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Physics of Instabilities in Amorphous Semiconductors*

Abstract: A four-fold classification of the current-controlled instabilities in amorphous semiconductors is proposed. The experimenta evidence supporting a simple band model for the amorphous covalent alloys is given. The present understanding of the reversible switching effects and of the switching with memory is discussed.

Introduction

Interesting electrical switching effects have been observed in a large variety of amorphous semiconductors when they are placed as a thin layer between two electrodes. Most of these switching effects have in common the fact that they are current-controlled so that the *I-V* characteristic is obtained with a protective load resistor R_L placed in series with the switching unit. The appearance of the observed *I-V* characteristics suggests the fourfold classification shown in Fig. 1.

Case (a) The *negative resistance device* has an *I-V* characteristic which is retraceable and which shows an extended negative differential resistance region. With a proper choice of R_L this negative resistance device can be kept at any point of the *I-V* curve. Some hysteresis is observed when the current is changed too rapidly for maintaining thermal equilibrium. With a small value of R_L this device can be made to switch along the load line from a point at which $-(dV/dI) = R_L$ to the point of intersection of the load line and the *I-V* characteristic.

Case (b) The *switching device* has no stable operating point between the original high resistance state and the conductive state to which the device switches at the threshold voltage V_T. The conductive state can be maintained only above a holding current I_H. When I is decreased below I_H, the device switches to its original high resistance state.

Case (c) The *negative resistance device with memory* has two states. The high resistance state resembles that of (*a*). The second state is conductive. It is established at higher currents and then remains without noticeable decay. The high-resistance state can be re-established by increasing the current above a certain value and switching it off rapidly.

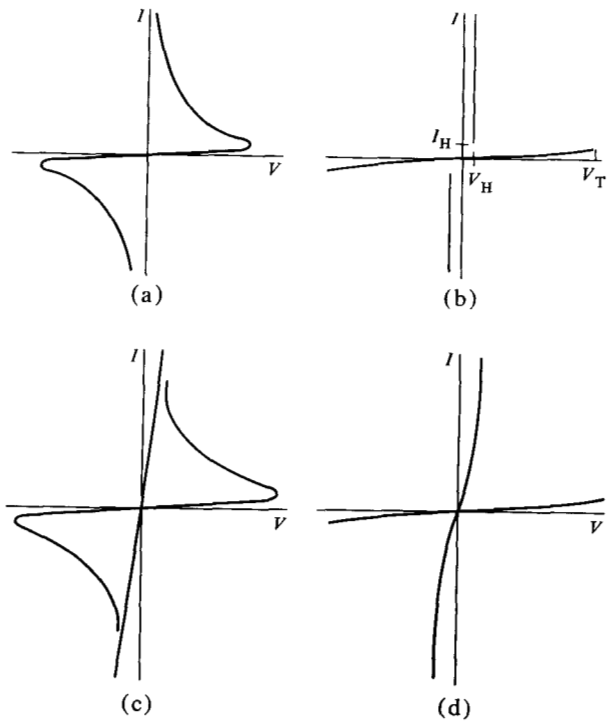

Figure 1 Classification of current-controlled breakdown characteristics. (a) Negative resistance device. (b) switching device. (c) Negative resistance device with memory. (d) Switching device with memory.

Case (d) The *switching device with memory* also has two stable states. The initial high-resistance state and the mode of switching resemble those of (*b*). The second state is conducting and persists without change. The high resistance state can be reestablished by applying a short current pulse.

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Almost all of these phenomena occur in the same manner for both polarities of the applied voltage. This phenomenological classification is, however, insufficient to separate the physical causes that give rise to the switching effects. Furthermore, these effects are not limited to amorphous semiconductors. The oldest case of a negative resistance device, case (*a*), known to me is boron, which was studied by E. Weintraub[1] in 1913 and later by F. W. Lyle,[2] J. H. Bruce and A. Hickling,[3] and by C. Feldman.[4] Some of the *I-V* characteristics reported by these authors are indistinguishable from those of Cu-doped Fe_2O_3 polycrystalline ceramic[5] and of thin polycrystalline films of VO_2.[6] In the latter case the switching effect has been identified as being caused by self-heating to a phase transition at 68°C, where the resistivity of VO_2 drops by more than four orders of magnitude.

