beams with similar good agreement between line shapes above 40 eV. The agreement obtained for each of these adsorbates in fourfold coordinated bonding sites is similar to that obtained for clean nickel surfaces[5] and is discussed and illustrated for these other beams in more detail elsewhere.[11] The good agreement between theoretical and experimental peak positions and line shapes of $(\frac{1}{2}\frac{1}{2})$, (01), and (00) beams for each adsorbate displacement d adds to our confidence in our determined structures.

In Table I we summarize the adsorbate displacements above the substrate, corresponding Ni-chalcogen bond lengths, and Ni-chalcogen bond lengths from other sources. Our determined bond lengths for O, S, and Se are slightly less than typical bond lengths found in bulk solids and are comparable to those of Ni-chelate complexes. However, the tellurium-Ni bond length is comparable to bulk bond lengths.

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Reversible Switching in Thin Amorphous Chalcogenide Films—Electronic Effects

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Experimental results suggest that (1) switching in thin chalcogenide glass films is fundamentally electronic, and (2) the regime of pure electronic initiation has been exposed.

We have investigated three aspects of switching in thin amorphous chalcogenide films[1]: (1) the response of unannealed virgin and "formed"[2] films to voltage pulses 2 nsec in duration, where heating is negligible; (2) the virgin threshold voltage as a function of pulse duration; (3) the phenomenon of "minor" switching.[3] The results indicate that (i) a critical electric field E_c must be reached in part of the film in order for conventional "delay-time" t_d switching to occur, and (ii) t_d has a shortest value t_s, the characteristic time required by the as yet unspecified electronic mechanism that produces switching.[1,4] The experimental results support the view that switching is fundamentally electronic,[1,4,5] and help elucidate the role of thermal effects under conditions where they can initiate the switching process.[6,7]

Samples were prepared in the following configurations: (a) $As_{49}Te_{51}$ glass prepared from 99.999%-pure elements was evaporated by electron beam onto a polished Al plate coated with 0.1 μm of Mo. These films were all of thickness l near 2 μm.[8] A spherical-tip graphite counterelectrode was set and maintained under slight pressure here and for samples in (b) below. "Off"-state resistances R_0 were typically between 10 and 50 kΩ.

(b) AsTe, As_2Te_3, and a few compositions in the Te-As-Si-Ge system were sputtered onto polished plates of Mo-coated Al in thicknesses of 0.5, 1.0, and 2.0 μm.[9] Here the R_0's ranged from

3 to 500 kΩ.

(c) Films of Si-Ge-In-As-Te glass were sputtered onto Mo through a 20-μm-diam hole (pore) etched into a SiO_2 film on Si. Mo was then sputtered over the top. These films were slightly less than 1 μm thick[10] and $R_0 = 4\times10^8$ Ω.

Experiments were performed with pulse widths t_p in the range $2\times10^{-9} \leq t_p \leq 10^{-2}$ sec, applied at a pulse repetition frequency of 25–1000 Hz. For configurations (a) and (b) the sample was considered to be the region of the film in the immediate vicinity of the counterelectrode. Samples (c) were diced and packaged in TO-5 headers with wire-bonded leads. Forming[2] occurred for all t_p's in all samples, and no effort was made to control it.[11]

Each datum bar in Fig. 1 represents the virgin threshold voltage V_{tv} for two or more individual samples prepared as in (c) above. Single-shot pulses verified that the constancy of V_{tv} for $t_p \geq 5\times10^{-5}$ sec is due to the fact that the virgin-switching delay time t_d is always less than about 2×10^{-5} sec. The important point is that as t_p decreases below about 10^{-7} sec, the rate of rise of V_{tv} tends to diminish, in contrast to the linear behavior expected from an electrothermal model.[6,7] By using a specific heat of 0.05 cal/g°K, a density of 5 g/cm^3, and assuming no heat flow out, we calculated a 0.1°K temperature rise at threshold throughout the sample volume of 12×10^{-12} cm^3 for $t_p = 2\times10^{-9}$ sec. Even if we assume pre–first-switch thermal channeling into 25% of the cross-sectional area of the virgin film, the temperature rise in this region at threshold is less than 2°K. We conclude that for short pulses the virgin event is electronically initiated. Figure 1 indicates an average critical field $\bar{E}_c \simeq 7\times10^5$ V/cm in these particular films at room temperature. Buckley and Holmberg[12] found that V_{tv} scales with thickness for $t_p \leq 10^{-5}$ sec, also suggesting the existence of an $\bar{E}_c$, and observed that as the temperature was

