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Bistable resistivity switching properties of the semiconducting glass As-Te-Ge

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OF THE SEMICONDUCTING GLASS As-Te-Ge.

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BISTABLE RESISTIVITY SWITCHING PROPERTIES

OF THE SEMICONDUCTING GLASS As-Te-Ge

by

Ronald Robert Uttecht

A Dissertation Submitted to the

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INTRODUCTION

In recent years, the semiconductor industry has been con-
cerned primarily with crystalline materials such as germanium
and silicon which exhibit nearly perfect long range period-
icity. Diodes and transistors are fabricated by very care-
fully doping these crystalline materials with precise amounts
of impurities to form p-n junctions. Recently, however, con-
siderable interest has been shown in a group of materials
known as amorphous semiconductors which do not have long
range periodicity.

Several phenomena have been observed which seem to depend
on the bulk properties of these amorphous materials rather
than on impurity doping or p-n junctions. One of these
phenomena, electrically reversible bistable resistivity, has
been observed in such widely varying materials as the chalco-
genide glasses As-Te-I (1) and As-Te-Ge (2), metal oxide
films such as Al_2O_3 (3), and epoxy films (4). Since the
resistivities of the two stable states differ by at least
three or four orders of magnitude, these materials are
potentially useful in digital memory applications. An ex-
perimental memory array has been fabricated by Sie (5)
using a thin film of As-Te-Ge glass, but the basic mechanism
governing the bistable resistivity switching process is not
fully understood. In an attempt to shed some light on the
switching mechanism, these pages report some observations on

the properties of bistable resistivity switching in As-Te-Ge glass and attempt to transform these observations into a model of the bistable switching mechanism in amorphous semiconductors.

A material which exhibits bistable resistivity can best be characterized by its current vs. voltage curves as shown in Figure 1. The two stable resistance states, R_h and R_l, are represented by the two slopes. Initially the material is in its high-resistance state, R_h, with a resistance typically on the order of several megohms. An external voltage, V_s, is applied through a series resistance, R_s. As V_s is increased from zero, the current also increases slowly in an ohmic fashion up to a threshold voltage, V_t. When V_t is exceeded, the material switches rapidly to its low-resistance state, R_l, following the load line of the external resistance, R_s. Note that the intersection of the load line with R_l should be below the current threshold, I_t for stable switching to occur. In its low-resistance state the material has a resistance typically on the order of 10 ohms. The material will remain in the low-resistance state even if the applied voltage is removed. To switch from R_l back to R_h, the value of R_s is decreased so that now the intersection of the load line with R_h is below V_t. Now when the applied voltage is increased from zero and the current reaches its threshold value, I_t, the material switches back to its high-
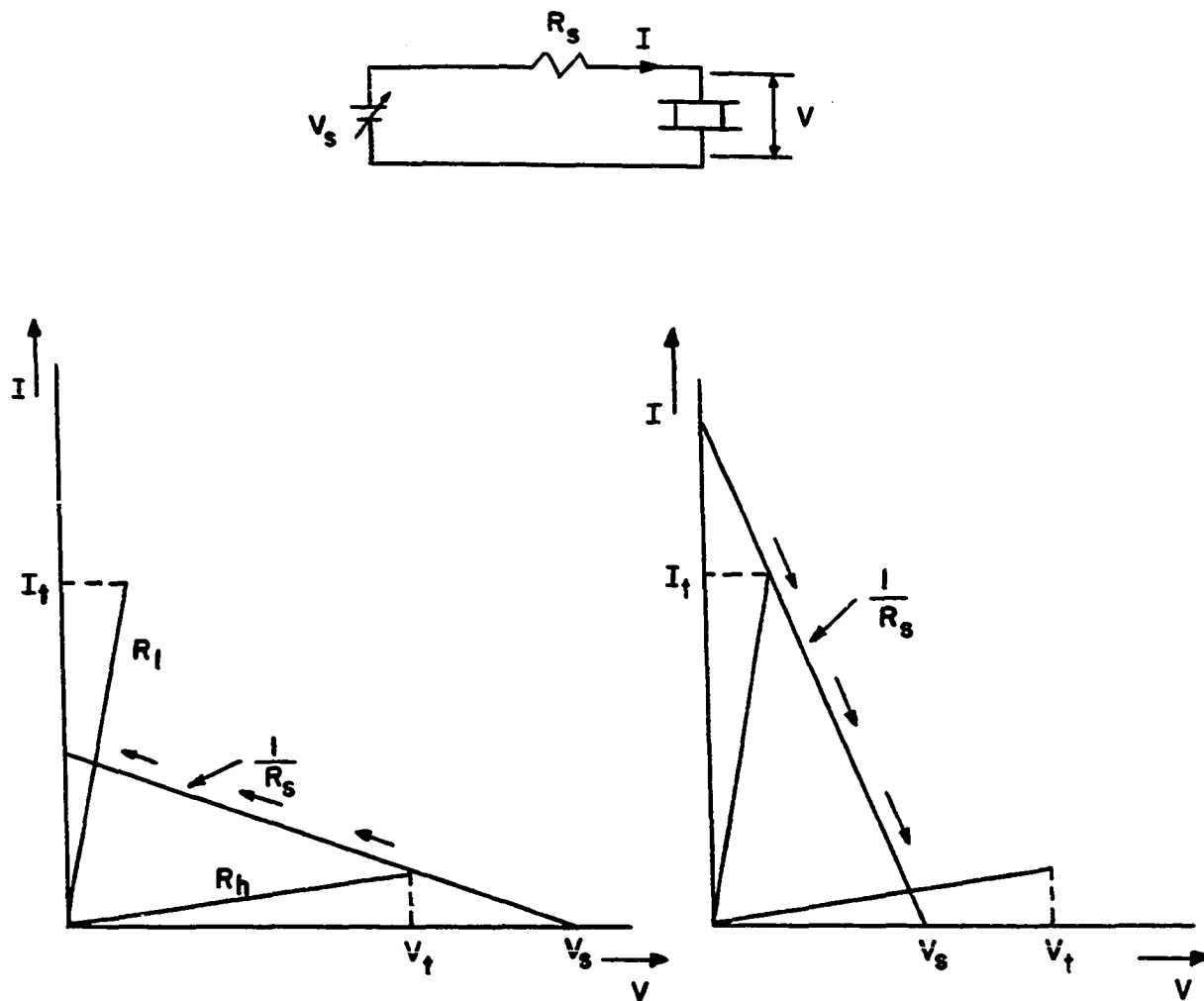
Figure 1. Current vs. voltage characteristics of
bistable resistivity switching

resistance state. These transitions can be repeated any number of times in the same sample if the proper cycle of applied voltage is used.

It is generally thought that an electrically induced conducting filament is responsible for the low-resistance state of amorphous semiconductors (6, 7). A method of forming a filamentary conducting path on the surface of bulk samples of amorphous As-Te-Ge is described in this study. This method allows direct visual observation of the filament growth. A cinematographic study was made of the filament formation and of the effect on filament formation of various parameters such as the duration and polarity of the applied voltage. The relationship between filament formation and the variation in the values of the threshold voltage and the high- and low-resistance states is reported. When the threshold voltage of an amorphous As-Te-Ge sample is exceeded for the first time, a certain amount of time passes before the material switches to the low-resistance state. It is observed that this delay time decreases each successive time the threshold voltage is exceeded and asymptotically approaches some iinal value. A relationship is thought to exist between the changing delay time and the formation of a conducting filament in the amorphous As-Te-Ge sample.

In switching from the low-resistance state back to the

high-resistance state, it is observed that the filament is disrupted by an amount which depends on the amplitude, width and shape of the applied voltage "pulse". Whether or not the material remains in the high-resistance state after the transition from R_l to R_h occurs is observed to depend on the speed with which the applied voltage is removed.

To further characterize these electric field-induced filaments, X-ray diffraction, electron microprobe and electron microscope techniques were employed. From these measurements and observations, the presence of crystallinity after many filaments had been formed on the surface of an amorphous As-Te-Ge sample and the composition and surface texture of the filaments were determined.

With all of the above observations on the bistable resistivity switching process in As-Te-Ge glass as a basis, a model of the switching mechanism in amorphous semiconductors is presented. This model is constructed around a crystalline conducting filament which is formed in amorphous semiconductors by an electric field-induced phase transformation. The first few transitions between R_h and R_l constitute a forming process during which a continuous filament grows between two external contacts. After a complete filament has been formed, subsequent bistable resistivity switching takes place within a very small portion of the total filament provided

that the correct type of applied voltage is used. Although
this model was based on observations made in bulk samples
it is thought that a similar process occurs on a much smaller
scale in the bistable resistivity switching observed in
thin films of amorphous semiconductors.

MATERIAL PREPARATION AND PROPERTIES

The first amorphous semiconductor considered for this study was As-Te-I glass as described by Pearson et al. (1). It was observed that this material decomposes noticeably in air over a period of a few weeks and therefore is unsuitable if consistent results are desired. It was suspected that the iodine was subliming.

The material actually used was As-Te-Ge glass in which Ovshinsky (8) had reported bistable resistivity switching taking place. The composition used for most of the investigations of this study was $As_{55} Te_{35} Ge_{10}$ (by atomic percent). As shown in Figure 2 this composition lies in the center of a glass-forming region of the ternary diagram for As-Te-Ge published by Hilton et al. (9). This composition is also the same one used by Sie (5) in his memory array. A few compositions slightly different than the one given above were used to determine the effect of varying the relative proportions of the three elements. Therefore the material will hereafter be referred to as As-Te-Ge without naming any specific composition.