Although self-heating of a semiconducting material whose resistivity drops rapidly with increasing temperature can easily lead to thermal run-away,[7] this need not be the only mechanism which yields a characteristic of type (*a*).

On the other hand, regardless of the physical mechanism and despite the obvious differences among the cases shown in Fig. 1, all of these have in common the transition from the high-resistive to the conductive state that occurs with a constriction or narrowing of the current path. Ridley[8] has shown in general that in the cases pictured in Fig. 1, the current will be confined in the conducting state to a channel whose cross section grows with the current until it equals that of the electrodes.

There may be several more such similarities among phenomena which currently appear to be different. These can be established only after we know more about the conduction mechanisms in the various amorphous materials.

Negative resistance characteristics of type (*a*) occur in transition metal oxides and have been discussed by K. L. Chopra.[9] A. D. Pearson et al.[10] described negative resistance devices with memory of type (*c*) made of different chalcogenide and oxide glasses. A. D. Pearson[10] (p. 510, this issue), reported that his materials were not homogeneous but contained a second phase and that characteristics with and without memory could be observed in all units.

Data on chalcogenide glasses

The following discussion is restricted to measurements performed in the laboratory of S. R. Ovshinsky on chalcogenide glasses.[11] These have the advantage, over other materials such as amorphous elements and oxides also studied in his laboratory, that they can be prepared in bulk as well as in thin film form.

Switching characteristics of type (*b*) and (*d*) were observed, but separately, and in quite different materials. The memory action, i.e., the persistence of two states in which resistances differ by many orders of magnitude, is possible in the switching devices with memory (*d*) only when a structural change can take place in the material. Simple binary or ternary glasses near eutectic or compound compositions are examples of suitable materials. Simpler structures like those of elemental semiconductors or stoichiometric compound materials were found impractical because of their excessive tendency to crystallize. In contrast to this, any structure change has to be inhibited in order to obtain the switching effect without memory (type *b*). Examples of these materials are multicomponent glasses of alloys of Group III, IV, V, and VI elements. These can be cooled very slowly from the liquid without showing traces of crystallite growth.

The switching devices (*b*) without and (*d*) with memory have in common that switching occurs very abruptly at a threshold voltage V_T when the applied voltage is increased slowly. When a square-wave voltage is applied, switching occurs after a delay time τ_D which decreases nearly exponentially with increasing square-wave voltage amplitude, as shown in Fig. 2. No switching appears possible below a certain voltage which for practical purposes is equal to V_T. The switching time τ_S measured in several laboratories is less than 10^{-9} sec. This upper limit is determined by the response time of the measuring equipment.

The conduction in the high-resistance state was found to be bulk limited rather than contact limited. All conductors tested were found to form low-resistance contacts with these amorphous semiconductors when precautions were taken to free the electrodes from oxide layers. Evidence for this was obtained by four-probe measurements and by testing the scaling of the resistance with the film thickness. Before switching occurs, the conductance increases approximately exponentially with applied voltage as shown in Fig. 3 for an 0.8 μm thick layer of amorphous $Te_{0.5}As_{0.2}Si_{0.1}Ge_{0.2}$. Pulse measurements show that the temperature of the semiconductor rises less than about 15°C above ambient, due to self-heating before switching under static conditions.

The dimensions of the unit, the specific heat per unit volume C of the amorphous layer, and the temperature dependence of its resistivity allow us to estimate whether self-heating is a possible mechanism for switching. We note that the apparently discontinuous change of slope from a positive differential resistance at the point of breakdown to a slope equal to that of the load line, already speaks against a thermal run-away. The Joule heat

$$\int_0^{\tau_D} I V \, dt$$

deposited in these devices prior to breakdown is not constant but decreases typically by a factor of 4 as the delay time τ_D is decreased by an order of magnitude by increasing the amplitude of the voltage pulse. This observa-

tion, however, rules out only the case for which thermal runaway occurs at a critical temperature, as for example in VO_2, but not the more general cases treated in Ref. 7.

