ELECTRICAL SWITCHING IN BULK SAMPLES
OF 0.15As-0.12Ge-0.73Te GLASS

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of 0.15As-0.12Ge-0.73Te glass

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Electrical switching in bulk samples
of 0.15As-0.12Ge-0.73Te glass

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Electrical switching which occurs as a result of the thermal mechanism has been studied both experimentally and theoretically. Switching in bulk samples of 0.15As-0.12Ge-0.73Te glass has been verified to be caused predominantly by the thermal switching mechanism for near threshold applied voltages. Also, switching in this bulk sample of glass occurred by the thermal mechanism even for applied voltages an order of magnitude above the threshold voltage of the sample. In order to investigate a switching event in this glass sample, a constant voltage pulse was applied to the sample and the delay time and the electrical energy input to the sample during the delay time were measured. A log-log plot of the energy input to the sample during a delay time of 1.00 s as a function of the electrode spacing on the sample's surface was found to have a slope of approximately 1.6. For the theoretical study of the thermal switching mechanism, a one dimensional calculation of the heat balance equation with radial heat flow was made and the results of the calculation followed the same trends as the

experimental data. The large scatter in parts of the data and the increase in the average resistance of the sample for a switching event with near threshold applied voltages were observed effects which could not be explained by the thermal switching mechanism. These effects could be a manifestation of the structural changes which probably occur in the sample as a result of the high temperatures present at the moment of switching.

I. INTRODUCTION

The most spectacular and oldest display of electrical switching is lightning. The electrical resistance between the clouds and earth suddenly decreases by orders of magnitude. Switching, which is the sudden decrease by orders of magnitude of the resistance of a material, has been observed for decades. Destructive breakdown in dielectrics was the first area of switching to be studied (1,2,3). One advantage of switching in amorphous materials is that the switching is nondestructive.

An amorphous material is a material which has only short range order. The long range order of crystalline solids is absent. Although the bond lengths are usually the same for a material in the crystalline state as in the amorphous state, the bonds in an amorphous material may be bent slightly from their usual crystalline bond angles. In an ideal amorphous material all bonds of the constituents are satisfied. Even though one has more freedom with the bond angles in an amorphous solid, it seems to be just as difficult, if not more so, to make a good reproducible amorphous material as it is to make a good crystal. An excellent review article (4) about switching and amorphous materials in general has recently been published.

Most switching in amorphous chalcogenide materials has current-voltage (I-V) characteristics similar to Fig. 1a.

This type of switching is known as current-controlled negative differential resistance (CCNR) switching. The other type of negative differential resistance switching is voltage-controlled negative differential resistance (VCNR) switching which has I-V characteristics similar to Fig. 1b. An example of a device which switches with a VCNR characteristic is the tunnel (Esaki) diode.

In order to have CCNR switching, one must have a sharp increase in the electrical conductivity which implies a sharp increase in the carrier concentration or a sharp increase in the mobility of the carriers or both. CCNR switching in glasses is usually known as threshold switching because a minimum or threshold voltage is required in order to have switching in a sample. If voltage less than the threshold voltage is applied, the sample will not switch. Immediately after the application of a voltage greater than threshold, the sample does not switch. Instead a certain amount of time, known as the delay time, must elapse before the sample switches. Several review articles on CCNR switching in amorphous materials have been published (3,4,5,6,7,8,9,10,11,12,13). Also, review articles on the electronic transport properties of amorphous materials are available (4,14,15,16,17,18,19).

Figure 2 is an actual oscilloscope photograph of a current-time trace showing switching in a bulk chalcogenide

FIG. 1a. Typical current-voltage (I-V) characteristic for current-controlled negative differential resistance (CCNR) switching.

FIG. 1b. Typical current-voltage (I-V) characteristic for voltage-controlled negative differential resistance (VCNR) switching.

FIG. 2. Oscilloscope photograph of a current-time trace showing CCNR switching in a bulk sample of glass. The vertical scale is 1.25 mA/div and the horizontal scale is 500 ms/div.

glass sample whose composition was 15 atomic-% As, 12 atomic-% Ge, and 73 atomic-% Te. The horizontal axis represents time and the vertical axis represents the current flowing through the sample. At $t = 0$ a constant voltage of 125 V was applied to the sample. At the moment of switching ($t = T_s$), the resistance of the sample rapidly decreased which caused the current through the sample to increase sharply. Thus, for this application of voltage, the delay time [T_s] is 3.516 s.

Immediately after the sample switched, the voltage was removed to reduce the sample's deterioration. If current is allowed to flow through 0.15As-0.12Ge-0.73Te glass after it has switched, a crystalline filament of low resistance forms between the two electrodes (20,21). The crystalline filament causes the sample to be in a low resistance state (memory state) and thereby prevents the sample from being switched again until the filament is broken. Other investigators (22,23) have also observed the formation of the memory state.

Previously (20), high-speed cinematography has been used to show that switching in bulk samples of 0.15As-0.12Ge-0.73Te glass occurs primarily by a thermal mechanism. The principal visual result of that experiment was that for an applied voltage near the threshold voltage, a high-temperature filament formed between the two pointed electrodes on the glass sample's surface before the sample

switched. Ridley (24) has shown that for materials which exhibit CCNR switching, high-current filaments must form during the switching of the material as a result of the assumption that switching obeys minimum entropy production.

The present investigation is a study of the thermal switching mechanism in bulk samples of 0.15As-0.12Ge-0.73Te glass. Specifically, the changes in some of the switching parameters were examined as the applied voltage and probe separation were varied. The switching parameters measured were the threshold voltage [V_t], the delay time [T_s], and the total electrical energy [E_s] put into a sample while voltage is applied to it.

The thermal switching mechanism needs to be studied in order to investigate nonthermal switching mechanisms. Since thermal effects (Joule heating) are always present any time a voltage is applied to a sample, the possibility always exists that a sample switched in part or wholly due to thermal effects (i.e. that the sample switched by the thermal switching mechanism).

II. SWITCHING MECHANISMS

Numerous mechanisms have been suggested to explain current-controlled negative differential resistance (CCNR) switching in chalcogenide glasses. All of the suggested mechanisms can be divided into two major categories, thermal and nonthermal. The nonthermal category is usually known as the electronic class of mechanisms. For the thermal category (including the electrothermal theories) to explain switching, a temperature rise in the sample is necessary. To produce a temperature rise, a thermal theory relies on the Joule heating created in the sample whenever a voltage is applied to it. To produce switching, the temperature rise must cause the sample's resistance to decrease which then increases the Joule heating until thermal runaway occurs. A necessary condition for a thermal mechanism to cause switching is that the sample's conductivity be a strongly increasing function of temperature. The conductivity of most semiconductors including the chalcogenide glasses is a strongly increasing function of temperature.

The electrothermal theories also rely on thermal runaway to effect switching, but some electronic phenomena are introduced in conjunction with the thermal theory. Since switching in thin film samples with heat sinking electrodes cannot occur by a thermal mechanism alone (25,26), some new or additional mechanism is needed. The simplest addition is

to introduce the electric field dependence of the electrical conductivity into the thermal theory (26,27,28). The electric field dependence of the electrical conductivity in chalcogenide glasses has been measured (29,30,31,32). With the electric field dependent factor added to the thermal theory, switching in thin film samples made from chalcogenide glass can occur.

