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[15]We are indebted to Dr. J. Kondo. Equation (4) is obtained as follows:

$$\frac{1}{\tau_{\uparrow}}=\frac{1}{\tau_0}+\mu_B H\frac{d}{d\epsilon}\frac{1}{\tau}$$

and

$$\frac{1}{\tau_{\downarrow}}=\frac{1}{\tau_0}+\mu_B H\frac{d}{d\epsilon}\frac{1}{\tau},$$

so that

$$\rho(H)\propto\frac{1}{\tau_{\uparrow}+\tau_{\downarrow}}=\frac{\tau_0}{2}\left[\left(\frac{1}{\tau_0}\right)^2-(\mu_B H)^2\left(\frac{d}{d\epsilon}\frac{1}{\tau}\right)^2\right].$$

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REVERSIBLE ELECTRICAL SWITCHING PHENOMENA IN DISORDERED STRUCTURES

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(Received 23 August 1968)

A rapid and reversible transition between a highly resistive and conductive state effected by an electric field, which we have observed in various types of disordered semiconducting material, is described in detail. The switching parameters and chemical composition of a typical material are presented, and microscopic mechanisms for the conduction phenomena are suggested.

We describe here a rapid and reversible transition between a highly resistive and a conductive state effected by an electric field which we have observed in various types of disordered materials, particularly amorphous semiconductors[1,2] covering a wide range of compositions. These include oxide- and boron-based glasses and materials which contain the elements tellurium and/or arsenic combined with other elements such as those of groups III, IV, and VI.

Such amorphous materials can be described as intrinsic semiconductors[3,4] with an optical energy gap E_g typically between 0.6 and 1.4 eV and an activation energy[5] for electrical conduction ΔE between 0.7 and 1.6 eV depending on composition.

Field-effect measurements[6] indicate that the "band gap" contains a distribution of trapping and recombination centers with densities in excess of 10^{19} cm^{-3} eV^{-1}.

The measurements shown below have been obtained with an amorphous semiconductor containing (in atomic percent) 48 at.% tellurium, 30 at.% arsenic, 12 at.% silicon, and 10 at.% germanium. The specimen was an evaporated film, 5×10^{-5} cm thick, between two carbon electrodes with a contact area of about 10^{-4} cm^2. This material has a resistivity at 300°K of $\rho=2\times10^7$ Ω cm, $\Delta E=1.0$ eV, and a positive thermopower.

Figure 1 shows oscilloscope pictures of (a) the I-V characteristic, (b) the voltage V across the unit, and (c) the current I passing through the above unit as a function of time. In this case, a 60-Hz ac voltage was applied across the unit and a 10^4-Ω load resistor was used. The I-V curve is independent of frequency to at least 10^6 Hz.

The major features of the switching phenomena shown are the following: (1) The I-V characteristic is symmetrical with respect to the reversal of the applied voltage and current. (2) The same switching characteristic is observed when the semiconducting materials is sputtered or hot-pressed between the electrodes. It remains symmetrical even when the electrodes are of differ-

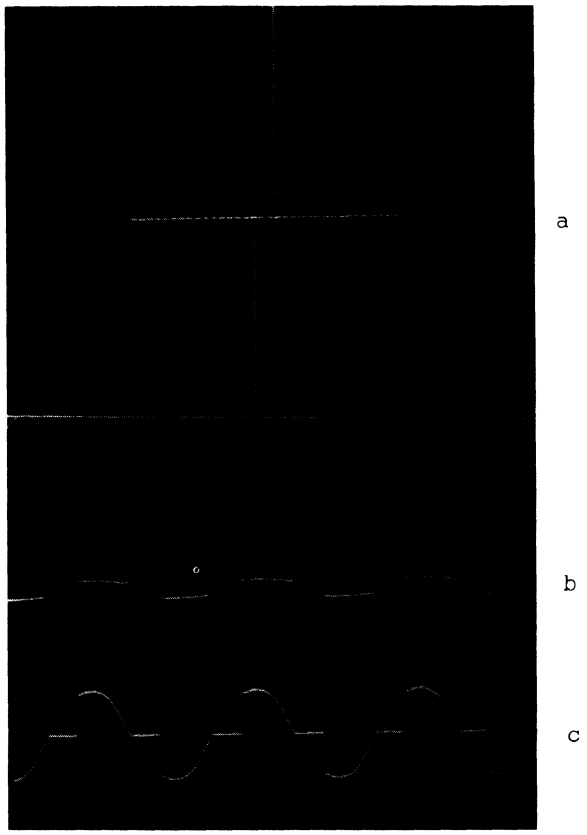

FIG. 1. Response of switching unit to 60-Hz voltage. (a) I-V characteristic: vertical, 2 mA/div; horizontal, 5 V/div. (b) Voltage: vertical, 5 V/div; horizontal, 5 msec/div. (c) Current: vertical, 20 mA/div; horizontal, 5 msec/div.