Let us assume as the best condition for self-heating that no heat is conducted away. Under this favorable circumstance we shall determine whether or not a sufficient volume of the amorphous layer is heated within the switching time τ_S to a sufficiently high temperature to yield the conducting state. As an example we take a point in the conducting state at $I = 10$ mA, $V_H = 1$ V, which yields $R = 100$ ohms. The resistivity of the material follows to a good approximation

$$\rho = \rho_0 \exp(\Delta E/kT),$$

with $\rho_0 = 5 \times 10^{-3}$ ohm-cm and $\Delta E = 0.50$ eV. Assuming a high but perhaps not impossible temperature increase of $\Delta T = 600°C$ above ambient, one obtains for the minimum cross section A of the current channel through a $t = 10^{-4}$ cm thick amorphous film $A \geq \rho t/R = 5 \times 10^{-6}$ cm^2. A smaller cross section than this would require a higher temperature to yield the observed current flow of 10 mA at $V_H = 1$ V after switching. We now ask to what temperature T can a volume element (At) be heated with the power available during the switching time τ_S. The temperature rise ΔT above ambient is

$$\Delta T = P\tau_S/CAt.$$

For $V_T = 20$ V one obtains as an upper estimate for the average power P during switching $P = 0.4$ W. With $C \approx 1$ Joule/cm^3°C and the upper limit of $\tau_S = 10^{-9}$ sec the temperature rise becomes $\Delta T \approx 1°C$. As mentioned above the temperature rise during the delay time τ_D was less than 15°C.

It therefore does not appear possible to find a value for the cross section of the current channel which is small enough to permit a sizeable ΔT but at the same time large enough to yield the low value of the resistance in the conductive state. Although the temperature in the current channel will rise above ambient as soon as switching has taken place, we conclude from the above argument that self-heating *cannot* be the initiating cause for breakdown in the switching devices of type (*b*) and (*d*).

Band model for amorphous covalent alloys

The task of discussing possible electronic breakdown mechanisms in amorphous semiconductors is burdened by the fact that the concepts needed for describing even the low-field electrical properties are just being formulated. A simple band model for amorphous semiconductors has recently been described.[12] It is based on a combination of some new ideas together with many ideas which have been expressed by N. F. Mott[13] over the last eight years, particularly on the notion that all atoms in amorphous covalently-bonded alloys have their valence bond requirements locally satisfied. As shown in Fig. 4 the principal