Another mechanism which has been employed in conjunction with the thermal theory to explain switching in thin films is the introduction of space charge layers next to the heat sinking electrodes (26,27). This electrothermal model is known as the virtual electrode model (VEM) which in effect replaces the heat sinking electrodes with electrodes which are not heat sinking.

Some other electrothermal models (33,34,35,36) employ an electronic instability at the time of voltage application to cause a local increase in the conductivity of the sample which results in a small local temperature rise. The switching of the sample then proceeds by thermal runaway.

One of the suggested mechanisms for switching in chalcogenide glasses in the nonthermal category is the avalanche process or impact ionization (10,37,38). In this model free carriers in the conduction band are accelerated by the applied field. When these carriers have sufficient kinetic energy to excite additional carriers into the conduc-

tion band, an avalanche of carriers is possible and switching of the sample occurs. An example of a device which switches by the avalanche mechanism is a reverse biased Zener diode.

Another proposed nonthermal switching mechanism is the double injection model by Henisch et al. (39). This model assumes the band structure for chalcogenide glasses suggested by Cohen, Fritzsche, and Ovshinsky (40). The CFO band structure postulates a high density of states at the Fermi level and, in addition, a high and equal density of positive and negative deep traps. In this switching model both holes and electrons are injected in equal amounts into a sample from their respective electrodes. The injected carriers quickly fall into the deep traps near their respective electrodes. Thus, a space charge builds up in the sample due to the trapped charge carriers. After a short while (on the order of a microsecond for a 1 micron thick sample) the space charge regions overlap causing a cancellation of the space charge in the overlap region. When the traps are all filled resulting in the neutralization of all the trapped space charge, the conductivity of the sample sharply increases and the sample switches.

Another proposed nonthermal switching mechanism is the single injection model by van Rocsbroeck (41,42). This model assumes that chalcogenide glasses are relaxation semiconductors (42,43). A relaxation semiconductor is

defined to be any semiconductor whose dielectric relaxation time is greater than the recombination time. This model postulates that the glasses are p type and that switching occurs via minority carrier (electron) injection. The injected electrons form a highly conductive space charge between the two electrodes at the moment of switching. The injected charge carriers, which form the space charge, are highly conductive because they are not screened by the material before they reach the other (positive) electrode. This switching model is applicable only for thin film samples (less than a few microns thick) because the injected minority carriers must reach the positive electrode before they recombine.

None of the aforementioned switching mechanisms can be expected to explain CCNR switching in all samples of chalcogenide glass. Although there is general acceptance of the idea that the thermal model is the predominant switching mechanism in bulk samples of glass, electronic effects can still have an effect on the switching of a sample. Likewise in thin film samples, there is considerable evidence to show that thermal effects can and do occur (27,34,44,45,46,47). Immediately after a voltage is applied to a sample, both electronic and thermal phenomena begin to occur. When the sample switches, the predominant mechanism which caused the switching is the one which resulted in the shortest delay

time. There is a definite possibility that in many samples, especially thin films with heat sinking electrodes, more than one mechanism synergetically effects the switching of the sample.

III. CALCULATION OF THERMAL MECHANISM

The thermal theory of switching has been theoretically studied by many investigators (3,26,27,28,32,33,44,48,49,50,51,52,53,54,55,56,57,58,59,60). Usually the investigation begins with the differential equations which embody the thermal theory. The first equation is Ohm's law or the current linear flow equation,

$$\bar{J} = \sigma \{ \bar{E} + S \overline{\text{GRAD}} (T) \},^1 \quad [1]$$

where $\bar{J}$ is the electrical current density, σ is the electrical conductivity of the material, $\bar{E}$ is the applied electric field, S is the Seebeck coefficient, and T is the temperature. The next equation is the thermal linear flow equation,

$$\bar{J}_q = S T \bar{J} - \lambda \overline{\text{GRAD}} (T), \quad [2]$$

where $\bar{J}_q$ is the thermal current density and λ is the thermal conductivity.

The third equation is the conservation of charge,

$$dp/dt = -\text{DIVG} (\bar{J}),^2 \quad [3]$$

where p is the charge density and t is the time. The fourth equation is the conservation of energy,

¹ $\overline{\text{GRAD}} (V)$ is defined to be the gradient of the scalar quantity $[V]$, i.e. $\overline{\text{GRAD}} (V) = \text{"del" operator operating on } V$.

² $\text{DIVG}_-(\bar{E})$ is defined to be the divergence of the vector quantity $[\bar{E}]$, i.e. $\text{DIVG}_-(\bar{E}) = \text{"del" operator dotted into } \bar{E}$.

$$C \cdot dT/dt = \bar{J} \cdot \{ \bar{E} + S \cdot \overline{\text{GRAD}}(T) \} - \text{DIVG}(\bar{J}q) - T \cdot (dS/dT) \cdot \bar{J} \cdot \overline{\text{GRAD}}(T), \quad [4]$$

where C is the heat capacity per unit volume which equals the density of a material times the heat capacity per unit mass. Since the charge density was introduced in equation [3], another equation involving the charge density is needed. Therefore, assuming a linear isotropic material, the last required equation is Poisson's equation,

$$p = -\epsilon \cdot \text{LAPN}(V),^1 \quad [5]$$

where ϵ is the permittivity of the material and V is the electric potential.

Of course, S , λ , and σ are temperature dependent and can be spatially dependent. Thus, solving equations [1] through [5], which are coupled nonlinear partial differential equations, is a formidable task. No one has even come close to solving them for even a simple sample geometry. Consequently, various simplifying assumptions are made.

First, all of the terms involving the Seebeck coefficient $[S]$ are dropped. The effect of dropping these terms is small and has been studied (27). Next, the material for which the calculations are being done is assumed to be isotropic which is a reasonable assumption for an amorphous

¹ $\text{LAPN}(T)$ is defined to be the Laplacian of the scalar quantity $[T]$, i.e. $\text{LAPN}(T) = \text{DIVG}(\text{GRAD}(T))$.

material. Using the previous assumptions, and substituting the two flow equations into the conservation of energy equation, the following equation results,

$$C \cdot dT/dt = \sigma \cdot E^2 + \lambda \cdot \text{LAPN}(T). \quad [6]$$

Thus, a nearly complete solution of the thermal theory involves the solution of equations [3], [5] and [6]. In order to avoid solving for the time-dependence of the charge and the electric field in equations [3] and [5], the next major assumption which is usually made is that the charge density at any time equals zero. Thus, $dp/dt = 0$ and equations [3] and [5] become,

$$\text{DIVG}(\bar{J}) = 0; \text{ and } \text{DIVG}(\bar{E}) = 0 \text{ or } \text{LAPN}(V) = 0.$$