ent contacting areas or of different materials. (3) In the highly resistive state, the material is Ohmic at fields below about 10^4 V/cm. At higher fields, the dynamic resistance decreases monotonically with increasing voltage. (4) When the applied voltage exceeds a threshold voltage V_t, the unit switches along the load line to the conducting state.[7] (5) In the conducting state, the current can be increased or decreased without significantly affecting the voltage drop, termed the holding voltage V_h, across the unit. Here the dynamic resistance is close to zero. (6) As the current is reduced below a characteristic value termed the holding current I_h, the unit switches back to the original highly resistive state along the load line. (7) The switching process is repeatable. Alternating or full-wave unfiltered rectified voltages have been applied continuously to units over periods of many months without noticeable change in their characteristics.

In the highly resistive state, the threshold voltage V_t of the unit increases nearly linearly with the thickness of the film.[8] This observation and also the fact that the symmetry of the I-V characteristic is preserved even when different electrode materials are used indicate that the current in the highly resistive state is not electrode limited but that the field is essentially uniform throughout the bulk of the material. In contrast to this, the holding voltage is weakly dependent on thickness, which suggests that in the conductive state the voltage drop occurs predominantly at one or both electrodes. A dependence of V_h on electrode material has also been observed.[9] Upon switching into the conductive state, a current filament appears to form, growing in diameter with increasing current flow.[10] Diameters of about 5×10^{-3} cm were observed by thermal probing for $I\approx100$ mA. Similar current filaments have been observed and discussed by Böer and co-workers[11] and are quite generally associated with S-shaped instabilities.[12]

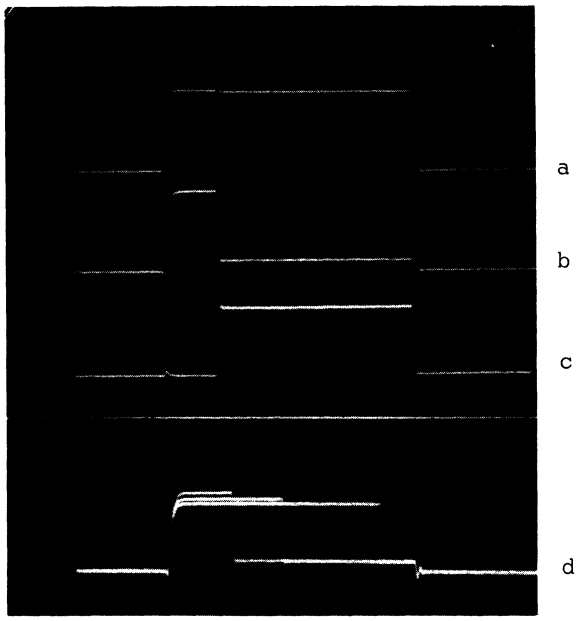

FIG. 2. Response of switching unit to square-wave pulse. Horizontal time scale 500 nsec/div. (a) Voltage applied across unit and 1000-Ω series resistor: vertical, 5 V/div. (b) Voltage across unit: vertical, 5 V/div. (c) Current through unit: vertical, 10 mA/div. (d) Same as (b) for different amplitudes of applied voltage pulse.

Figure 2 shows the switching phenomenon which follows the application of a rectangular voltage pulse [Fig. 2(a)]. Because the load resistance is much smaller than that of the unit before switching, the applied voltage appears across the unit

until switching occurs, as seen in Fig. 2(b). Note that switching occurs after a delay time t_d. The duration of the switching process is less than 1.5×10^{-10} sec. After switching, the holding voltage V_h is observed across the unit until the end of the applied pulse. Figure 2(c) shows the abrupt increase of current after t_d and the sudden drop at the end of the pulse. Figure 2(d) shows the decrease of t_d with increasing voltage V. The functional form is approximately $t_d = \text{const} \times \exp(-V/V_2)$.

The switching processes can be analyzed in terms of a nucleation theory wherein the nucleation rate is dependent on the applied voltage. In this model,[13] nucleation precedes the process leading to the delay time t_d. A statistical analysis of the distribution of threshold voltages for 30 000 successive switching events recorded on one unit operated with 60-Hz ac voltage showed the nucleation probability per unit time to be a constant for a given applied voltage and to depend on voltage as $\exp(V/V_1)$, where V_1 was about 0.1 V for the unit examined. The peak of the probability distribution occurred at 13.9 V; we take this as the definition of V_t.[14,15] The nucleation rate at the peak is 7×10^4 sec^{-1}.