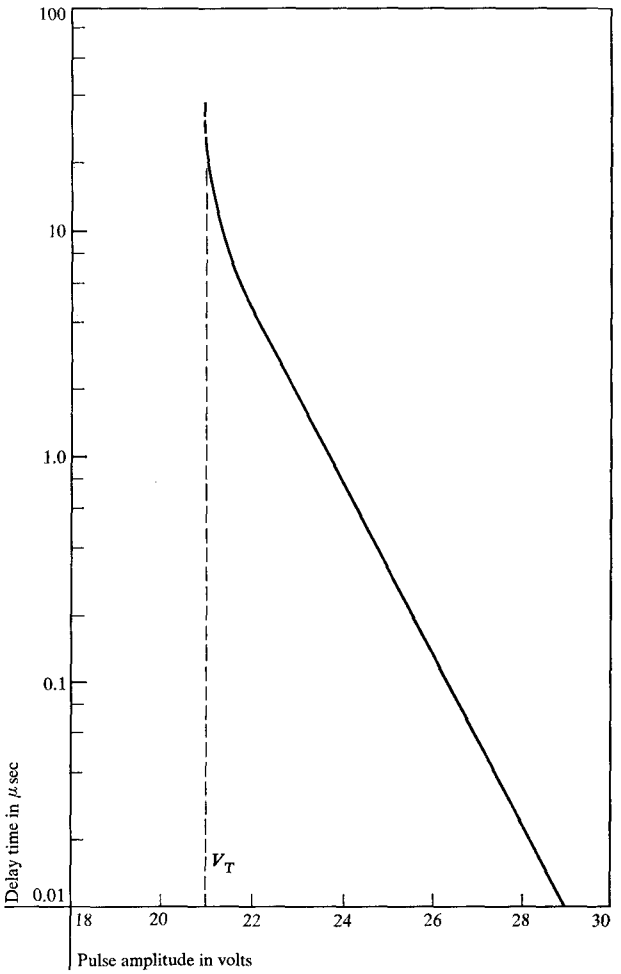

Figure 2 Delay time between onset of square-wave pulse and switching vs. pulse height.

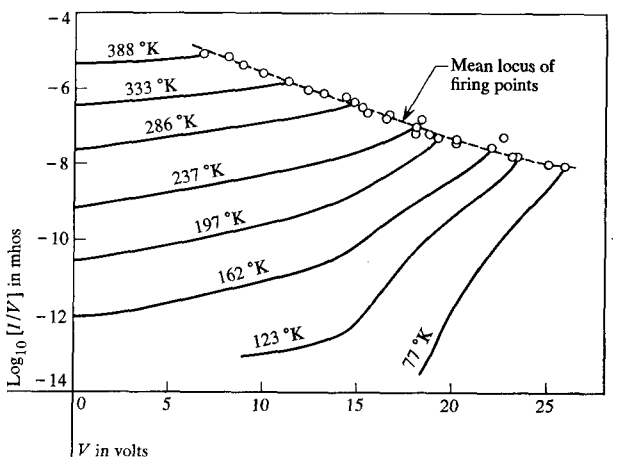

Figure 3 Conductance of a 0.8μm thick chalcogenide alloy as a function of bias voltage. The conductance is the same for either polarity.

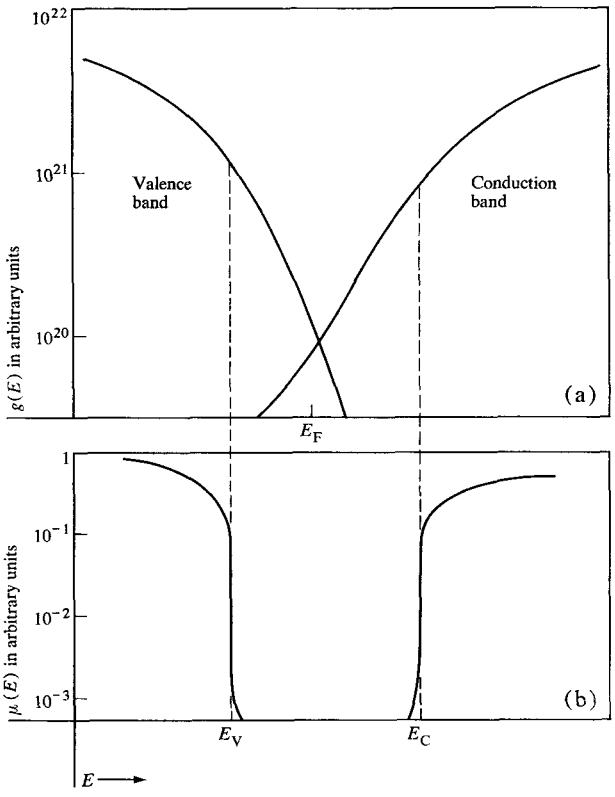

Figure 4 Sketch of the partial density of states of the conduction and valence bands (a) and of the electron and hole mobility (b). The units of the ordinates are indicated as arbitrary because no quantitative calculation has been made.

features of the model are overlapping conduction and valence band tails of localized states and sharp mobility edges at the energies E_c and E_v. In this model the mobility gap rather than a forbidden energy gap gives rise to the well defined thermal activation energy of the electrical conductivity.