Since the materials involved in switching are semiconductors, their electrical conductivity $[\sigma]$ has the form,

$$\sigma = \sigma_0 \cdot \text{EXP} \{-dE/(k \cdot T)\}, \quad [7]$$

where σ_0 is the preexponential factor and dE is the activation energy. Many times an electric field dependent factor is added to the conductivity equation [7]. This factor has been observed (29,30,31,32,61) and is needed for the thermal theory to explain switching in samples with perfect heat sinking electrodes (26,27). With the field dependent factor the electrical conductivity equation becomes,

$$\sigma = \sigma_0 \cdot \text{EXP} \{-dE/(k \cdot T)\} \cdot \text{EXP}(E/E_0), \quad [8]$$

where E_0 is a measured constant. The measured values of E_0

for chalcogenide glasses usually range from 10^6 to 10^7 V/m (29,30,31,32). The thermal theory for switching has now been reduced to basically equation [6], the heat balance equation. Equation [6] is an nonlinear parabolic partial differential equation with four independent variables (three spatial variables). In order to simplify the problem further, cylindrical geometry is used for the two electrodes across which the voltage is applied. Since the sample is assumed to be isotropic, there is no theta dependence for any variable. Thus equation [6] becomes, after substituting for sigma,

$$C \cdot dT/dt = \text{sigc} \cdot \text{EXP} \{-dE/(k \cdot T)\} \cdot \text{EXP} (E/E_c) \cdot E^2 + \lambda \cdot \{d^2T/dr^2 + (1/r) \cdot dT/dr + dT/dz\}. \quad [9]$$

The two electrodes on the sample are assumed to be perfect electrical and thermal conductors. Since the charge density between the electrodes is assumed to be zero, Laplace's equation ($\nabla^2 V = 0$) can be solved for a particular electrode geometry to find the electric field everywhere in the sample. Usually the electrodes are assumed to be two parallel plates, each having an infinite radius, which are separated by a distance [d] (26,27,32,48,49). Thus, the magnitude of the electric field between the plates is simply the voltage across the plates divided by the distance between them.

The parallel plate electrode geometry is a reasonable geometry for thin film samples sandwiched between two metal

electrodes. Even for parallel plate electrode geometry and constant thermal conductivity of the sample, no one has satisfactorily solved equation [9]. In order to make the problem still easier, one of the terms in equation [9] is usually set to zero. Either the thermal loss term is neglected ($LAPN(T) = 0$) or the time dependence of the equation is neglected ($dT/dt = 0$) and the equation solved for the steady state temperature profile as the applied voltage is increased. Instead of setting one of the terms to zero, C. Culp (32) has replaced the thermal loss in equation [9] with a term of the form, $constant \cdot (T - T_0)$, where T_0 is the sample's ambient temperature.

The calculation which is presented in this section also neglects neither the thermal loss term nor the time dependence. Instead the axial dependence of the electric field and temperature are ignored. The axial heat flow term ($dT/dz = 0$) is dropped from equation [9] and the axial dependence of the electric field ($d\bar{E}/dz = 0$) is neglected, i.e. this calculation only allows for uniform axial current flow and radial heat flow. Thus, the present calculation numerically solves the equation,

$$C \cdot dT(r,t)/dt = \text{sigo} \cdot \text{EXP} \{-dE/(k \cdot T)\} \cdot E^2(r,t) + \lambda \cdot \{d^2T(r,t)/dr^2 + (1/r) \cdot dT(r,t)/dr\}. \quad [10]$$

The electric field dependent part of the electrical conductivity has been dropped to make the computations some-

what easier. The effect of dropping the electric field dependent factor is discussed at the end of this section.

The present calculation uses spherical electrodes imbedded in the sample rather than parallel plates. The spherical electrode geometry represents pointed metal electrodes placed on a sample. Figure 3 shows the hypothetical spherical electrode geometry and the coordinate system. The origin of the coordinate system is at the midpoint of the line connecting the centers of the two spherical electrodes and the axial axis (z-axis) runs along that line. The radial axis (r-axis) is perpendicular to the axial axis. Before equation [10] can be solved, the electric field needs to be known as a function of radial distance. The spherical electrodes are assumed to be equipotential surfaces with a voltage of 1 V between them. Also, the space charge at any time between the spheres is assumed to be zero which is probably not always a good assumption. Certainly at $t = 0$, the time of the application of voltage to the electrodes, the assumption is valid but for times near the time of switching, the assumption is probably not valid.

With these previous assumptions the electric field anywhere between the spheres can be obtained by the method of image charges (62). Due to symmetry the radial component of the electric field along the radial and axial axes is zero (i.e. $|\bar{E}(z=0)| = E_z$ and $|\bar{E}(r=0)| = E_z$). Figures 4 and 5 are

FIG. 3. Diagram of the spherical electrode geometry and the coordinate system employed in the calculation of the thermal switching mechanism.

FIG. 4. Graph of electric field as a function of distance in the axial direction (z-axis) for two different radii [Re] of the spherical electrodes in Fig. 3. A potential of 1 V was applied across the spherical electrodes.

FIG. 5. Graph of electric field as a function of distance in the radial direction (r-axis) for two different radii [Re] of the spherical electrodes in Fig. 3. A potential of 1 V was applied across the spherical electrodes.

graphs of the electric field as a function of distance in the axial and radial direction for two different cases of electrode radius $[R_e]$ (50 microns and 500 microns).

For the numerical calculation of equation [10], the heat capacity, the preexponential factor of the electrical conductivity, the activation energy, and the thermal conductivity of the hypothetical sample were assumed to be constant. Reasonable or measured values of the various constants were used. Also, initial conditions and boundary values need to be chosen. The initial conditions are: at $t = 0$, the voltage is applied (i.e. $E(r,0)$ is a function whose shape is shown in Fig. 5) and the temperature of the hypothetical sample has no spatial variation and is equal to room temperature (i.e. $T(r,0) = 300$ K). The boundary condition which is needed is that at a distance sufficiently far from the axial axis, the temperature of the sample remains constant (300 K). Since the high temperature filament will center on the axial axis, the thermal loss from the filament region to the boundary must be kept at a minimum. For this calculation the constant temperature boundary varied from 3 mm to 12 mm from the axial axis. The large distances to the boundary were necessary to keep the thermal loss to the boundary at less than 1% of the total electrical energy $[E_s]$ into the hypothetical sample during the voltage application.

Equation [10] was solved numerically using a special type of trapezoidal predictor in conjunction with a similar type of trapezoidal corrector. Knowing the temperature profile $[T(r,t)]$ at each radial grid-point at a time $[t]$, the predictor equation is used to calculate the temperature profile at a new time $[t+ts]$. The corrector equation is then used to correct the new temperature profile. Only one iteration of the corrector was used for each application of the predictor.

The predictor-corrector difference equation for equation [10] is based on the Crank-Nicolson method (63,64) for numerically solving heat conduction problems. For a one dimensional heat conduction problem, the following differential equation is applicable,

$$dT(x,t)/dt = d^2T(x,t)/dx^2. \quad [11]$$

The Crank-Nicolson difference equation for equation [11] is

$$\begin{aligned} \{T(x,t+ts) - T(x,t)\}/ts = \{T(x+xg,t+ts) + T(x-xg,t+ts) - \\ 2*T(x,t+ts) + T(x+xg,t) + T(x-xg,t) - \\ 2*T(x,t)\}/(2*xg*xg), \end{aligned} \quad [12]$$

where ts and xg are the time step-size and distance grid-size respectively. In equation [11] the heat flow term $[d^2T(x,t)/dx^2]$ has been replaced in the difference equation by the mean value of the second difference quotients evaluated at times $[t]$ and $[t+ts]$. Replacing a function by its mean value evaluated at two points is essentially the trapezoidal

rule used in numerical integration. Equation [12] is an implicit difference equation since $T(x+xg, t+ts)$, $T(x, t+ts)$, and $T(x-xg, t+ts)$ are unknown and appear on the right hand side of the equation. In the predictor equation of my predictor-corrector scheme, the new temperature profile at time $[t+ts]$ is unknown and must be obtained by solving one difference equation for each radial grid-point.