The desired quantities of reagent grade arsenic, tellurium and germanium were weighed and placed in a quartz tube. The tube was evacuated with a mechanical pump for about 5 minutes and then sealed with a hydrogen torch. The sealed tube was placed in a rocking furnace, heated to 950-
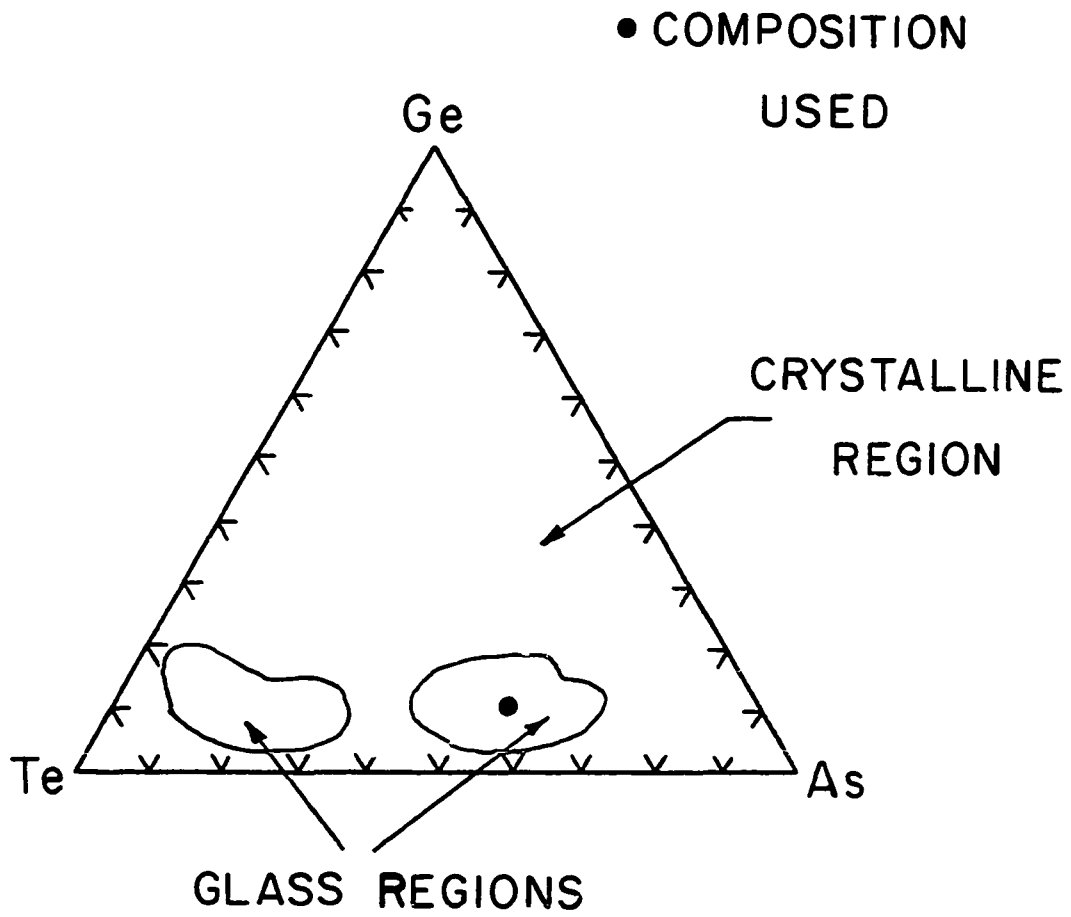
Figure 2. As-Te-Ge composition diagram

1000°C and allowed to react for about twenty-four hours.
Glass ingots were then formed by lifting the tubes out of the
furnace and air quenching them to room temperature.
Crystalline ingots used for resistivity measurements and
for X-ray diffraction were obtained by heating the glass
ingots in air to 400°C and then letting them cool to room
temperature in about four hours. Identification of an ingot
as amorphous or crystalline could usually be done by visual
examination. If there was any doubt, X-ray diffraction of
the sample provided a means of positive identification.

The electrical resistivity of the amorphous and
crystalline As-Te-Ge ingots was measured to be 1.1×10^6
ohm-cm and 0.98 ohm-cm respectively. The magnetic sus-
ceptibility of amorphous and crystalline As-Te-Ge was
measured by the Faraday method to be -28×10^6 emu/g.at.
and -14×10^6 emu/g.at. respectively. Both the amorphous
and crystalline samples were diamagnetic.

TRANSITION FROM HIGH- TO LOW-RESISTANCE STATE

Observation of filament formation

After applying a voltage pulse of 700 volts across the
ends of a 7 mm by 3 mm rod of crystalline stibnite (Sb_2S_3)
doped with 1% of antimony, Gildart (10) observed the formation
of a "metal-like thread" inside the body of the rod connecting
the ends. It was thought that the conductivity of this thread
accounted for a resistance decrease of five orders of
magnitude observed in the doped Sb_2S_3 after the voltage
pulse was applied. The formation of a similar metal-like
thread or filamentary conductor has been proposed (7, 11)
to explain the large resistance decrease observed in
chalcogenide glasses, such as As-Te-Ge, upon application of
a sufficiently large voltage. A method of forming such a
filamentary conducting path in As-Te-Ge by applying a
voltage between two point contact probes (12) is described
here. The point contact probes are placed on the surface
of a flat sample of As-Te-Ge thus allowing direct visual
observation of the growth of the filament between the probes.
Also the effects on filament formation of various parameters
such as the duration and polarity of the applied voltage can
easily be observed.

The electrical circuit used in this study is shown in
Figure 3. The symbol used to represent the material was
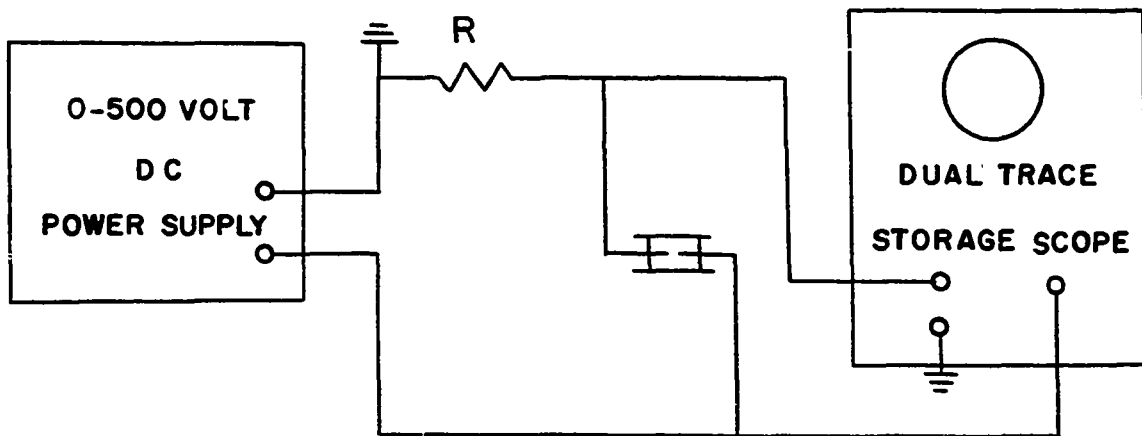chosen to illustrate the fact that a dc voltage was applied

Figure 3. Test circuit for the observation of bistable resistivity switching

to a bulk sample of As-Te-Ge by means of two tungsten carbide
probes in contact with the surface of the sample. The
tips of the probes were about 25 microns in diameter and
were spaced approximately 600 microns apart on the surface.
The probes were connected to a 0-500 volt dc power supply
through the current limiting resistor R of Figure 3. For
the transition of the material from the high-resistance state
to the low-resistance state, the value of R was 43k ohms.
The applied voltage, V_s, and the current through the material
between the probes, I_d, were monitored with a Tektronix
Model 564 dual trace storage scope.

The filament formation phenomena occurring in the material
were observed both visually using a Micro-Tech Model 2080
microprobe and cinematographically by taking 16mm films
simultaneously of the phenomenon in the material and the
storage scope traces. The films were taken in such a way
that they could be processed and printed together with the
material phenomenon appearing in the top half of a frame and
the storage scope traces in the bottom half. The composite
film (13) could then be studied to relate the growth character-
istics of a filament with the material's electrical
characteristics.