All states which correspond to covalent bonds are considered part of the valence band. The valence-band states must therefore be considered neutral when they are occupied, whereas the conduction-band states are neutral when they are empty. In certain regions of the material the valence-band states may have higher energy than nonbonding states in other regions. Consequently, electrons will fall from the top of the valence-band tail into spatially distinct states of the lower conduction-band tail. This will create positively charged states above and negatively charged states below the Fermi level E_F. The resulting Coulomb potential fluctuations will change the energies of all states and have to be treated self-consistently. This model, therefore, includes neutral and charged traps for electrons above E_F, and neutral and charged traps for holes below E_F.

The density of localized states near E_F can be estimated from field effect measurements[14] and from the small magnitude of the hopping conduction[15] at low temperatures to be between 5×10^{19} and 10^{20} (eV-cm^3)$^{-1}$. Such a large density of states will effectively pin the Fermi level and hence explain why contacts between metals and amorphous semiconductors are of low resistance and nonrectifying.

The problem is to understand how a highly conductive state can be maintained after breakdown occurs in a material in which recombination and trapping processes are accelerated by such a high concentration of gap states. Furthermore, the low, temperature-independent Hall mobility[16] in these materials suggests that the mean free path of the carriers above the mobility edges is too small for impact ionization across half the mobility gap.

Photostimulated and field-stimulated excess photoconductivity

It should be noted that the model predicts that most of the electron traps will be located above the Fermi level and most of the hole traps below. As a consquence, one might expect that a nonequilibrium distribution of carriers not only decays relatively slowly but also leads to a higher conduction, because the electrons and holes can be reexcited into their respective bands more easily from the higher lying traps than from the states occupied under equilibrium conditions.

This indeed appears to take place, as shown in Fig. 5. The same material as that used for the switching experiments was illuminated[17] at 78°K with light of sufficient energy to produce electron-hole pairs beyond the mobility edges. At this temperature the virginal sample had a conductivity too low for the current to appear on this graph. Illumination produced photoconduction of sufficient magnitude to increase the current by more than five orders of magnitude. After illumination part of the photoconduction decreased with a short relaxation time but an appreciable fraction remained with a very long time constant. The short illumination was repeated with $\lambda_1 = 0.93$ μm and later with $\lambda_2 = 1.5$ μm light to study the equilibration and decay times. Although one deals here with a distribution of many relaxation times one can distinguish fast and very slow relaxation processes. The first seem to govern the equilibration of the photoexcited carriers with the traps, whereas the very slow processes might correspond to a slow return to equilibrium via tunneling and recombination. Such a trap-limited excess conductivity was seen in chalcogenide glasses by A. M. Andriesh and B. T. Kolomiets.[18]

E. A. Fagen[17] has produced the same excess conductivity not only by light excitation but also by applying a transient high electric field which brings the material into its non-ohmic region. Both the photostimulated and the

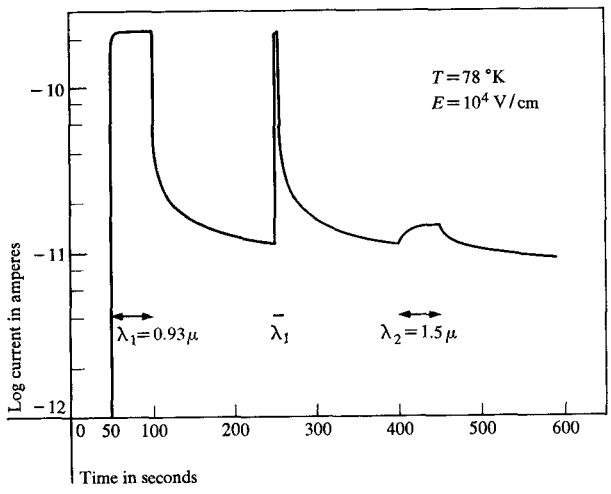

Figure 5 Photocurrent produced at 78°K in a film of chalcogenide alloy. Note the fast and the very slow components in the decay of the photocurrent after illumination.

electric-field stimulated excess conductivity disappears rapidly as the material is heated. The relaxation times become of the order of hours at 150°K and minutes at 200°K. At room temperature these relaxation processes will, of course, be accelerated but they might still remain sufficiently slow for trap limited conductivity to yield a substantial increase in conduction in the presence of a sufficient excitation process.