In addition to the heat flow term, equation [10] also has a nonlinear term in T , the Joule heating term. For the present solution of equation [10], the Joule heating term in equation [10] was replaced in the difference equation by the mean value of the Joule heating evaluated at times $[t]$ and $[t+ts]$. In order to simplify the solution of the predictor difference equations for the new temperature profile, the Joule heating term was linearized, i.e. the Joule heating term was made linear in $T(r, t+ts)$. The linearization is as follows,

$$\text{EXP } (C/T) + \text{EXP } \{C/(T+dT)\} = \{2 - C*dT/T^2\} * \text{EXP } (C/T),$$

where $T = T(r, t)$ and $dT = T(r, t+ts) - T(r, t)$. This linearization is valid only if $dT \ll T$, i.e. if the time-step $[ts]$ is small.

The difference equation for the Crank-Nicolson method, equation [12], has only the nearest grid-point neighbors for the approximations of the second derivatives for the heat flow term. For my predictor equation the next-nearest and

nearest grid-point neighbors were employed for the approximations of the derivatives for the heat flow term. The corrector difference equation which was used for the present calculation was very similar to the predictor difference equation. The Joule heating term did not need to be linearized and the next-next-nearest, next-nearest, and nearest grid-point neighbors were all employed for the approximations of the derivatives in the heat flow term.

The size of the time-step at each point in time was automatically varied in order that the relative root-mean-square difference between the predicted new temperature profile and the corrected new temperature profile was always less than 0.01%. A uniform mesh (usually 601 grid-points) constituted the discretization of the radial distance from the midpoint of the line connecting the two spherical electrodes to the constant temperature boundary. The grid-size varied from 5 microns to 20 microns. Stability (65,66) of the solution near the constant temperature boundary became a problem for smaller grid-sizes.

Before equation [10] can be numerically solved, either measured or appropriate values for the parameters in the equation (C , σ , dE , and λ) have to be chosen. Since the switching experiments were done on a chalcogenide glass which had a composition of 15 atomic-% As, 12 atomic-% Ge, and 73 atomic-% Te, the parameters in equation [10] were

chosen to represent as closely as possible the actual physical constants of the glass used for the switching experiments. The heat capacity was calculated with the Dulong and Petit value ($3 \cdot R$), where R is the gas constant and equals 8.314 J/(K-mol) . This value of heat capacity is usually appropriate for most solids near room temperature (300 K). In order that the heat capacity $[C]$ in equation [10] have the correct units (J/m^3), the density of the hypothetical glass sample needs to be known. The density of the actual glass for the switching experiments was calculated by interpolation from the measured densities (67) of glasses with a very similar composition.

For the purposes of the present calculation, the measured values of the electrical conductivity constants for the actual glass were employed. The measured electrical conductivity constants are the preexponential factor $[s_0]$ and the activation energy $[dE]$ in equation [7]. A more complete description of the resistivity measurement can be found in the sample preparation and experimental results sections.

The thermal conductivity of the hypothetical glass sample had to be estimated. An average value was chosen between the values for fused quartz and other traditional laboratory glasses, and a measured value for one chalcogenide glass. The thermal conductivity of laboratory glasses at room temperature ranges from $0.7 - 1.5 \text{ W/(m-K)}$ (68) and the

one measured value of a chalcogenide glass is 0.22 W/(m-K) (69). The following numbers are the values of the various parameters which were used for numerically solving equation [10]. The calculated heat capacity per unit mass for the particular glass composition in the switching experiments is $221. \text{ J/(kg-K)}$ and the interpolated value of the density is $5590. \text{ kg/m}^3$. For the electrical conductivity constants the measured values of the preexponential factor and the activation energy for the actual glass are $5000. \text{ ohm/m}$ and 0.368 eV respectively. The estimated value for the thermal conductivity is 0.5 W/(m-K) .

In order that the calculation more closely represents the switching experiments of the actual sample, a load resistor was placed in series with the hypothetical sample and power supply. Figure 6 is a schematic of the arrangement of the sample, power supply, and load resistor. The value of this load resistor was 10 kilohms for the 50 micron electrode radius calculations and 1 kilohms for the 500 micron electrode radius calculations. With the load resistor the voltage on the sample $[V_s]$ is given by

$$V_s = V_p - I \cdot R_l, \quad [13]$$

where V_p is the power supply voltage, I is the current flowing through the sample and load resistor, and R_l is the load resistor. The electrical power $[P_s]$ into the sample at any time is simply the product of the sample voltage and

FIG. 6. Diagram of the arrangement of the hypothetical sample, power supply, and load resistor for the calculation of the thermal switching mechanism.

sample current. The sample resistance $[R_s]$ at any time is the quotient of the sample voltage and the sample current.

The next series of figures (Fig. 7 - Fig. 14) show the results of numerically solving equation [10] for the set of parameters stated above and using the aforesaid initial and boundary conditions with the 50 micron radius electrodes. Figure 7 is a graph of the calculated sample voltage versus sample current. For the calculation which resulted in Fig. 7, the output of the hypothetical power supply was given by

$$V_p = 500 \cdot t + 1.$$

Since Fig. 7 is similar to Fig. 1a rather than to Fig. 1b, switching by a thermal mechanism is current-controlled negative differential resistance (CCNR) switching. Figure 8 is a graph of the calculated sample current $[I_s]$ and voltage $[V_s]$ as a function of time $[t]$. The power supply was set to a fixed voltage of 750 V which is approximately 150 V above the threshold voltage of the hypothetical sample. The similarity in the shape between the sample current curve in Fig. 8a with the actual sample current curve in Fig. 2 shows that the thermal mechanism does have a sharp increase in the sample current at the moment of switching even for near threshold voltages.

The sample current at any time is calculated by numerically integrating, in cylindrical coordinates, the sample current density $[J]$ along the radial axis ($z = 0$) from

FIG. 7. Current-voltage (I-V) characteristic of a calculated CCNR switching event. For this characteristic the hypothetical power supply in Fig. 6 generated a ramp output voltage with a slope of 500 V/s.

FIG. 8a. Graph of the calculated current through a hypothetical sample as a function of time for one switching event. For this calculated event the hypothetical power supply in Fig. 6 generated a constant output voltage of 750 v.

FIG. 8b. Graph of the calculated voltage across a hypothetical sample as a function of time for the same switching event as for Fig. 8a.

FIG. 9. Graph of the calculated resistance of a hypothetical sample as a function of time for the same switching event as for Fig. 8.

FIG. 10a. Graph of the electrical power into a hypothetical sample as a function of time for the same switching event as for Fig. 8.

FIG. 10b. Graph of the electrical energy into a hypothetical sample until a point in time as a function of that point in time. The switching event for this graph is the same one as for Fig. 8.

FIG. 11. Graph of the temperature at different times along the radial axis (r-axis) of a hypothetical sample as a function of distance. The switching event for this graph is the same one as for Fig. 8.

