oscillations in the NDR region, principally chaotic in nature.

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