The observation that the excess conductivity can be field stimulated suggests that the non-ohmic conduction shown in Fig. 3 is associated with a nonequilibrium distribution of carriers over the trapping centers. The required excess carriers can be generated internally by various field-ionization processes or can be injected at the electrodes, or both.

The field distribution is most likely still uniform in the high-resistive state before breakdown because of the observed rough proportionality of V_T and film thickness. This is presumably a simple consequence of the short screening length discussed above. If there is a regeneration or feeding mechanism for electrons and holes that is a strongly increasing function of the field, then, as shown by Gunn,[19] a second stable state in which the high-field regions are concentrated near the electrodes is established. Such a mechanism is provided by the strongly field-dependent tunneling of electrons and holes from the Fermi level of the metal, through the potential barrier near the electrodes, into the semiconductor. The highly conductive state is then sustained by field emission from the electrodes, which provides double injection of holes and electrons so that the material remains essentially neutral. As soon as the injection current falls below a critical value, the equilibration processes in the bulk material will predominate and return the material to the original high-resistance state. Some Joule heating in the bulk of the semiconductor will occur after switching has taken place and increase its temperature. This will contribute to a lower voltage drop in the material and a concentration of the potential fall near the electrodes.

The only prediction this qualitative model permits one to make is that the voltage drop across the switching device in the conductive state should be larger than but of the same magnitude as the mobility gap, i.e., twice the conductivity activation energy. This is indeed observed; the holding voltage is between 1 to 1.5 V.

Switching effects

All experimental observations so far suggest that the same process leads to switching from the high-resistive to the conductive state in both the switching device and the switching device with memory. The switching device of type (*b*) returns to its original high-resistance state as soon as the current falls below a certain value I_H. The switching device with memory [type (*d*)] remains in the conductive state after a certain "set" energy of about 0.5×10^{-6} joules has been deposited while the device is in the conductive state. This energy causes the necessary transformation of the material. In order to re-establish the high resistance state of the memory switch, a "reset" pulse is applied, whose current must exceed a certain minimum value. The "reset" pulse is of less than a microsecond duration and deposits an energy comparable to that of the "set" pulse. Switching devices with memory have been cycled in this manner for more than 3×10^8 times with no loss in performance.

As explained above, the amorphous covalent alloys are intrinsic and highly resistive because of the near-perfect local satisfaction of the valence requirements of each atom. This high degree of bond completion is made possible (a) by the choice of glass forming, multivalence elements comprising the alloy, and (b) by the positional and compositional disorder. These two factors make the occurrence of dangling bonds and of acceptor and donor states unlikely. As soon as one of these factors is eliminated the Fermi level is likely to move away from the gap center, and the material becomes a low-resistivity semiconductor.

In the present case of covalent amorphous alloys used for memory switches, one can achieve the loss of bond completion by a slight shift in compositional disorder, using a properly multivalent element in a matrix of an otherwise stable covalent alloy glass. In this case the transformation energy is minimized and reversibility is optimized. The persistence of either state requires a structural change that involves atomic movement (diffusion) from one stable state to the other.