FIG. 12. Graph of the temperature at the origin of the coordinate system in Fig. 3 as a function of time. The switching event for this graph is the same one as for Fig. 8.

FIG. 13. Graph of the current density at different times along the radial axis (r-axis) of a hypothetical sample as a function of distance. The switching event for this graph is the same one as for Fig. 8.

FIG. 14. Graph at different times of the integrand for the calculation of the current flowing through a hypothetical sample as a function of distance along the radial axis (r-axis). The switching event for this graph is the same one as for Fig. 8.

r equals zero to infinity. The sample current density at any point along the radial axis and at any time can be calculated from Ohm's law and is given by

$$J(r,t) = s_{iq0} \cdot \text{EXP} \{-dE / (k \cdot T(r,t))\} \cdot E(r,t). \quad [14]$$

Figure 9 is a graph of the sample resistance $[R_s]$ as a function of time $[t]$. This graph shows that the rate of switching at the time of switching $[T_s]$ for a thermal mechanism near the threshold voltage is quite rapid.

Figure 10a is a graph of the power into the sample $[P_s]$ as a function of time. For a constant voltage power supply the power curve will reach a maximum (i.e. $dP_s/dt = 0$) when the sample resistance equals the total load resistance. Figure 10b is a graph of the time-dependent electrical energy put into the sample as a function of time. The time-dependent energy is the total electrical energy put into the sample from the application of voltage until some later time $[t]$ (i.e. the time-dependent energy is the integral of the sample power from time = 0 until time = t). The total energy into the sample $[E_s]$ is the total electrical energy put into the sample from the application of voltage until the time of switching $[T_s]$. Thus, the total energy $[E_s]$ for this particular solution is the maximum time-dependent energy in Fig. 10b.

Figure 11 is a graph of the temperature at different times along the radial axis of the hypothetical sample as a

function of distance. A high-temperature filament forms along the axial axis near the time of switching $[T_s]$ and, once the filament starts to form, the temperature in the filament increases very sharply. Figure 12 shows the speed of the temperature rise in the filament more clearly. This figure is a graph of the temperature at the origin of the coordinate system as a function of time.

Figure 13 is a graph of the current density $[J]$ at several different times along the radial axis as a function of distance. Near the time of switching the high-temperature filament is also a region of high current density. Since this calculation was done in cylindrical coordinates, the integrand for the calculation of the current through the hypothetical sample at any time is given by

$$\text{Integrand} = 2\pi r J(r,t),$$

where $J(r,t)$ is given by equation [14].

Figure 14 is a graph of the value of the integrand at several different times as a function of distance along the radial axis. Thus, the current through the hypothetical sample at each of the times is simply the integral of the integrand from $r = 0$ to $r = \text{infinity}$.

It is interesting to note that when equation [10] was solved with the same conditions as stated above but with λ equal to zero, the hypothetical sample did not switch. A high-temperature filament formed, but the region of high

current density was not wide enough to support an appreciable sample current. Thus, the sample current increased very little and by definition the sample did not switch.

The following series of figures (Fig. 15 - Fig. 19) displays the results of solving equation [10] as before but for different applied voltages and two different electrode radii ($R_e = 50$ and 500 microns). The values of the parameters for equation [10] and the initial and boundary conditions were the same as the solution displayed in the last series of figures. The voltage from the power supply was constant during each pulse (i.e. square voltage pulses) and only voltages greater than the threshold voltage for each electrode radius were applied.

For a thermal model and near threshold applied voltages, delay times are very long because the initial Joule heating rate of the sample is quite small. The initial rate of the Joule heating is proportional to the square of the applied sample voltage [V_s]. As the applied voltage increases for each successive pulse, the delay time becomes shorter since less time is required to form the high-temperature filament. The relationship between the power supply voltage [V_p] and delay time [T_s] for the present calculation is shown in Fig. 15. Since the load resistor for these calculations and experiments is small, the power supply voltage is nearly equal to the applied sample voltage. Since the slopes of the

FIG. 15. Graph of the delay time from the calculation of the thermal switching mechanism as a function of the output voltage of the hypothetical power supply. The calculations were done with two different electrode radii $[Re]$.

FIG. 16. Graph of the calculated electrical energy into a hypothetical sample until the sample switches as a function of the power supply output voltage. The calculations were done with two different electrode radii [Re].

FIG. 17. Graph of the calculated electrical energy into a hypothetical sample during the delay time as a function of the delay time. The calculations were done with two different electrode radii [Re].

FIG. 18. Graph of the calculated average electrical power into a hypothetical sample during the delay time as a function of the power supply output voltage. The calculations were done with two different electrode radii [Re].

FIG. 19. Graph of the calculated average resistance of a hypothetical sample during the delay time as a function of the power supply output voltage. The ambient temperature (300 K) resistances of the sample are also shown. The calculations were done with two different electrode radii [Re].

theoretical curves in Fig. 15 are not even near vertical for low voltages, there is some difficulty in determining the threshold voltages for this calculation of the thermal switching mechanism. This same difficulty exists in the experimental results of switching in bulk samples of 0.15As-0.12Ge-0.73Te glass.

If equation [10] is solved with $\lambda = 0$ and $R_l = 0$, then a simple relationship between the power supply voltage and the delay time is obtained,

$$V_p \cdot T_s^2 = \text{constant}.$$

In Fig. 15 the nonlinear relationship between the power supply voltage and the delay time demonstrates the effect of the thermal loss term in equation [10]. For near threshold voltages the delay time is longer than would be expected due to the thermal loss term.

Since the solution of equation [10] with $\lambda = 0$ does not exhibit switching, the definition of switching has to be altered for the $\lambda=0$ calculations. When the hypothetical sample reaches a predetermined high temperature profile, the sample is said to have switched. Whenever the $\lambda=0$ solution of equation [10] is mentioned, the load resistor [R_l] was also set equal to zero for the calculation.

For the thermal model all of the electrical energy put into a sample is converted into Joule heating, but not all of the Joule heating contributes to the switching of a sample.

Some of the Joule heating is conducted away from the filamentary region before the sample switches. For applied voltages near threshold (i.e. longer delay times), the total electrical energy put into a sample before switching is larger because more heat is conducted away from the filamentary region. For applied voltages much greater than threshold (i.e. shorter delay times), the total energy tends to be independent of voltage and delay time, because a finite amount of energy is required to form the high-temperature filament and hence switch the sample. For the $\lambda=0$ solution of equation [10], the total electrical energy $[E_s]$ is a constant independent of power supply voltage and delay time. The relationship for the full solution of equation [10] between the total electrical energy $[E_s]$ and the power supply voltage $[V_p]$ is shown in Fig. 16 and the relationship between the total energy $[E_s]$ and the delay time $[T_s]$ is shown in Fig. 17.

The effect of the load resistor in the present calculation is a small one. For each electrode radius (50 microns and 500 microns) the load resistor is approximately 1% of the ambient temperature resistance of the hypothetical sample. For one voltage pulse the electrical energy dissipated in the load resistor for near threshold voltages is approximately 6% of the total electrical energy $[E_s]$ into the sample and for much larger applied voltages the energy into the load

resistor is only 1.4% of E_s .