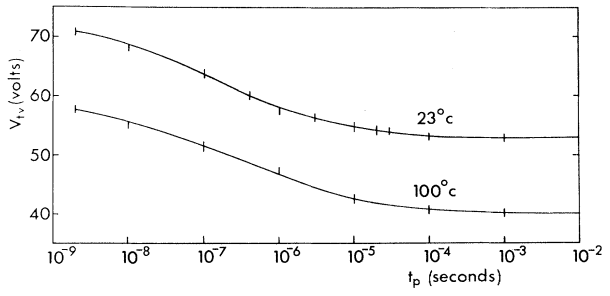

FIG. 1. Virgin threshold voltage as a function of pulse width.

reduced to liquid N_2 values, V_{tv}/l approached a constant value $\simeq 5\times10^5$ V/cm in films of higher conductivity than the ones discussed here.

Switching in *formed* films can occur in times that are limited by the risetime ($\leq 10^{-9}$ sec) of the SKL-model 503-A pulser employed in the short-pulse experiments. To study the current rise in such short times it is necessary to minimize the load resistor R in order to reduce the width of the displacement current spike that appears during the risetime. The price paid for the reduction in R, however, is that the switch evolves to a very high value of current, which alters the samples "off" characteristics.[13] Thus, when data are taken for increasing and then decreasing voltages, a hysteresis is observed in the V_t-versus-t_d plots.

In Fig. 2(a) we show the voltage (across the sample and R) and current (voltage across R divided by R) versus time for a type-(c) sample as measured on a Tektronix 7504 sampling oscilloscope. The voltage difference between the traces is the voltage across the sample. For $V_t \simeq 26$ V, t_d is about 1.5×10^9 sec. For slightly higher voltages, however, the conventional delay-time concept is inapplicable since the current starts its rise before the peak voltage is reached. The current rise also becomes much "cleaner," indicating that the statistical fluctuations associated with the delay-time event have disappeared. For peak voltages higher than about 27 V the data can be interpreted as an instability initiated at a critical voltage $\simeq 26$ V. Here the switch occurs in the time t_s. Figure 2(b) is a typical plot of V_t versus t_d for increasing and decreasing voltages.

We estimate a temperature rise of less than 5°K within the formed filament just prior to the switching that occurs in less than 10^{-9} sec. It appears that if $\bar{E}_c$ can be reached prior to the onset of appreciable heating, the sample will switch to a higher-conductance state. Delay-time (D) switching in samples with well heat-sunk electrodes also appears to be a consequence of E_c. For longer constant-voltage pulses at lower voltages the sample starts to heat in its central portion[6,7] during the preswitching "off" state.[13] Heating increases the conductivity, lowers the field in the center, and increases the fields near the cooler electrodes. When an electrode field exceeds E_c, D switching can occur.[14] In electrothermal calculations, the "virtual electrode" model of Kaplan and Adler is quite similar to the effect of an E_c. Their numerical calculations showed that without a field-activated conductiv-

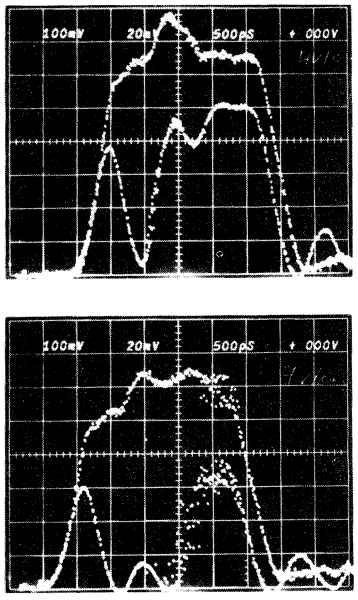

FIG. 2. (a) Voltage (top trace) and current (bottom trace) versus time for two values of peak applied voltage (26 V, bottom figure; 31 V, top figure). Voltage scale, 4 V/div; current scale, 40 mA/div; horizontal time scale, 0.5×10^{-9} sec/div. (b) Threshold voltage versus time at which the current is observed to rise sharply. Crosses, increasing voltage; circles, decreasing voltage; bar, range of times obtained with six different values of the peak voltage (> 27 V) and interpreted as occurring at 26 V.

ity,[15] switching would not occur unless high fields existed near the electrodes.