A filming sequence began by bringing the probes into
contact with the surface of an As-Te-Ge sample as shown in
Figure 4a and starting a slow sweep of about 3 sec/cm on the

Figure 4a. Original surface

Figure 4b. Initial transformation

Figure 4c. Filament partially grown

Figure 4d. Filament completely grown
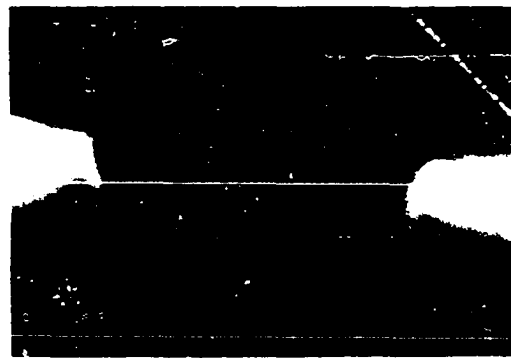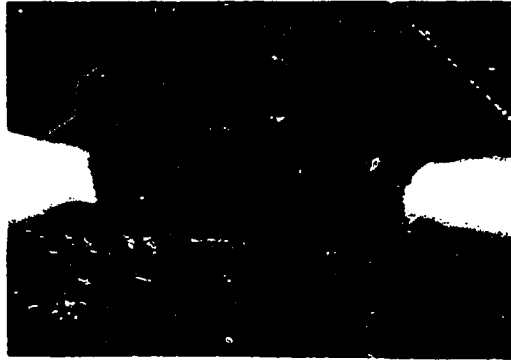
storage scope. The applied voltage was then increased manually from zero until a certain voltage threshold, V_{t_1}, was exceeded. At this instant a transformation, which was characterized by a change in the reflectivity of the surface, took place in the material. This transformation started at a line joining the probes and moved out in a direction perpendicular to that line as shown in Figure 4b. It can be seen that the transformation has removed the scratches which were originally on the surface as shown in Figure 4a. At the instant the transformation occurred, the resistance of the material between the probes dropped by about six orders of magnitude to what shall hereafter be referred to as the low-resistance state. If the applied voltage, V_s, was maintained at a value greater than the threshold voltage, V_{t_1}, a filamentary path started to grow along the surface from the positive probe toward the negative probe. If the applied voltage was then reduced to zero, the growth of the filament stopped as shown in Figure 4c and the material returned to its original high-resistance state. If the applied voltage was again increased from zero a new voltage threshold, V_{t_2}, was reached at a voltage which was somewhat less than V_{t_1}. When V_{t_2} was exceeded the resistance of the material dropped again and the filament started to grow from the spot where it had stopped. When this process was repeated a number of times, the filament continued to grow

each time the successively lower threshold voltage was
exceeded. The material changed to the low-resistance state
each time the threshold voltage was exceeded and returned
to the high-resistance state when the applied voltage was
removed. When the filament had completed its growth as
shown in Figure 4d, it was observed that the voltage threshold
had decreased to zero and that the material remained in the
low-resistance state, even after the applied voltage was
removed.

Variation of switching properties during filament formation

The electrical characteristics of the material can be
seen in Figure 5 which is an illustration of the storage
scope traces. The top trace is the applied voltage, V_s,
as a function of time and the bottom trace is the current
through the material, I_d, (i.e. the voltage across the current
limiting resistor R of Figure 3) as a function of time. Until
the first threshold voltage is reached, the voltage across
the current limiting resistor R is essentially zero as
shown in the bottom trace. This indicates that the re-
sistance of the material is much greater than R. When the
first threshold voltage is exceeded, the voltage across R
suddenly increases to a value slightly less than the applied
voltage, V_s. This indicates that the resistance of the
material has suddenly decreased to a value much less than R.
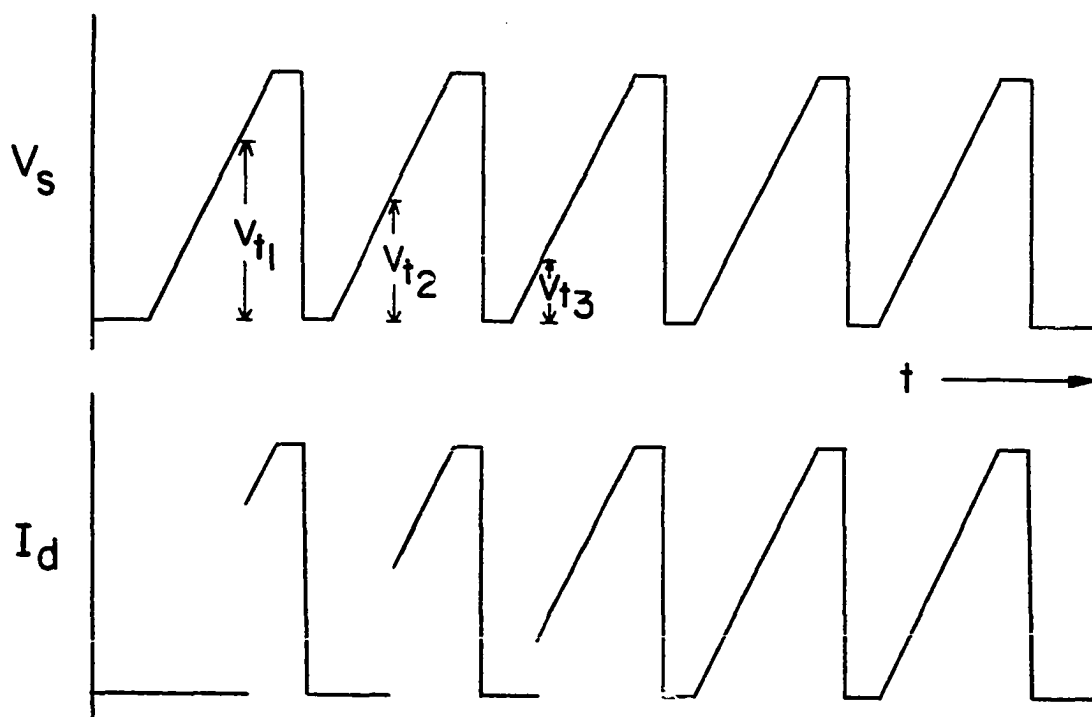The decrease in the threshold voltage as the applied voltage

Figure 5.   Illustration of storage scope traces indicating decreasing threshold voltage

is manually cycled up and down can also be seen in the
bottom trace of Figure 5. In this example after the third
cycle of applied voltage the threshold voltage has decreased
to zero and the material has been fixed in the low-
resistance state.

If the applied voltage was not decreased to zero after
exceeding the first threshold voltage but was maintained
at some value greater than V_{t_1}, then the filament grew all
the way over to the negative probe, thereby establishing
the low-resistance state in the material. This is illustrated
in Figure 6 which shows the absence of a second threshold
voltage after the applied voltage is maintained greater than
V_t for a time, decreased to zero and then increased. There-
fore the growth of a continuous filament between the two
probes is related to a stable non-vanishing transition of
the material from the high-resistance state to the low-
resistance state.

The visible growth of the filament always started
at the positive probe and proceeded toward the negative
probe. Many times the filament would appear to stop growing
before it reached the negative probe, while the scope traces
indicated that a continuous filament had been formed. It
was postulated that part of the filament had formed beneath
the surface. Polishing the surface after a filament of this
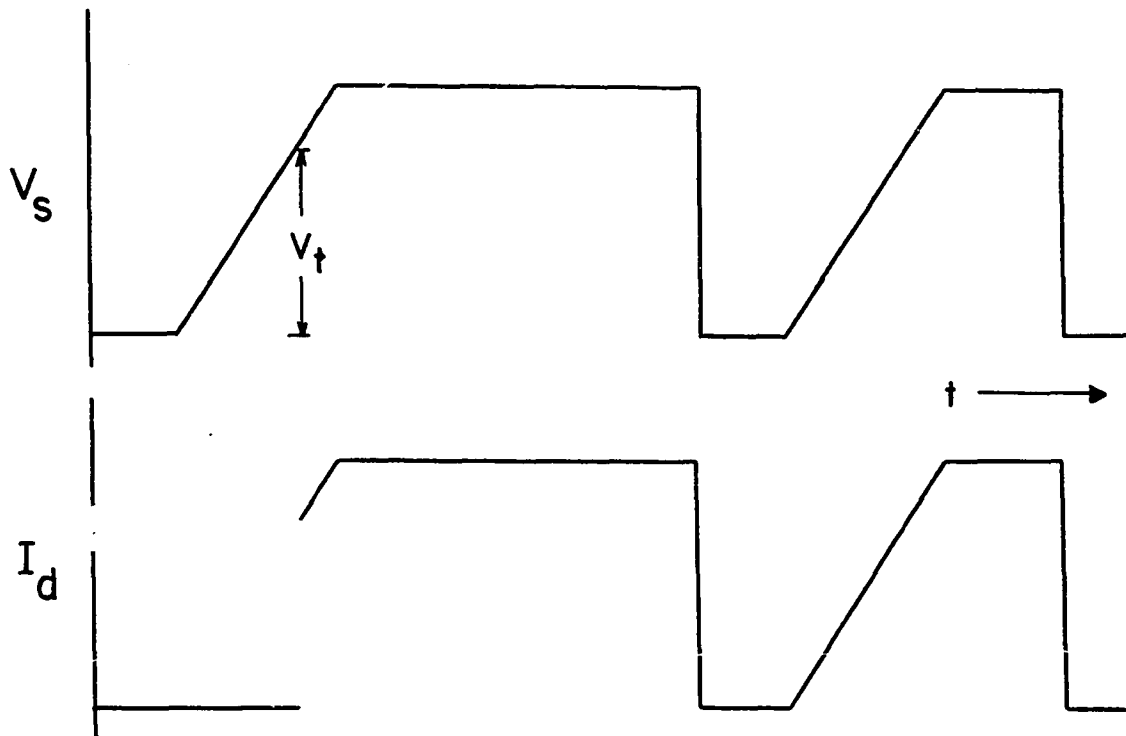type had been formed revealed a continuous path from one probe

Figure 6. Illustration of storage scope traces indicating completion of filament formation

mark to the other. This indicated that a continuous filament had originally been formed partially on the surface and partially beneath the surface. It is not known at the present whether the filament continued growing beneath the surface toward the negative probe or whether a second filament grew beneath the surface from the negative probe out to meet the first filament.