Both the total electrical energy [E_s] and the delay time [T_s] are sample dependent quantities which are not totally independent of the sample independent quantities such as the applied voltage. Thus, it is convenient to graph the relationship between E_s , T_s , and V_p . In order to plot the three quantities on a two dimensional graph, the average power quantity must be introduced. The average power into the sample [Avg_P_s] during the delay time is defined to be the quotient of the total electrical energy and the delay time (i.e. $Avg_P_s = E_s/T_s$). The relationship between the average power and the power supply voltage is shown in Fig. 18. The most interesting point about the graph is that the graph is almost a straight line with a slope of 2. If the sample had a constant resistance while the constant voltage was applied, the graph would be exactly a straight line with a slope of 2. The power or average power into the sample for a constant sample resistance is given by

$$P_s = V_s^2/R_s = V_p^2 * R_s / (R_s + R_l)^2. \quad [15]$$

For the $\lambda=0$ solution of equation [10], the average power [Avg_P_s] is directly proportional to the square of the applied voltage. Thus, the nonlinear relationship in Fig. 18 between the power supply voltage and the average power again shows the effect of the thermal loss term.

Using equation [15] to calculate an average sample resistance $[Avg_Rs]$ from an average sample power $[Avg_Ps]$ allows one to determine the deviation of the average power curve in Fig. 18 from a straight line with a slope of 2. For the present calculation Fig. 19 shows the relationship between the average sample resistance and the power supply voltage. The average sample resistance is below the sample's ambient temperature resistance since Fig. 9 clearly shows that the sample resistance $[Rs]$ during the application of voltage is not constant. Thus, the average resistance plotted in Fig. 19 is a pseudo time average of the resistance in Fig. 9. If the sample resistance in Fig. 9 were constant and equal to the ambient temperature resistance during the voltage pulse, then the average resistance in Fig. 19 would be equal to the ambient temperature resistance and independent of applied voltage.

The average resistance for applied voltages near threshold is less than the average resistance for greater voltages because of the thermal conduction from the filamentary region during the long delay times with the near threshold voltages. For longer delay times the thermal conduction from the filamentary region widens that region. The resistance of the filamentary region decreases as that region increases in area because more area is available through which current can flow. Since the resistance of the sample

and the filamentary region does not decrease significantly until the sample switches, as can be seen in Fig. 9, the average resistance of the sample is to a large extent determined by the resistance of the filamentary region before the sample switches. As would be expected for the $\lambda=0$ solution, the average resistance is a constant independent of the power supply voltage. Its magnitude is the asymptotic value of the average resistance curves in Fig. 19 as the voltage is increased.

If an exponential field dependent factor is included in the electrical conductivity (equation [8]) for the $\lambda=0$ calculations, then the average resistance is no longer constant. Instead the average resistance has a dependence on the power supply voltage which is the reciprocal of the exponential field dependent factor. Thus, if the field dependent factor is included in equation [10], the average resistance curves in Fig. 19 will curve downward (lower Avg_Rs) for applied voltages much larger than threshold (32).

IV. APPARATUS

A minicomputer-controlled data acquisition system was employed to measure the switching properties of bulk samples of 15 atomic-% As, 12 atomic-% Ge, and 73 atomic-% Te glass. Figure 20 is a schematic of the equipment which comprises the switching measurement system and a diagram of the logical connections between the various pieces of apparatus. The lines between the pieces of equipment indicate information connections between them and the arrows on the lines indicates the direction of information flow. The solid lines are signal lines from the sample and the dashed lines are control lines for communication between the various items of apparatus. A Hewlett-Packard [HP] 2114B minicomputer is the central controlling unit. The experimenter communicates with the equipment through a teletypewriter [TTY] which is connected to the minicomputer. Through the teletypewriter, the experimenter can vary the load resistor, the voltage applied to the sample, the maximum length of time voltage is applied to the sample, and the elapsed time between voltage applications.

Basically, this apparatus is a constant voltage pulse generator and signal processor. The amplitude of a voltage pulse can be varied from 0 V to 900 V and the maximum duration of the pulse can be varied from 10 microseconds to 300 seconds. If a sample switches to a low resistance state

FIG. 20. Block diagram of the hardware employed for the measurement of switching in samples.

during a voltage pulse, this equipment automatically detects the event and removes the voltage from the sample to prevent sample deterioration.

The length of time that voltage is applied to the sample is measured with two different clocks. For times shorter than 900 ms, the output of a gated 250 kHz oscillator is counted by an HP 2401B integrating digital voltmeter [DVM]. The gating of the oscillator corresponds to the application and removal of voltage from the sample. For times longer than 900 ms, the crystal-controlled interrupt clock in the minicomputer is used. The elapsed time between voltage applications is also measured with the computer's interrupt clock.

Figure 21 is a schematic of the basic circuit containing the sample. The transistorized switch applies and removes the voltage from the sample. The transistorized switch removes the voltage from the sample either when the sample switches or when the maximum length of time for voltage application to the sample elapses. The sample is assumed to have switched when the voltage $[V_c]$ across the current-sensing resistor $[R_c]$ is greater than 4 V. Since the current-sensing resistor is usually 400 ohm, a voltage of 4 V across this resistor corresponds to a current of 10 mA flowing through the sample. A current of 10 mA is at least an order of magnitude greater than the current before the

FIG. 21. Block diagram of the closed circuit containing the sample and a schematic of the transistorized high voltage switching circuit.

sample switches.

The Kepco operational power supply (OPS-500) determines the magnitude of the voltage $[V_p]$ which is applied to the sample and can be varied under computer control from 0 to 900 V in 0.25 V increments. The load resistor can also be varied under computer control from 1 kilohm to 1023 kilohms in 1 kilohm increments. The current-sensing resistor $[R_c]$ has to be changed manually. The current through the sample is measured with the voltage $[V_c]$ across the current-sensing resistor. The voltage across the sample can then be determined from the following equation,

$$V_s = V_p - (R_l + R_c) * V_c / R_c.$$

The power into the sample, which is the product of the sample current and voltage, is then given by

$$P_s = V_p * V_c / R_c - (R_l + R_c) * V_c^2 / R_c^2. \quad [16]$$

Since the electrical energy put into the sample $[E_s]$ during the application of voltage is the time integral of equation [16], the voltages $(V_c$ and $V_c^2)$ must be integrated.

The voltage $[V_c]$ across the current-sensing resistor is amplified and integrated with an analog integrator. Also, this voltage is squared and integrated. The integrators are controlled to integrate during the application of voltage to the sample. After the integrators have completed their integrations, the computer directs the input-scanner to connect the output of each integrator sequentially to the DVM

and then for the DVM to measure the voltage on each integrator. The voltage on the linear integrator [V1] is directly proportional to the amount of charge [Q] which flowed through the sample during the application of voltage. The voltage on the square integrator [V2] is directly proportional to the time integral of the square of the current which flowed through the sample during the application of voltage.

Thus, the total electrical energy into the sample [Es] during the application of voltage is calculated from the following equation which is the time integral of equation [16],

$$E_s = V_p * K_1 * V_1 / R_c - (R_1 + R_c) * K_2 * V_2 / R_c^2 \quad [17]$$

where K1 and K2 are the constants of proportionality for the linear and square integrators respectively. Following the voltage application and the measurement of the integrators, the results of the voltage pulse are printed by the teletypewriter. The information about each voltage application includes the power supply voltage, the value of the load resistor plus current-sensing resistor, an indication of whether the sample switched, the length of time that voltage was applied, the output voltage of each integrator, the charge through the sample, the energy into the sample, the ratio of the second term in equation [17] to the first term, and the time-of-day.