The exact nature of the structural transformation that leads to the conducting state of the memory-type switching device has not yet been elucidated. It appears likely that

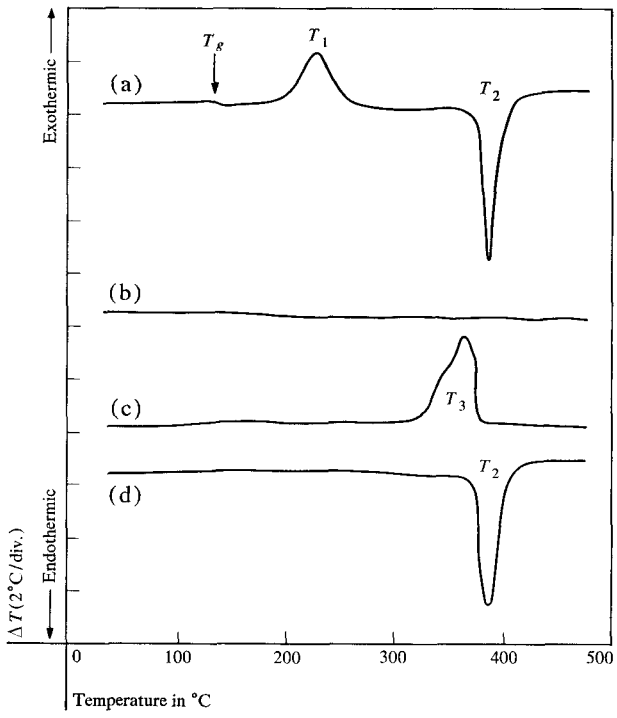

Figure 6 Differential thermal analysis of a chalcogenide alloy used for switching devices with memory. Traces (a) and (c) are heating curves, (b) and (d) are cooling curves.

the thermal gradients and the electric fields present in and around the current channel during the "setting" of the conducting state strongly influence the diffusion which is necessary for the structural transformation. One should bear in mind these differences in condition before one uses conclusions drawn from the behavior of memory-type material under heat treatment, which will be discussed later, to explain the memory action. Furthermore, the thin films used in switching devices with memory were deposited by cathode sputtering whereas the differential thermal analysis measurements were made on the cathode material.

Figure 6 shows differential thermal analysis data obtained with memory type material of composition $Ge_{16}Te_{82}Sb_2$. The starting material was of high resistivity ($\rho = 5 \times 10^6$ ohm cm at 300°K). One observes a glass transition near 130°C. Around $T_1 = 230$°C an exothermic transformation occurs. If the material is cooled from this temperature either slowly or rapidly, a highly conductive state is retained. Upon further heating, the material undergoes an endothermic transformation near $T_2 = 370$°C. The material is more ordered below T_2 and disordered above T_2. When the material is sufficiently rapidly cooled from $T > T_2$, at a rate in this case of 50°C per minute (curve *b*), the disordered state is retained and one obtains the original amorphous and highly resistive state which will yield the DTA curve (*a*) upon heating. Very slow cooling, in this case at 10°C per minute, leads to the more ordered and conductive state through an exothermic transformation occurring near $T_3 = 350$°C, as shown by DTA curve (*c*). Heating this transformed material yields DTA curve (*d*), which shows only the T_2 endotherm above which the option of slow or fast cooling is available. X-ray diffraction studies[20] reveal Te crystallites after the material is heated to a temperature between T_1 and T_2. The original material as well as the material rapidly cooled from $T > T_2$ were found to be amorphous. Although there are endothermic reactions possible without melting in which precipitates are dissolved at higher temperatures, the temperature T_2 is close to the eutectic melting temperature of the Ge-Te system.

The "set" pulse has a voltage which is sufficiently high to overcome the threshold voltage. After breakdown and the formation of a current channel, which is believed to be similar to that in switching devices, the "set" pulse continues and delivers about 0.5×10^{-6} J to the current carrying region. The temperature reached is probably only slightly in excess of T_1. After the "set" pulse is over, the material in the channel region remains more ordered and conductive. The "reset" pulse is short so that the Joule heat is concentrated in the limited dimensions of the channel region and that a quick cooling results after the end of the pulse. This restores the original disordered and high-resistance state.

None of the materials investigated which were prepared for switching devices of type (*b*) of Fig. 1 exhibited an exothermic or endothermic reaction at any temperature.

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