The polarity dependence of filament growth was demonstrated by first letting a filament grow from the positive probe halfway across to the negative probe and then stopping further growth by removing the applied voltage. The polarities of the probes were then reversed and the voltage applied again. When a critical value of applied voltage was reached, the filament appeared to grow backwards into the new negative probe and then a new filament started to grow out of the new positive probe toward the new negative probe.

Polarity reversal did not have any effect on a filament which had been completely formed. Therefore it is the filament formation process which is dependent on the polarity of the applied voltage. A possible explanation of this would be that ion migration is involved in filament formation. The ions, which are electrically charged, would respond to changes in the polarity of the applied voltage.

The size of a growing filament was observed to depend

directly on the amount of current flowing through the material. If the value of the current limiting resistor, R, was increased while a filament was forming, the diameter of the filament was smaller from that point on. If the value of R was decreased while a filament was forming, the filament would completely vanish and then would start growing again from the positive probe with a larger diameter than it had before.

In order to determine the speed of response of the material to an applied voltage "pulse", a switch was connected between the dc power supply and the current limiting resistor, R, to provide faster rise times than could be obtained by manually increasing the applied voltage. The storage scope was used in a single sweep mode to monitor the applied voltage and the voltage across the current limiting resistor. After initiating a sweep and then closing the power supply switch, a delay was observed from the time the power supply was switched on until the material transformed to the dynamic low-resistance state. The first time the voltage "pulse" was applied to a sample, the time delay was about 7 msec as shown in Figure 7a. Since the power supply was on for only a short time, the material did not stay in the low-resistance state but returned to the high-resistance state as soon as the voltage pulse was removed. When additional voltage pulses were applied to the

Figure 7a.   Storage scope traces for first application
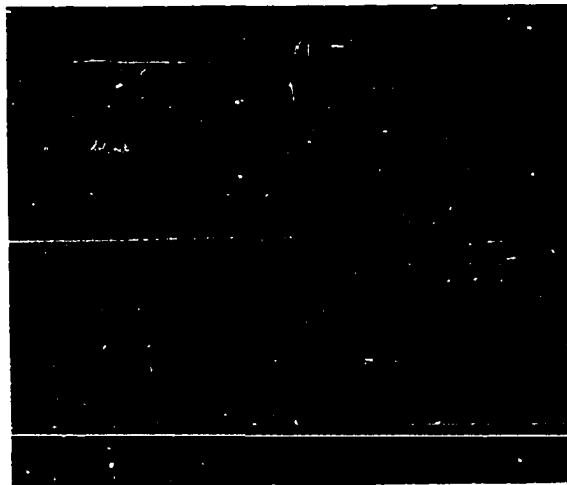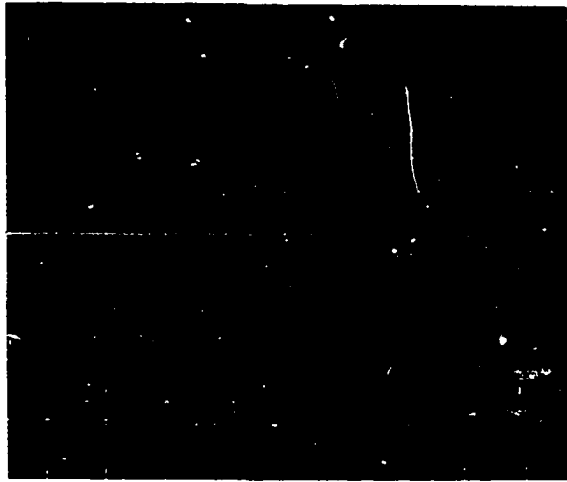of voltage pulse

Vertical scale: 100 v/cm
Horizontal scale: 2 msec/cm

Figure 7b.   Storage space traces for third application
of voltage pulse

Vertical scale: 100 v/cm
Horizontal scale: 2 msec/cm

Figure 7c.   Storage scope traces for twentieth applica-
tion of voltage pulse

Vertical scale: 100 v/cm
Horizontal scale: 1 msec/cm

same sample, the time delay was observed to decrease.
The time delay decreased to about 3 msec after the third
voltage pulse and decreased to about 0.1 msec after the
twentieth voltage pulse as shown in Figures 7b and 7c
respectively. The speed of the actual transition from the
high-resistance state to the low-resistance state, not in-
cluding the time delay, was too fast to be reasonably
estimated by this method.

It is thought that the time delay and its decrease are
directly related to the formation of a filament. Each time
the voltage pulse was applied, the filament grew a little
longer and the distance across which the voltage was applied
decreased. With the same value of voltage applied across a
decreasing distance, the maximum value of electric field
intensity will increase for each pulse until the filament
has completely grown. A decrease in delay time with an
increase in the applied voltage pulse observed by Ovshinsky
in his threshold switch was thought to be due to a nucleation
process which preceded the actual switching (11). A similar
mechanism may be operative in the example reported here.

TRANSITION FROM LOW- TO HIGH-RESISTANCE STATE

Observation of filament disruption

Gildart (10) reported the formation of a "metal-like thread" connecting the ends of a rod of doped crystalline stibnite when he applied a 700V voltage pulse across the rod. He also observed that when the stibnite rod was heated to 200-300°C or when a sufficiently large current pulse was passed through the rod, the original high-resistance state was restored and the thread vanished. Ovshinsky (11) also reported using a current pulse exceeding a threshold value to switch from the low-resistance state to the high-resistance state in a chalcogenide glass containing arsenic, tellurium, germanium and silicon. In both of these examples the switching action took place inside the bulk of the material so that a complete investigation of the process could not be made. The switching action reported here, however, took place through the formation of conducting filaments on the surface of the material. Therefore the transition from the low-resistance state back to the high-resistance state and its relation to the conducting filament could be observed and studied.

The first method used to switch back to the high-resistance state after a continuous filament had been formed was to change the current limiting resistor R of Figure 3

from 43k ohms to 500 ohms and then apply a dc voltage. When a current threshold, I_t, was reached the filament vanished and the high-resistance state was restored. If the applied voltage was quickly reduced to zero after I_t was reached, the material would remain in the high-resistance state. If, however, the applied voltage was maintained or increased after I_t was reached, the material would not stay in the high-resistance state.

The second method of switching back to the high-resistance state after a continuous filament had been formed utilized a Tektronix Model 575 Curve Tracer. The full-wave rectified 60 cycle ac voltage source and the 500 ohm series resistor were internal to the curve tracer. As the amplitude of the ac voltage was increased from zero and the current threshold was reached, the material returned to the high-resistance state with no visible change in the structure of the filament. If the amplitude of the ac voltage was then increased so that the current threshold was exceeded, the filament would either be disrupted along a small portion of its length or would completely vanish. In either case the material would transform back to and remain in the high-resistance state.

The transition from the low-resistance state to the high-resistance state without a visible change in the structure of the filament was observed only when the curve tracer with

its 60 cycle ac voltage supply was used. The reason for this and the other phenomena observed during the transition from R_l to R_h is thought to involve the difference in the speeds with which the ac and dc applied voltages were removed after the current threshold was reached. This hypothesis will be expanded and discussed further in a later section where a proposed switching mechanism is presented.

Variation of switching properties during filament disruption

The values of R_h and R_l were estimated from the slopes of the current vs. voltage curves displayed on the curve tracer for the various types of transition to the high-resistance state. The resistance was 10k ohms before any filament formation had taken place and 0.4 ohms after a continuous filament had been formed. After switching back to the high-resistance state the value of R_h was 1.2k ohms if the filament had not been visibly changed, 1.7k ohms if the filament had been visibly severed and 5.0k ohms if the filament had completely vanished. The value of R_l after each of these transitions was about 0.6 ohms.

The threshold value for switching back to the low-resistance state also depended on what type of transition was made to the high-resistance state. The value of V_t was 45 volts for the filament which appeared unaltered, 55 volts for the filament which was visibly severed and 115 volts for the filament which had completely vanished compared to 140

volts for the threshold voltage of the initial transformation. For all three types of transition to R_h, the bistable resistivity switching was completely repeatable over many cycles. For any practical application, however, the best type of transition to R_h is the one with no visible change in the filament. Since the switching here is evidently taking place in a very small region, the transitions would be faster and would require less applied voltage.

CHARACTERIZATION OF FILAMENTS

X-ray diffraction

Several of the speculations on the mechanism of bi-stable resistivity switching in amorphous semiconductors involve crystallization processes (5, 14). It was observed that the thermal crystallization of an amorphous sample of As-Te-Ge, by heating it to 400°C and then slowly cooling it to room temperature, also transformed the sample to the low-resistance state. Sie (5) proposed that the bistable resistivity switching in amorphous As-Te-Ge was due to a reversible amorphous to crystalline phase transition. It does not seem unreasonable, therefore, that the filament formation observed during the electric field-induced trans-formation of amorphous As-Te-Ge to the non-vanishing low-resistance state is also a crystallization process.

X-ray diffraction analysis provides an excellent means for investigating the crystallization of amorphous materials. Crystalline materials produce sharp X-ray diffraction peaks which can be used as a positive means of identification by comparison with standard data such as the A.S.T.M. Index (15). Amorphous materials, on the other hand, show rather broad X-ray diffraction peaks with the complete absence of sharp peaks. An unknown material may be identified by com-paring its diffraction pattern with those in the A.S.T.M.

Index to find one that matches. Identification of several substances in a mixture is often possible, since the diffraction pattern for the mixture is a superposition of the patterns for the individual constituents of the mixture.