The constants of proportionality (K1 and K2) used in equation [17] were calibrated by replacing the sample by a

known resistance. By the application of a known voltage to a known resistance for a known time, the output voltages on the integrators can be calculated. A linear relationship exists between the calculated voltage and the measured voltage on each integrator. By least-squares-fitting to a straight line the calculated voltage versus the measured voltage, a constant of proportionality can be calculated from the slope of the fit line. A good measure of the scatter in the calibration points is the relative root-mean-square [rms] error. The relative rms errors of the calibration points from the straight lines are less than 2% for the linear integrator. For the square integrator the relative rms errors are less than 40%. However, the magnitude of the second term in equation [17] is usually less than 5% of the magnitude of the first term for small load resistors, so this error is not serious. The errors in the square integrator are larger than those in the linear integrator owing to the instability of the squaring amplifier. Further information about the equipment and its operation is given in the system manual (70).

For the resistivity measurement of the glass sample, a small thermoelectrically heated and cooled sample chamber allowed the ambient temperature of the sample to be varied. The sample chamber was capable of varying the temperature of

the sample from -30°C to 50°C . A standard Leeds and Northrup wheatstone bridge (catalog no. 4735) measured the resistance of the sample at various temperatures.

V. SAMPLE PREPARATION

The samples of 0.15As-0.12Ge-0.73Te glass were prepared from reagent grade constituents by a method used by several other investigators (22,23,71,72,73). Each number in the formula for this glass composition is the fraction of each constituent in the glass. The constituents were sealed into a 25 mm diameter quartz tube which was placed in a rocking furnace and heated to 950°C. The rocking period was 4.5 minutes. In addition the tube was rotated at 3 RPM to insure thorough mixing of the constituents. After 24 hours in the rocking furnace the glass was quenched by ejecting the tube from the furnace onto a bed of sand which had been precooled with liquid nitrogen. Usually most or all of the ingot was in the amorphous state. Sometimes a narrow region along the center of the ingot was polycrystalline. The amorphous and polycrystalline regions could be distinguished by x-ray analysis, visual observation, and resistance measurements.

The sample for the resistivity measurement was prepared by breaking a chip from the amorphous part of the ingot and shaping the chip into a wafer approximately 1.0 mm thick and 4.4 mm square with the wire saw, lapping machine, and polishing wheel. Each of the two parallel plate electrodes to this sample consisted first of liquid Ga-In eutectic dabbed onto the sample's surface, then a thin sheet of gallium placed on the eutectic, next a thin sheet of indium

placed on the gallium sheet, and last a thick sheet of copper as the outer electrode. A spring-loaded sharpened tungsten wire made contact with each copper sheet.

Each sample for the switching experiments was prepared by breaking a chip of material from the amorphous part of the same ingot and mounting this chip in Quickmount self-setting resin.¹ The mounted chip was lapped flat and then polished with a 600 grit wet polishing wheel. Two pointed tungsten wires on the sample's surface served as electrodes to the sample. The pointed tungsten electrodes were made by dipping tungsten wire into fused sodium nitrite.

¹Resin is manufactured by Fulton Metallurgical Products Corp., Pittsburgh PA 15220.

VI. EXPERIMENTAL RESULTS AND DISCUSSION

The electrical resistivity of a 1 mm thick wafer of 0.15As-0.12Ge-0.73Te glass was measured with a two electrode technique. Each electrode consisted of liquid gallium-indium eutectic on a copper sheet. Since metal electrodes form ohmic contacts with chalcogenide glasses, a two electrode resistance measurement has been demonstrated (74,75,76) to work almost as well as a four probe technique in measuring the resistivity of a sample. Thus, by measuring the electrode areas, the sample thickness, and the sample's resistance, the resistivity of a sample can then be calculated. Figure 22 is a graph showing the calculated conductivity of the glass wafer as a function of the reciprocal of the temperature. From the graph the activation energy [dE] and the preexponential factor [sigo] of the electrical conductivity were calculated to be 0.368 eV and 5000 mho/m respectively.

An attempt was made to sputter molybdenum electrodes onto the same glass wafer as above and then to remeasure the resistivity of the sample. After the electrodes were sputtered onto the glass wafer, a remeasurement of the sample's resistance showed that the activation energy and the preexponential factor of the sample had changed. Although only 150 W of rf power over a 6 inch substrate were used, the sputtering operation seemed to give the glass wafer an irre-

FIG. 22. Graph of the electrical conductivity of a wafer of 0.15As-0.12Ge-0.73Te glass as a function of the reciprocal of the temperature. The activation energy [dE] and the preexponential factor [sigo] from the graph are 0.368 eV and 50 mho/cm respectively.

versible heat treatment. The glass transition temperature for this composition of glass is 130 °C and the first crystallization peak in a DTA analysis of the glass occurs at 220 °C (67). In spite of the fact that these temperatures are considerably higher than the temperature of the water-cooled base plate of the substrate holder, the sample was apparently not very well heat sunk to the base plate.

The potted bulk samples for the switching experiment were taken from the same ingot as the sample for the resistance measurement. Two sharpened tungsten wires served as electrodes to the polished sample's surface. Throughout the switching measurement the potted samples were kept in an air environment and at room temperature (23 °C). For the switching experiment a known voltage was applied across the sample through the electrodes and two switching parameters, the delay time [T_s] and the energy input [E_s], were measured. From these two parameters, the power supply voltage [V_p], and the load resistor [R_l], two more quantities can be calculated, the average power input [Avg_{Ps}] and the average resistance [Avg_{Rs}]. The average power input equals the energy input for a switching event divided by the delay time for that event. The average resistance of an event equals the square of the applied voltage to the sample divided by the average power input for that event.

After the first switching event at a new electrode location on the sample's surface, a change in the surface texture between the electrodes was noticeable. This change in the surface texture resulted from the formation of a high-temperature filament which occurs during each switching event in a bulk glass sample (21).

The next series of figures (Fig. 23 through Fig. 27) shows the results of measuring numerous switching events at one electrode location on a sample. The distance on the sample's surface between the electrodes for these switching events (i.e. the probe separation [psep]) was 3.0 mm.

Figure 23 is a graph of the delay time as a function of the power supply voltage for switching in one bulk sample of 0.15As-0.12Ge-0.73Te glass at one electrode spacing (psep = 3.0 mm). The graph shows the results of the thermal switching mechanism in an actual sample. The data would parallel the straight line with a slope of -2 if thermal loss from the filamentary region of the sample did not occur. Thus, the deviation of the data at lower power supply voltages from a slope of -2 is directly due to the thermal conductivity of the sample. The thermal conductivity of the sample removes heat from the high-temperature filament between the electrodes which is forming during the application of voltage. The electrical energy put into a sample during the application of voltage raises the temperature of the

FIG. 23. Graph of the delay time for a switching event as a function of the applied power supply voltage. The distance between the electrodes [psep] on the surface of the glass sample was 3.0 mm. Figures 23 - 27 are different plots of the same set of data points.