The conduction and switching processes appear closely tied to the structures of disordered and amorphous materials which in turn are associated with the local bonding characteristics of the constituent chemical elements. A high density of localized states in the forbidden energy gap is split from the conduction and valence bands by the translational and compositional disorder. The disorder allows most atoms to complete their valence state and thereby establish a high degree of compensation, yielding the observed intrinsic behavior of these materials. A large overlap in energy of those levels stemming from the valence band with those from the conduction band is expected with self-compensation of charges producing a large density of traps. These traps when occupied can easily be ionized at moderate fields by lowering the trap depth and reducing the capture cross section.[16] A rapid increase of carrier concentration results, and can explain the observed non-Ohmic behavior in the low-conductivity state.

The relatively close spacing of these localized states in both space and energy makes it likely that internal-field ionization and emission from these localized states play an important role in the carrier generation necessary to initiate the conducting state at threshold values of the order of 10^5 V/cm. We feel the exponential dependence of the current on voltage in the highly resistive state before switching supports this contention. The low mobility and high number of localized states offer, in principle, the possibility of the dramatic conductance changes observed.

We believe that after switching, a redistribution of carriers as a result of oppositely charged carriers having very different mobilities and transition rates through the electrode interfaces gives rise to a space charge and field enhancement near one electrode and to the small value of V_h.

An unusual memory effect is observed[2,17] in materials in which structural changes are facilitated by the removal of cross-linking elements from the above formula—for example, the reduction of arsenic to 5 %. After switching from a highly resistive state, structural changes result in the preservation of a conductive state even when the current is totally removed. The material can be reversibly switched back to the highly resistive state by application of a current pulse of either polarity exceeding a threshold value.

I particularly wish to acknowledge the early advice, help, and encouragement given by H. Fritzsche, the valuable assistance and discussions of M. H. Cohen and K. W. Böer and also of D. Turnbull and A. Bienenstock, and the devoted help of my wife and colleague, I. M. Ovshinsky, and the staff of Energy Conversion Devices, Inc.

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[1]Parts of this work were presented earlier: S. R. Ovshinsky, at the Fourth Symposium on Vitreous Chalcogenide Semiconductors, sponsored by the Academy of Sciences of the USSR, Leningrad, 23-27 May 1967 (unpublished), and at the International Colloquium on Amorphous and Liquid Semiconductors, sponsored by the Rumanian Academy of Science, Bucharest, 28 September-3 October 1967 (unpublished), and in Proceedings of the Electronic Components Conference, Washington, D. C., May 1968 (McGregor and Werner, Inc., Washington, D. C., 1968), p. 313 ff.

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[5]The conductivity is expressed as $\sigma = \sigma_0 \exp(-\Delta E/kT)$.

[6]H. Fritzsche, E. A. Fagen, and S. R. Ovshinsky, to be published.

[7]Even in a circuit that is current stabilized by a 10^8-Ω load resistor, the unit cannot be held at an operating

point between the highly resistive and the conducting state. In some cases, relaxation oscillations governed by the load resistor and the unit's capacitance ($C \approx 3$ pF) have been observed.

[8]By changing the film thickness, values of V_t between 2.5 and 300 V have been obtained.

[9]Nichrome electrodes yield a particularly low value, $V_h = 0.5$ V. A more detailed study is in progress.

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SECOND-ORDER STARK EFFECT OF A RESONANT MODE IN NaI:Cl^- †

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The anharmonicity associated with a lattice resonant mode has been identified by means of a second-order Stark-effect measurement.

Large frequency shifts of a lattice resonant mode[1] in NaI:Cl^- caused by an external-electric-field perturbation have been observed.[2] These frequency shifts determine the symmetry of the defect site and give a direct measure of the anharmonicity of the interionic potential for the impurity ion. Although large electric-field–induced shifts have been predicted[3] and observed[4] previously for a defect-induced tunneling mode, such shifts have not yet been reported for local,[5] gap, or resonant modes.[6]

The far-infrared absorption measurements were made using a Strong-type lamellar interferometer and a He^3-cooled bolometer detector[1]; instrumental resolution was 0.2 cm^{-1}. To maintain a uniform electric field across the sample, a special sample configuration has been devised. The doped sample is framed by four pieces of pure crystal so that the fringing fields occur mostly in the pure crystal, and the field on the sample is as uniform as possible. Sample thickness is about 1.4 mm. Two such samples are mounted with the high-voltage electrode between them. Up to 12 kV could be applied without electrical breakdown. Incident radiation is polarized by a 500-lines/in. Ni grid deposited on Mylar film[7] placed in the light path just before the sample.