There exists further evidence for the existence of a critical-field phenomenon. On rare occasions formed samples (a) and (b) would exhibit "minor" (M) switching,[3] which we studied using an EH model 132A-8 pulser (risetime $\simeq 10\times10^{-9}$ sec). A typical room-temperature M-D switching sequence proceeded as follows for $R>100\ \Omega$ (refer to Fig. 3(a)]: (I) At the first threshold, $V=V_a$ (1–5 V), an M switch occurred (usually symmetric with respect to pulse polarity) in a time limited by the pulse risetime. (II) With further increase in bias ($V_a \rightarrow V_c$), the total current I increased. Here the product IVt_p increased with increasing t_p. (III) At V_t (2–15 V) another switch to a higher-current state occurred. This process was a D switch with $IVt_p \simeq$ const, and was characterized by its onset at the trailing edge of the pulse.

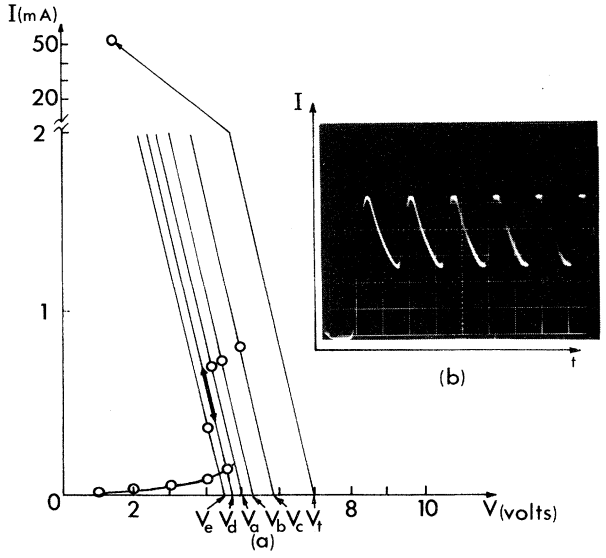

FIG. 3. (a) Total current I versus voltage V for a type-(a) configuration. The load line is shown at various values of bias. The heavy double arrow denotes the I-V excursion during the relaxation oscillations. (b) Total current versus time in the M-switch relaxation oscillation mode. Frequency, 3 MHz; $R=1$ kΩ; $t_p=5\times10^{-6}$ sec. Vertical scale, 0.1 A/div; horizontal scale, 2×10^{-7} sec/div.

When the bias was reduced after M switching at V_a, the sample often simply switched back to its "off" state. However, we also observed many of the following events: (A) At V_d ($< V_a$) a high-frequency relaxation oscillation[16] appeared at a frequency that increased as V increased and decreased as R increased. The observed frequency range was from 3–20 MHz [see Fig. 3(b)], which is 1 to 2 orders of magnitude higher than the typical relaxation oscillation frequencies observed in a D mode.[16] (B) At V_e the oscillation quenched and another small stable range of currents appeared. (C) Finally, a switch back to the "off" state occurred.

We interpret the results as follows: We assume that the formed filament in configurations (a) and (b) is partially crystallized,[13] leading to a smaller active volume and grossly inhomogeneous field distribution. The distribution is such that E_c is reached locally by flux concentration before it is attained by Joule heating in the center of the filament. At this point part of the sample shorts (here the voltage redistribution does not cause other parts of the sample to reach E_c), and the conductance exhibits an upward step.