The X-ray diffraction patterns of powdered amorphous and crystalline As-Te-Ge obtained with a General Electric Model XRD-5 diffractometer using nickel-filtered Cu K_{α} radiation are shown in Figures 8a and 8b respectively. The crystalline sample was obtained by heating an As-Te-Ge glass ingot to 400°C, letting it cool slowly to room temperature, and then crushing it to a fine powder. Figure 8a shows the broad peaks which are typical of an amorphous material and Figure 8b shows a set of sharp peaks which are characteristic of crystalline As-Te-Ge. The d-spacings of the crystalline peaks of Figure 8b are listed in Table 1. A Debye-Scherrer powder pattern was obtained using finely powdered crystalline As-Te-Ge. This method gave essentially the same set of d-spacings as obtained from the diffractometer trace, but the relative intensities of the peaks were somewhat different. It was not possible to determine the specific phase or phases present in the crystalline sample of As-Te-Ge by comparing the d-spacings and relative intensities obtained by both methods with those in the A.S.T.M. Index. It is quite possible, however, that a crystalline compound or compounds are present which have not been previously indexed.

Figure 8a. X-ray diffraction pattern of amorphous As-Te-Ge powder

Figure 8b. X-ray diffraction pattern of thermally induced crystalline As-Te-Ge powder

Figure 8c. X-ray diffraction pattern of amorphous As-Te-Ge bulk surface

Figure 8d. X-ray diffraction pattern of amorphous As-Te-Ge bulk surface with about 10% of its area covered with electrically induced filaments
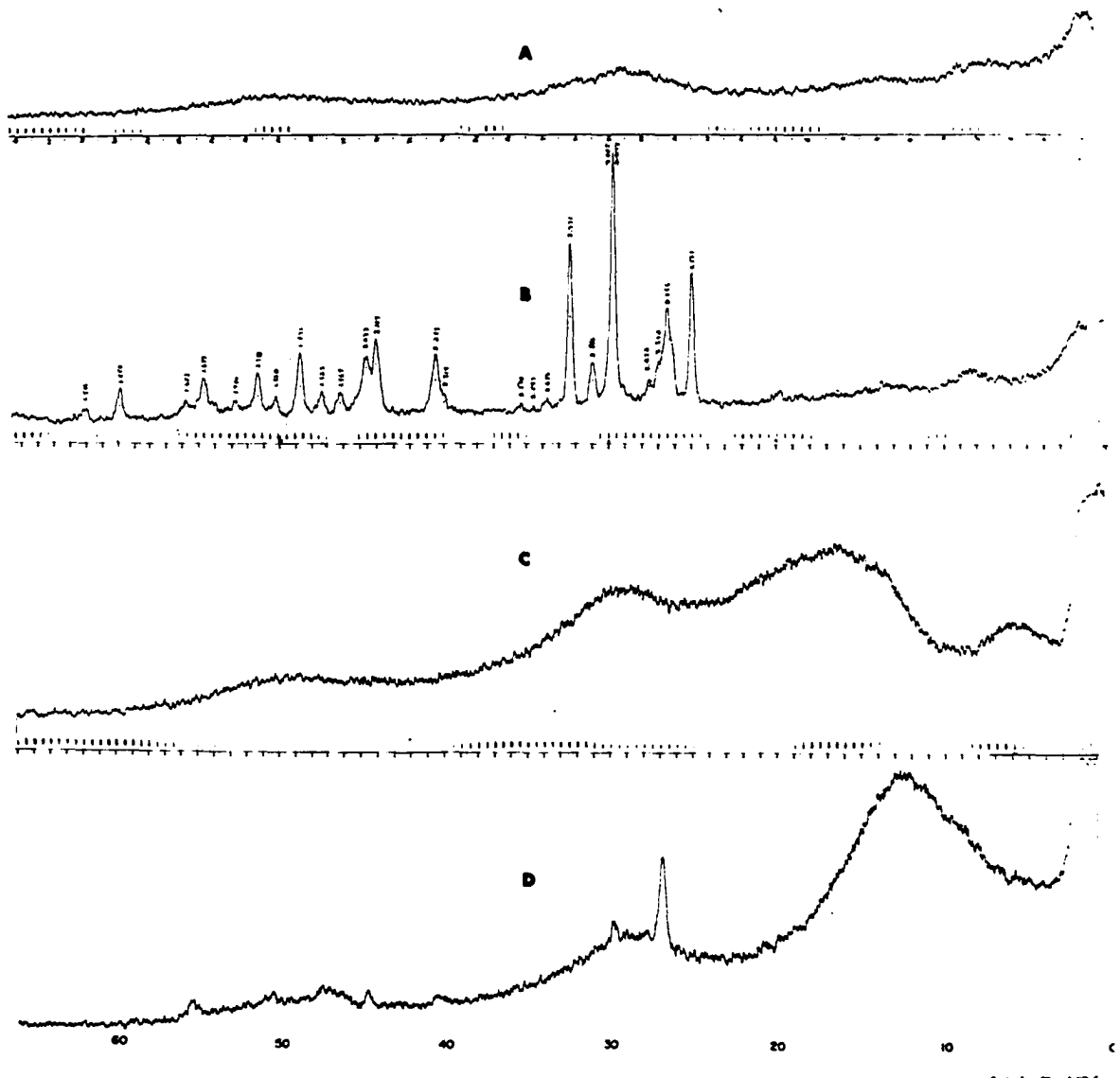
Table 1. d-spacings of thermally and electrically induced
crystalline As-Te-Ge

| Thermally Induced (B) (in $\overset{o}{A}$)	Electrically Induced (D) (in $\overset{o}{A}$)
3.56	3.32
3.37	3.00
3.30	2.29
3.23	2.03
3.00	1.93
2.89	1.90
2.77	1.80
2.66	1.65
2.60	
2.54	
2.31	
2.29	
2.10	
2.03	
1.97	
1.92	
1.87	
1.82	
1.78	
1.74	
1.68	
1.65	
1.56	
1.50	
1.38	
1.29	
1.22	
1.21	
1.19	

In order to check the hypothesis that filament formation
in amorphous As-Te-Ge involves a crystallization process, an
X-ray diffraction analysis of some filament material had to
be made. Since a single filament was too small to reflect a
sufficient amount of X-rays to be detected by the available
equipment, it was necessary to use a large number of fila-

ments. Approximately 1500 filaments, each about 600 microns long and 30 microns wide, were electrically induced end to end in parallel lines on the surface of an amorphous As-Te-Ge sample using the tungsten carbide probes and dc power supply as described previously. The surface of this specimen, which was approximately 1" by 3/4", is shown in Figure 9a. An enlarged view of a portion of the surface, showing the details of the filament arrangement, is shown in Figure 9b.

The diffraction patterns of the specimen before and after the 1500 filaments were formed are shown in Figures 8c and 8d respectively. The broad peaks which appear between the angles of 0° and 20° in both of these patterns were due to the acrylic plastic in which the As-Te-Ge specimen was mounted and should be disregarded. Figure 8c shows two broad amorphous peaks centered on angles of about 29° and 49°. Figure 8d shows two crystalline peaks superimposed on the broad amorphous peak at 29° and a number of smaller crystalline peaks superimposed on the broad amorphous peak at 49°. The d-spacings of these crystalline peaks are also given in Table 1. Identification of a specific crystalline compound by a comparison of these d-spacings with those of the A.S.T.M. Index again failed. It should be noted, however, that all of the peaks of Figure 8d occur at the same angle as does some peak in Figure 8b. The fact that

Figure 9a.   Amorphous As-Te-Ge bulk surface with about
              1500 electrically induced filaments for X-ray
              diffraction purposes

Figure 9b.   Enlarged view of Figure 9a
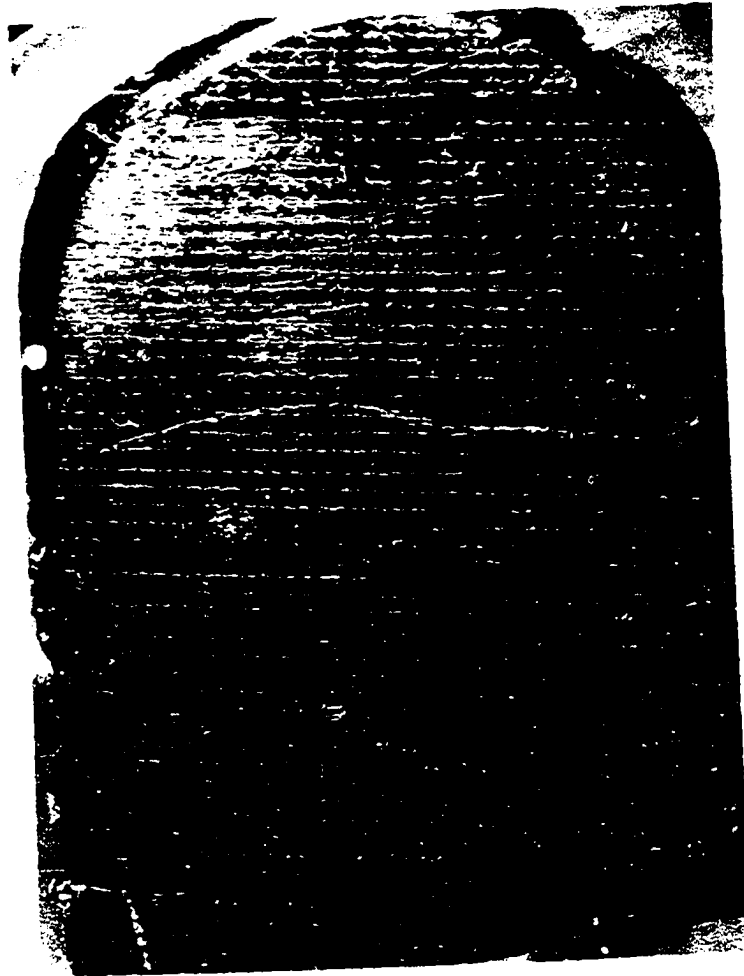
the intensities of comparable peaks are quite different is
not surprising since a great deal of preferred orientation
was probably present in the bulk specimen compared to that
present in the powder specimen. It is possible, therefore,
that at least one of the crystalline phases present in the
thermally crystallized sample of As-Te-Ge was also present
in the conducting filaments electrically induced on the
surface of the sample of amorphous As-Te-Ge. Even though
a positive identification of the specific crystalline phase
could not be made, the presence of sharp peaks in Figure 8d
indicated that some type of crystallization was involved in
the filament formation process.