The transmission spectrum of the sample was measured for several different values of electric field E_{dc} applied in the [100] and [110] crystal directions, for incident radiation polarized both perpendicular and parallel to the dc electric field. The frequency of the E-shifted line was determined by dividing the transmission spectrum by the zero-field unshifted spectrum and forming the absorption constant $\alpha(E, \omega)$ from

$$I(E, \omega) = I(0, \omega) \exp[-\alpha(E, \omega)t],$$

where $I(E, \omega)$ and $I(0, \omega)$ are the transmitted intensities for E- and zero-field, respectively, at frequency ω, and t is the sample thickness. The absorption constant of the unperturbed line was then added to $\alpha(E, \omega)$. This indirect process is necessitated by the difficulty of making a pure sample which has a geometry, hence an optical interference pattern, identical to that of the doped sample.

Typical results of this data reduction process are shown in Fig. 1 for the case of $E_{ir} \| E_{dc} \| [100]$, where ir denotes infrared. Applied volt-

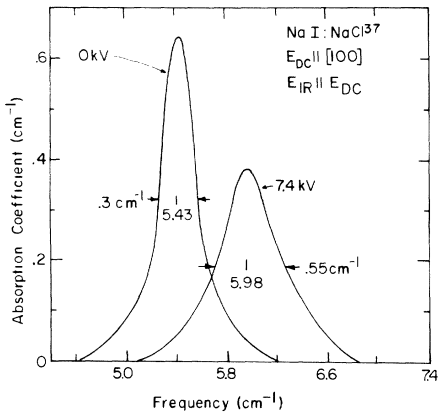

FIG. 1. Typical electric-field–induced frequency shift. Instrumental resolution is 0.2 cm^{-1}.

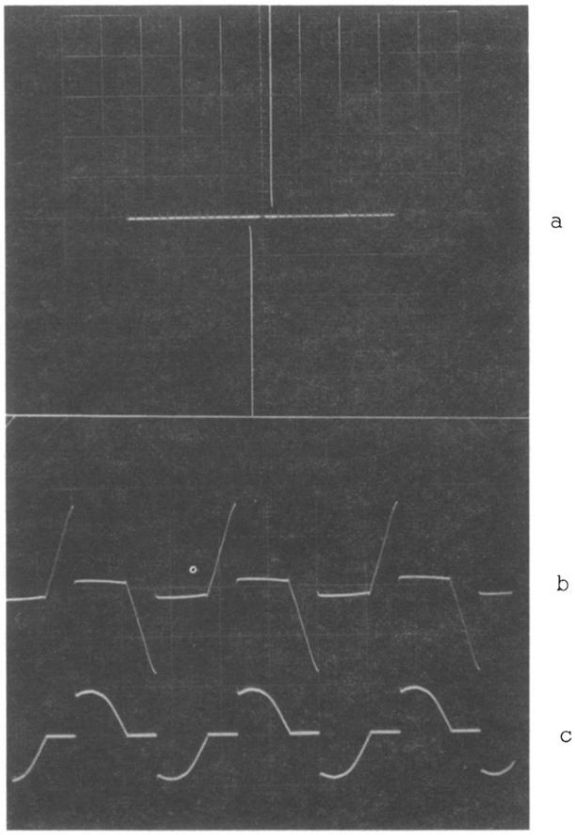

FIG. 1. Response of switching unit to 60-Hz voltage. (a) *I-V* characteristic: vertical, 2 mA/div; horizontal, 5 V/div. (b) Voltage: vertical, 5 V/div; horizontal, 5 msec/div. (c) Current: vertical, 20 mA/div; horizontal, 5 msec/div.

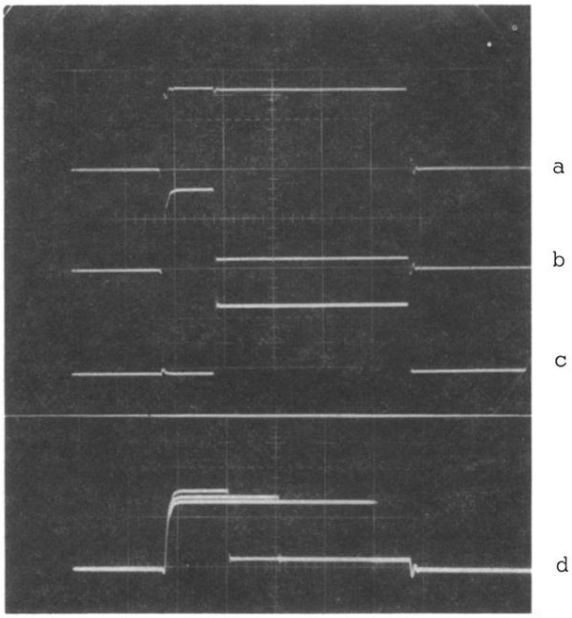

FIG. 2. Response of switching unit to square-wave pulse. Horizontal time scale 500 nsec/div. (a) Voltage applied across unit and 1000-Ω series resistor: vertical, 5 V/div. (b) Voltage across unit: vertical, 5 V/div. (c) Current through unit: vertical, 10 mA/div. (d) Same as (b) for different amplitudes of applied voltage pulse.