In summary, we find that reversible switching in thin amorphous chalcogenide films is fundamentally electronic and can occur by electronic initiation if (1) E_c is reached fast enough so that heating is negligible, or (2) large inhomogeneities produce local fields greater than E_c. For the case where the field is initially below E_c, but Joule heating causes a hot spot to initiate, then E_c can be reached near the electrodes and D-mode switching will occur.

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[9]D. Sarrach of E. C. D., Inc., prepared these samples.

[10]W. D. Buckley of E. C. D., Inc., prepared these samples.

[11]Both D. Adler and S. R. Ovshinsky (private communication) have prepared samples where the virgin threshold voltage was maintained. S. R. Ovshinsky and H. Fritzsche [IEEE Trans. Electron Devices 20, 91 (1973)] have suggested means of sample preparation designed to control the forming process. Our results indicate that forming is an artifact of, rather than necessary for, switching.

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[13]M. P. Shaw, S. C. Moss, S. A. Kostylev, and L. Slack, Appl. Phys. Lett. 22, 114 (1973).

[14]A possible sequence of events: If we assume a central hot spot, when an electrode field exceeds E_c the conductivity there will increase dramatically to a level well above the central region. The excess voltage from the electrode region then appears across the center (propagating disturbance), causing both the field and the heating there to increase.

[15]Use of a field-activated conductivity to explain switching has proved quite successful (see Refs. 6 and 7). It is therefore important to produce results using an E_c model in order to determine whether, at the very least, equivalently successful agreement can be obtained. Perhaps E_c will augment the field-activated conductivity model, since Kaplan found a best fit to the data with a virtual electrode-field activated conductivity model [T. Kaplan, Ph. D. thesis, Massachusetts Institute of Technology, 1972 (unpublished)].

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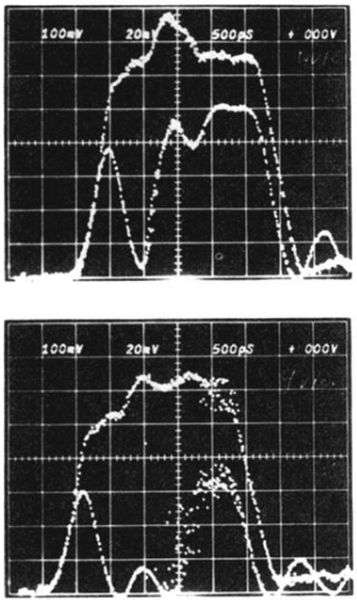
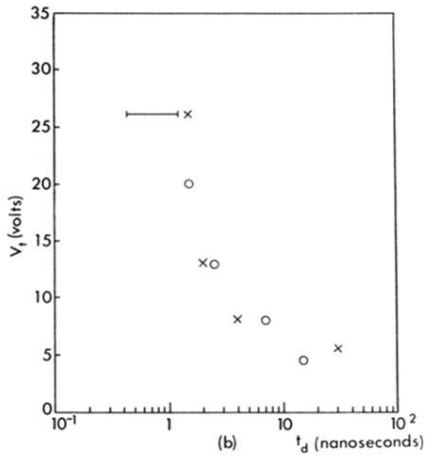


(a)



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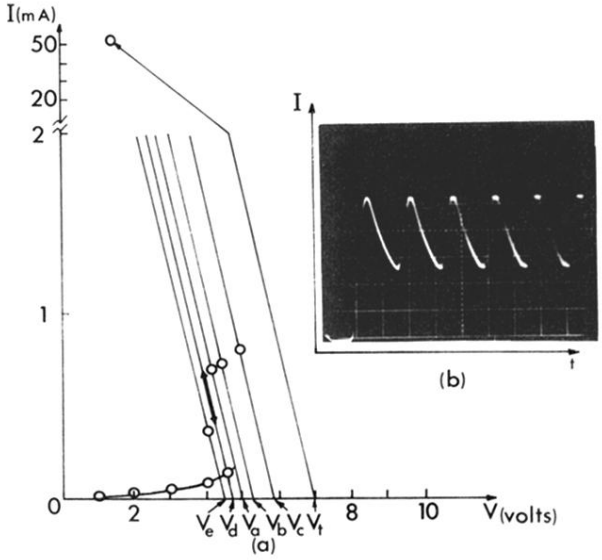

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