Electron probe microanalysis

In order to determine whether any compositional change
had taken place during filament formation, a Hitachi XMA-5
Electron Probe Microanalyzer with a two channel X-ray
spectrometer capability was used. An accelerating voltage
of 30 kV with an absorbed electron current of 0.01 μA
at the specimen was held constant throughout the study. Under
these circumstances the resolution of the beam is about 2 μ.
A LiF crystal was used to detect the Te L_α line and the Ge
K_α line and a KAP crystal was used to detect the As L_α line.

The beam was first focused on standard polished samples
of As, Te and Ge and the X-rays emitted by each element

counted for 20 seconds. Then the beam was focused on an amorphous sample of As-Te-Ge which had a filament formed on its surface. The beam was focused on a spot in the center of the filament and on a spot far removed from the filament. In each case the X-rays emitted by each element were counted for 20 seconds. The surface of the specimen was polished flat with 0.05 micron alumina grit to ensure the detection of as much emitted radiation as possible.

By scanning the beam across a filament and the area on each side of the filament, the spatial distribution of each element near the surface was determined. Since only two elements could be studied simultaneously it was necessary to make one scan examining Te and As and a second scan examining Ge and As. The beam was held stationary and the specimen moved at 10 μ/min. The amplitude of the emitted X-rays detected in counts/sec was recorded on a chart moving at 60 mm/min.

By using the equation

$$\text{Relative X-ray Intensity} = \frac{N - B}{N_o - B}$$

where

      N = number of counts for 20 seconds from the unknown specimen using radiation of a particular wavelength

      N_o = number of counts for 20 seconds from the standard specimen using the same radiation as for N

B = background correction obtained by taking the number of counts for 20 seconds from the standard specimen using radiation of wavelength on either side of the peak value

we can calculate relative X-ray intensities of the various elements for the spot at the center of the filament and for the spot far away from the filament. Since the relative X-ray intensity from any element will not normally correspond to its weight percentage, it is necessary to convert the former to the latter. This was done by a method of successive approximations as suggested by Birks (16, 17). In carrying out the calculations, no corrections were applied for fluorescence, atomic number effect or dead time of the counter. These were expected to make only an insignificant contribution. When the weight percentages of each element were calculated for various spots in the vicinity of the filament, the spatial distribution of the elements could be determined.

Table 2 gives the relative X-ray intensities and the calculated composition in weight percentages inside a typical filament and far away from the filament. The assumed starting composition by weight percentage is also given for comparison purposes. It is possible, however, that the actual composition of the As-Te-Ge sample used here was not the same as the assumed starting composition. This would explain the difference observed between the weight per-

Table 2.   Electron probe microanalysis results

| | Relative X-Ray Intensity | | Calculated Composition in Weight % | | |
	Far Away From Filament	Inside Filament	Far Away From Filament	Inside Filament	Starting
As	0.1632	0.0888	37.74	22.36	44.27
Te	0.4574	0.6468	52.78	72.61	47.92
Ge	0.0829	0.0430	9.48	5.03	7.80

centages found at a spot far away from the filament and the weight percentages of the assumed starting composition.

Figure 10 shows the spatial distribution of weight percentages of As, Te and Ge obtained from a scan across a typical filament and the surrounding area.   Inside the filament there has been an increase of 37.6% of tellurium, a decrease of 40.8% of arsenic and a decrease of 47% of germanium for this particular example.   A slight accumulation of germanium is also noted on each side of the filament.

The weight percentages calculated inside the filament for arsenic and tellurium are close to those of As_2Te_3, which is a highly crystalline compound (18).   The crystalline filament, therefore, could be As_2Te_3 in a matrix of germanium. Another possibility is that the filament is crystalline tellurium in an arsenic-germanium matrix.   Neither of these speculations could be correlated exactly with the X-ray diffraction results, however.

Figure 10.   Weight percentage distribution of arsenic,
             tellurium and germanium across a filament
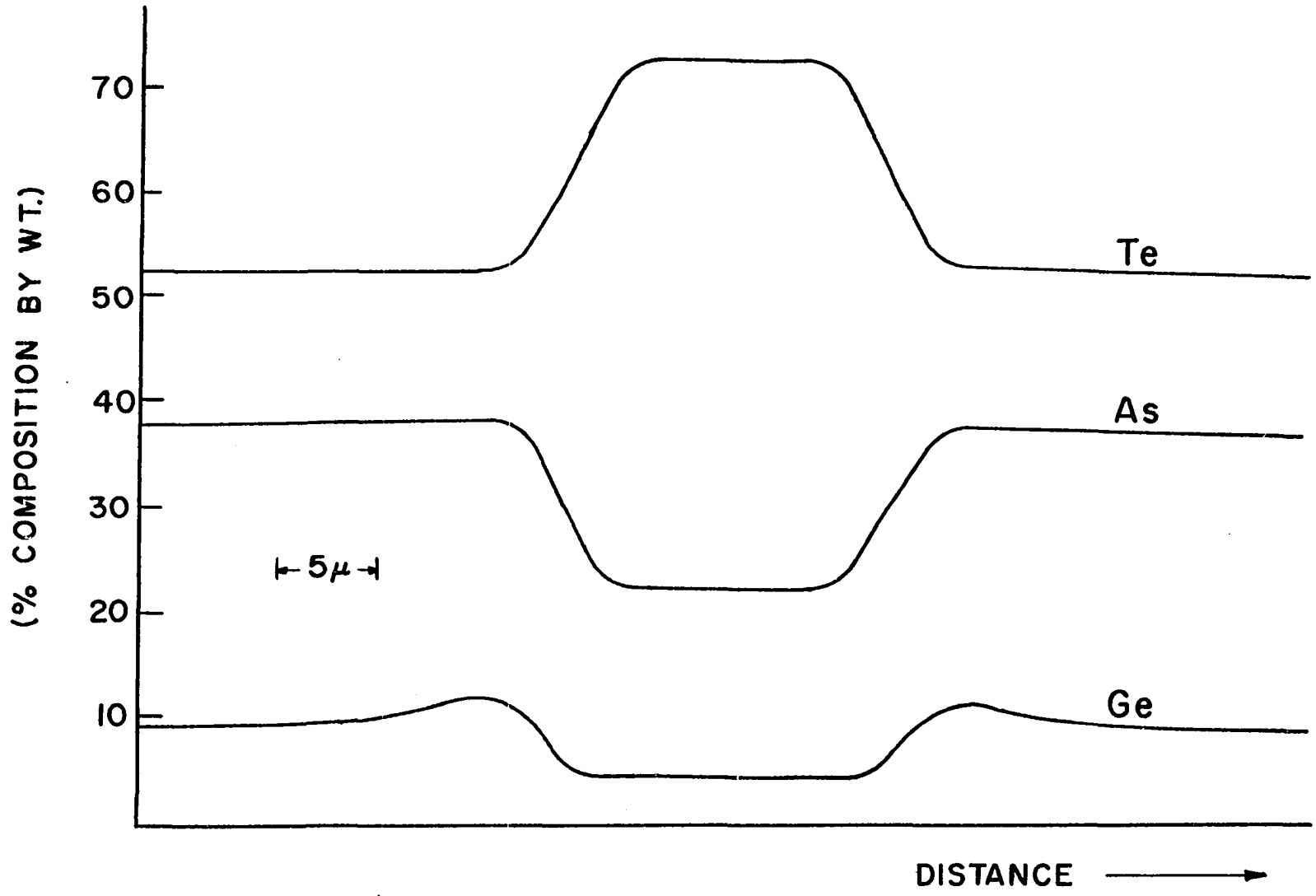
It should be noted that the penetration of the beam into the material was only about one micron so that the results given here are indicative only of what had taken place near the surface examined. The original surface was lapped down after the filament had been formed, however, so that the results still show qualitatively what had taken place farther down inside the material. The electron microprobe analysis indicated, therefore, that a spatial rearrangement of the elements occurred during filament formation.

Electron microscopy

Carbon replicas were made of the surface of an As-Te-Ge sample which was polished with 0.05 micron alumina grit after many filaments had been formed on its surface. These replicas were then examined in a Siemens Elmiskop I electron microscope at an accelerating voltage of 80 kV. Electron optical magnifications of up to X60,000 were employed in this study.

The first step in the replicating process was to cover the polished surface with a drop of 4% parlodian solution. When the parlodian had completely dried it was stripped off very carefully with a pair of tweezers. This plastic replica was then placed in a vacuum evaporator with the surface which had been in contact with the As-Te-Ge sample facing upward. Then thin layers of Victawet, germanium and carbon

were deposited in that order onto the plastic replica. The germanium was deposited at a 45° angle to cast shadows which improve the contrast of the image seen in the electron microscope. The germanium also makes the carbon replica more stable. The layer of Victawet was a wetting agent which allowed the shadowed carbon replica to float free of the parlodian layer when the combined replicas were immersed in water. The shadowed carbon replica was then removed from the surface of the water on a 200-mesh copper grid and allowed to dry. The shadowed carbon replica adhered to the copper grid and was then ready for observation in the electron microscope.

An example of a micrograph obtained by this technique is shown in Figure 11. The total magnification, including photographic enlargement, is X7,700. The filament shown in Figure 11 is about 12 μ wide. A topographical analysis of the micrograph's shadows indicated that the filament was slightly raised in relation to the rest of the surface pictured. It can also be seen that the scratches from polishing did not affect the surface of the filament. One interpretation of this is that the filament material is harder than the surrounding material and, therefore, has a different structure than the surrounding material.

A definite change in the direction of the surface texture can be seen in going from one side of a filament boundary to

Figure 11. Micrograph from surface replica of a filament
            Total magnification: X7,700
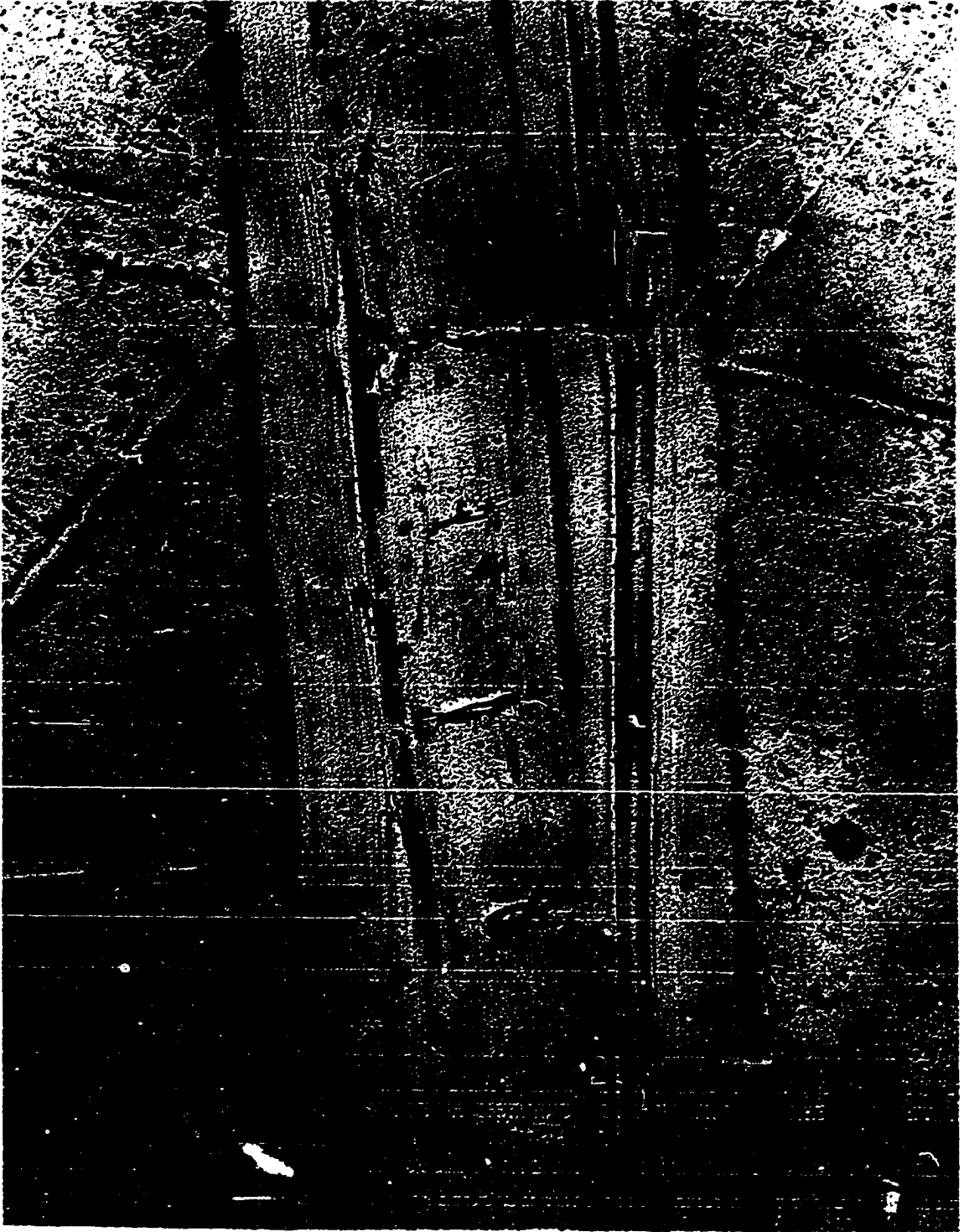
the other. The texture inside the filament seems to be
aligned with the direction of the growth of the filament.
The large surface irregularities horizontal to the filament
are thought to be due either to cracking caused by stresses
in the filament or to the segmented growth observed during
filament formation. Since the surface of the As-Te-Ge
sample was not chemically etched before the replica was
taken, a detailed analysis of the different surface textures
present could not be made.

PROPOSED BISTABLE RESISTIVITY SWITCHING MECHANISM

It should be pointed out that there are two distinct types of resistivity switching in amorphous semiconductors. The first type is known as threshold switching (11). It requires a bias voltage to maintain the low-resistance state, does not involve a structural change of the material, is extremely rapid and is probably electronic in nature. The other type, which is known as memory switching (11), is the bistable resistivity switching investigated here. As has been observed, this type of switching does not require a bias voltage to maintain the low-resistance state and does involve a change in the structure of the material. It is quite likely, therefore, that the mechanisms of the two types of resistivity switching are quite different. Although there is some evidence that both mechanisms are involved in establishing bistable resistivity switching in amorphous As-Te-Ge, the model proposed here will describe only the memory or bistable resistivity switching mechanism.

All of the observations of the properties of bistable resistivity switching in amorphous As-Te-Ge which have been reported here provide clues to the as yet unexplained mechanism. These observations were centered around the electric field-induced formation of conducting filaments on the surface of bulk samples of As-Te-Ge. It was demonstrated that the resistance changes remained fixed in the material

only after a continuous filament had been formed between the two external contacts. It is felt, therefore, that any model of the bistable resistivity switching mechanism must include these conducting filaments.

The proposed model starts with the transformation observed when the threshold voltage of an As-Te-Ge sample is reached for the first time. This transformation is thought to be initiated by a process similar to the "thermal pinching" of an electron-hole plasma as reported by Ancker-Johnson and Drummond in InSb (19). In this process, localized heating raises the temperature of the material to such an extent that melting may occur, resulting in irreversible changes to the solid structure. This may explain why the scratches on the surface of the As-Te-Ge sample appeared to vanish after the threshold voltage was reached and the transformation started.

Shortly after the initial transformation occurs, the resistance of the material drops by several orders of magnitude. If the applied voltage is removed before a filament has formed between the external contacts, the material returns to the high-resistance state. This phenomena is similar to threshold switching (11) and, therefore, will not be included in the model of the memory switching mechanism presented here.

The model next takes into account the forming process

during which the growth of a conducting filament from the positive contact to the negative contact occurs. These filaments were found to be crystalline by X-ray diffraction and electron microscope techniques. Therefore the filament growth must involve an amorphous to crystalline phase transformation, which implies that a thermal process is involved. It was also observed that the direction of growth of the filament depended on the polarity of the applied voltage. This implies that some type of charged carriers, such as ions, are moving in response to the applied electric field during filament formation. The results of the electron microprobe analysis showed that a rearrangement of the three elements had taken place during filament formation with tellurium increasing and arsenic and germanium decreasing inside the filament. This implies that atoms are diffusing through the material in such a manner that tellurium atoms accumulate and arsenic and germanium atoms diffuse away from a line joining the external contacts. The exact manner in which this is accomplished, however, is not obvious. The diffusion would proceed until a certain stoichiometric ratio was reached, after which the crystalline filament would start to grow. The forming process of the proposed model therefore, includes both thermal and electric field dependent phenomena. The manner in which these phenomena interact to form a crystalline conducting filament is not understood at the present time.

The last part of the model accounts for the bistable resistivity switching mechanism after a continuous filament has been formed between the external contacts. As has been observed, the transition back to the high-resistance state after a continuous filament has been formed takes place by disrupting the filament. The current limiting resistor is decreased so that a large amount of current passes through the filament. When the current threshold is reached, Joule heating causes the filament to disrupt somewhere along its length.

When dc voltages are applied and the current is increased to the critical value, Joule heating causes the entire filament to disrupt. If the current is quickly removed, the heated material quenches into the amorphous state and the high-resistance state is restored. If the current is left at the critical value or is slightly increased, a new phase transformation will occur, the material will return to the low-resistance state and a new filament, larger than the first, will start to grow.

When ac voltage is applied and the current is increased to the critical value, Joule heating causes the filament to disrupt at its weakest point when the ac voltage is at its maximum amplitude at the top of a cycle. Since the amplitude of the ac voltage decreases rapidly from this point on, only a small amount of material is heated. This small

amount of material immediately quenches to the amorphous state and the high-resistance state is restored. If the amplitude of the ac voltage is now increased so that the current goes past the critical value, a larger amount or all of the filament is disrupted. Since the amplitude of the ac voltage quickly drops after the filament is disrupted, the heated material quenches into the amorphous state and the high-resistance state is restored.

In general, the amount of filament disrupted in the transition from the low-resistance state to the high-resistance state depends on the amplitude and duration of the applied voltage. Whether the transformation to the high-resistance state is maintained depends on the speed with which the applied voltage decreases to zero. An optimum combination of the amplitude, duration and fall time of applied voltage pulses could be found which would permit switching to the high-resistance state with a minimum disruption of the filament. Switching back again to the low-resistance state would then be accomplished by restoring the disrupted filament. This would be done by applying the original low-current voltage pulse to the external contacts. At a new voltage threshold, somewhat lower than the original, the disrupted portion of the filament would recrystallize and the low-resistance state would be restored. If the proper applied voltage pulses were used, a very small volume

of a filament could be cycled between the amorphous and crystalline phases almost indefinitely. In doing this we would also be going back and forth between the high- and low-resistance states, which is bistable resistivity switching.

SUMMARY

The preceding pages have presented a series of observations on the bistable resistivity switching properties in bulk amorphous samples of As-Te-Ge. A relationship was developed between these bistable switching properties and the formation and disruption of electrically induced crystalline filaments between the external contacts. A method of forming and disrupting these crystalline filaments on the surface of bulk amorphous As-Te-Ge samples was presented which allowed direct visual observation of the switching action. A characterization of the filaments themselves was attempted by means of X-ray diffraction, electron probe microanalysis and electron microscopy. Taking all of the above observations into account, a model of the bistable resistivity switching mechanism in amorphous semiconductors was presented.

Crystalline conducting filaments were formed on the surface of bulk samples of amorphous As-Te-Ge by applying a voltage between two point contact probes. When a certain threshold voltage was reached, a transformation occurred in the material between the probes and a filament was observed to grow from the positive probe toward the negative probe. A cinematographic study was made of the relationship between filament formation and the changes observed in the electrical

characteristics of the material. It was observed that the material would stay in the low-resistance state only after a continuous filament had been formed between the probes. Once this occurred, however, the applied voltage could be completely removed without affecting the low-resistance state fixed in the material.

To transform back to the high-resistance state after a filament had been formed, a large amount of current was passed through the filament. The joule heating then increased the temperature of the filament to the point that it disrupted, much as in the manner of blowing a fuse. The amount of filament which disrupted depended on the amplitude and duration of the applied voltage. Whether the material was transformed into the high-resistance state or whether it stayed in the low-resistance state depended on the speed with which the applied voltage was removed. In the case of a full-wave rectified 60 cycle ac voltage "pulse", the amplitude, width and fall time were such that the transition back to the high-resistance state occurred with no visible change in the filament. Evidently the switching here was taking place in a very small area.

A study was made of the filaments themselves in an attempt to learn more about the switching process. X-ray diffraction of a large number of filaments on the surface of an amorphous As-Te-Ge sample showed that a certain amount of

crystallinity had been introduced by the filament formation. Identification of the specific crystalline substance present was not possible. An electron microprobe scan across a filament and surrounding area showed that a spatial redistribution of elements had taken place during filament formation. Inside the filament the amount of tellurium increased and the amounts of germanium and arsenic decreased. The weight percentages of the three elements inside the filament indicated that the filament material was possibly As_2Te_3 in a germanium matrix or tellurium in a germanium-arsenic matrix. Examination in an electron microscope of a surface replica taken from an As-Te-Ge sample with filaments on its surface indicated that the filament material was harder than the surrounding material and, therefore, probably had a different structure.

Using all of the above observations as a basis, a model of the bistable resistivity switching mechanism in amorphous semiconductors was presented. The model first took into account the transformation observed upon reaching the threshold voltage for the first time. It was hypothesized that this transformation was initiated by an electron-hole plasma pinching process in which localized heating occurs.

The model of the switching mechanism was then further developed in two stages. The first stage was a forming process during which a crystalline conducting filament was

established between the external contacts. The crystallization process, which was driven by the local heating and the electric field, depended on the diffusion of the different atoms in the material in such a manner as to form the required stoichiometric ratio. The conducting filament provided a low resistance path connecting the external contacts, thereby establishing the low-resistance state in the material.

The second stage in the development of the model involved the bistable resistivity switching after a continuous filament had been formed between the contacts. After passing a sufficient amount of current through the filament, Joule heating caused a portion of the filament to melt. If the applied voltage was then quickly removed, the melted material was quenched into the amorphous phase, thereby re-establishing the high-resistance state in the sample. Switching back again to the low-resistance state was accomplished by restoring the disrupted filament. This was done by applying the original low-current voltage to the external contacts. At a voltage threshold somewhat lower than the original, the disrupted portion of the filament recrystallized and the low-resistance state was restored. If the proper applied voltage pulses were used, a very small volume of the filament could be cycled between the amorphous and crystalline phases (i.e., the high- and low-resistance

states) almost indefinitely.

Certainly the study of bistable resistivity switching
in amorphous semiconductors is still in its infancy. The
experimentalist in this field is faced with a seemingly
endless array of variables, most of which are not thoroughly
understood. The effects of starting composition, quenching
conditions, impurity level, ambient temperature and pressure,
the electrode material, contact resistance, etc., are very
difficult to isolate. Consequently, the model of the bi-
stable resistivity switching mechanism presented here should
not be taken as the final mechanism, but only as a first
attempt at understanding some of the experimentally ob-
served bistable resistivity switching properties.

The engineering applications of bistable resistivity
switching are apparent. A few devices have been offered
commercially and several more are in the development stage.
All of the devices considered so far have been fabricated
from thin amorphous films. Although the switching in thin
amorphous films takes place in a geometry which is vastly
different from that used in this study, it is not inconceiv-
able that similar mechanisms are operative in both cases.

It is hoped that the observations reported in these pages
will contribute to the understanding of the mechanism
responsible for bistable resistivity switching in all types
of amorphous semiconductor. At the very least the work re-

ported here has opened up a wide range of possibilities for further research in this area.

ACKNOWLEDGMENTS

BIBLIOGRAPHY

1. Pearson, A. David, W. R. Northover, Jacob F. Dewald, and W. F. Peck, Jr. Chemical, physical, and electrical properties of some unusual inorganic glasses. In Advances in Glass Technology. Pp. 357-365. New York, New York, Plenum Press. 1962.

2. Ovshinsky, S. R. Symmetrical current control device. Patent No. 3271591. September 20, 1963.

3. Cline, R. L. Anodized aluminum film switches. Sandia Corp. Tech. Memo. 228-62-72. 1962.

4. Sie, C. H. A memory cell using bulk effect in amorphous semiconductor. Unpublished paper presented at the Sixth Annual Report, Affiliate Program in Solid-State Electronics, Iowa State University, Ames, Iowa, May 22, 1968. Ames, Iowa, Engr. Research Inst., Iowa State University. 1968.

5. Sie, C. H. Memory cell using bistable resistivity in amorphous As-Te-Ge film. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1969.

6. Ridley, B. K. Specific negative resistance in solids. Proc. Phys. Soc. (London) 82: 954. 1963.

7. Pearson, A. David, W. R. Northover, Jacob F. Dewald, and W. F. Peck, Jr. Chemical, physical, and electrical properties of some unusual inorganic glasses. In Advance in Glass Technology-Part 2. Pp. 144-145. New York, New York, Plenum Press. 1963.

8. Ovshinsky, S. R. Amorphous semiconductor switches (Abstract). Ceram. Bull. 47, No. 4: 383. 1968.

9. Hilton, A. R., C. E. Jones, and M. Brau. Nonoxide IVA-VA-VIA chalcogenide glasses. Part 1. Glass-forming regions and variations in physical properties. Phys. Chem. Glasses 7, No. 4: 106. 1966.

10. Gildart, Lee. Hypothesis of orbital overlap shifting. Journal of Applied Physics 36: 335. 1965.

11. Ovshinsky, S. R. Reversible electrical switching phenomena in disordered structures. Physical Review Letters 21, No. 20: 1450. 1968.

12. Uttecht, R., H. Stevenson, C. H. Sie, J. D. Greiner, and K. S. Raghavan. Electric field-induced filament formation in As-Te-Ge glass. Paper presented at SEAS Symposium, New York, New York, May 17, 1969. To be published in Journal of Non-Crystalline Solids. ca. 1969.

13. Electric field-induced formation of low resistance paths in As-Te-Ge. Motion picture film P-66. Ames, Iowa, Film Production Unit, Iowa State University. 1969.

14. Eaton, D. L. Electrical conduction anomaly of semi-conducting glasses in the system As-Te-I. J. Am. Ceram. Soc. 47, No. 11: 554. 1964.

15. Smith, Joseph V., ed. Index (Inorganic) to the powder diffraction file. 1966. ASTM Publication No. PDIS-16i. Philadelphia, Pa., American Society for Testing and Materials. 1966.

16. Birks, L. S. X-ray spectrochemical analysis. New York, New York, Interscience Publishers. 1959.

17. Birks, L. S. Electron probe microanalysis. New York, New York, Interscience Publishers. 1963.

18. Uphoff, H. L. and J. H. Healy. Semiconducting properties of inorganic amorphous materials. Journal of Applied Physics 32, No. 5: 952. 1961.

19. Ancker-Johnson, Betsy and James E. Drummond. Thermal pinching in electron-hole plasma. Physical Review 131, No. 5: 1961. 1963.