FIG. 24. Graph of the energy input to the sample during the delay time as a function of the applied power supply voltage. The distance between the electrodes [psep] on the surface of the glass sample was 3.0 mm. Figures 23 - 27 are different plots of the same set of data points.

FIG. 25. Graph of the energy input to the sample during the delay time as a function of the delay time for a switching event. The distance between the electrodes [psep] on the surface of the glass sample was 3.0 mm. Figures 23 - 27 are different plots of the same set of data points.

FIG. 26. Graph of the average power input to the sample during the delay time as a function of the applied power supply voltage. The distance between the electrodes [psep] on the surface of the glass sample was 3.0 mm. Figures 23 - 27 are different plots of the same set of data points.

FIG. 27. Graph of the average resistance of the sample during the delay time as a function of the applied power supply voltage. The distance between the electrodes [psep] on the surface of the glass sample was 3.0 mm. Figures 23 - 27 are different plots of the same set of data points.

sample and thus forms the high-temperature filament. The formation of the high-temperature filament is a prerequisite for the switching of the sample by the thermal mechanism. With some of the heat removed from the filamentary region, more energy is needed to compensate for the loss. In order to obtain this additional energy which comes from the electrical power put into the sample, more time is needed. At the higher power supply voltages, the data does have a slope of -2 because the thermal conductivity of the sample for the shorter delay times is not important in the switching process.

A comparison can be made between the actual data points in Fig. 23 and the calculated points in Fig. 15 in the calculation of the thermal mechanism section. Although switching in the data points occurred at a much lower voltage than the calculated points with the small electrodes ($R_e = 50$ microns), the trends in the data follow the same trends as the calculated points do. The fact that the trends in the two figures are similar reaffirms that switching in a bulk sample of 0.15As-0.12Ge-0.73Te glass occurs predominantly by the thermal switching mechanism. Also, switching in this bulk sample of glass occurs principally by the thermal mechanism even for voltages an order of magnitude larger than the threshold voltage.

Several reasons are possible for the discrepancy between the power supply voltages required to cause switching in the data points and those voltages in the calculated points. The first reason is that the axial dependence of the electric field (z-axis in Fig. 3) was ignored in the calculation. As can be seen from Fig. 4, the electric field is considerably larger near the electrodes than at the midpoint between them, especially for the small electrodes. Thus, the Joule heating would be larger near the electrodes which would cause the regions around the electrodes to be hotter sooner. The observation has been made that the regions around pointed electrodes have the quickest rise in temperature (20,21). The conductivity in these hot regions is orders of magnitude lower than the rest of the sample and these regions can then act like larger electrodes. As can be seen from Figs. 4 and 5, larger electrodes have a larger electric field at the midpoint between the electrodes and thus the calculated points with the larger electrodes switch at a lower voltage. Hence, the hot regions which form around the tungsten electrodes would lower considerably the switching voltages of the data points as compared to the calculated points. The calculated points with the large electrode radius ($R_e = 500$ microns) in Fig. 15 agree quite well with the experimental points in Fig. 23.

Also, since the electric field present around the experimental pointed electrodes during the voltage application is quite large (probably greater than 10^6 V/m), electronic effects such as injection from the electrodes could very easily occur. Injection could cause an accumulation of space charge around the electrodes, which would result in an increase in the effective size of the electrodes, and thus a reduction of the switching voltages for the data points.

Another reason for the discrepancy in the values of the power supply voltages between the data points and the calculated points is the neglect of the field dependent factor in the electrical conductivity (equation [8]) of the calculated points. Inclusion of the factor in the calculation would decrease the threshold voltage for the small electrodes by a factor of approximately 2. In addition, due to the large electric field near the small electrodes, the field dependent factor would significantly increase the conductivity of the material near the electrodes and consequently increase the effective size of the electrodes.

Another possible reason for the difference between the data points and the calculated points is that some electronic instability could initiate switching in the sample. Any electronic effect which initiated a thermal switching mechanism would cause switching to occur at a lower voltage than by the thermal mechanism alone.

Figure 24 is a graph of the energy input to the sample as a function of the power supply voltage for the same set of data points displayed in Fig. 23. The deviation of the data near the lower voltages from a horizontal line again shows the effect of the thermal loss from the filamentary region. If the sample experienced no thermal loss, then there would be no variation in the energy input as a function of the power supply voltage. All of the energy put into the sample would go into forming the high-temperature filament. Thus, the energy input for the larger voltages (approximately 70 mJ) is the energy required to form the high-temperature filament and hence, the energy necessary for the sample to switch by the thermal mechanism.

The experimental data in Fig. 24 can be compared to the calculated points in Fig. 16. Although the numerical values of the energy input for the data points are lower than those values for the calculated points, the trends exhibited in the data are the same as those in Fig. 16. Possible reasons for the discrepancy between the experimental and the calculated points are the same as stated above for the difference between the voltages required to switch the actual and the hypothetical samples.

Figure 25 is a graph of the energy input to the sample as a function of the delay time for the same set of data points as before. This graph shows that the delay time

becomes larger as more energy is put into the sample. Once again, the additional energy is needed to compensate for the thermal loss in the filamentary region. Without the thermal loss the energy input would be independent of the delay time as it would be for the applied voltage. For this sample the thermal loss becomes unimportant for delay times less than approximately 100 ms.

Figure 26 is a graph of the average power input to the sample as a function of the power supply voltage. The straight line with a slope of 2 shows the slope the data would have if there was no thermal loss in the sample. Since there is not a great deal of deviation of the data from a slope of 2, the effect of the thermal loss, although large for near threshold voltages, is not as evident on this graph as it is on others (Fig. 23 - Fig. 25).

As can be seen from this graph, plotting the average power input versus some other quantity reduces the scatter in the data. The scatter in the energy input of a data point is not independent of the scatter in the delay time. For a given power supply voltage, if one switching event takes longer to switch than another (i.e. the delay time is larger) then more energy is put into the sample with the larger delay time. One reason for the larger energy input for the longer delay time is that for a given resistance of the sample (i.e. constant power input), there is more time for energy to be

put into the sample. A second reason is that the longer a sample takes to switch, more energy is lost due to the sample's thermal conductivity. Then, additional energy is needed to compensate for the energy loss. The second reason partially explains the larger absolute scatter in the data for near threshold voltages as compared to larger power supply voltages.

If a sample's resistance obeyed Ohm's law (i.e. the resistance is constant independent of applied voltage and time), then a log-log plot of the sample's power input versus applied voltage would be a straight line with a slope of 2. The data in Fig. 26 suggests that the resistance of the actual glass sample for a switching event was almost constant with respect to the power supply voltage. The sample's resistance certainly was not constant with respect to time during a switching event, but changed by more than an order of magnitude. This large change in resistance can be seen from the oscilloscope photograph of a switching event (Fig. 2) or from the calculated resistance versus time graph (Fig. 9). From the average power input of a data point, the average resistance of the sample for a switching event can be calculated.

Figure 27 is a graph of the average resistance for a switching event as a function of the power supply voltage. The average resistance is remarkably constant. The value of

the average resistance is approximately one and a half orders of magnitude lower than the resistance of the sample as measured by a wheatstone bridge or vclt-ohm meter. But again, the deviation of the average resistance from a constant value is due to thermal loss. The thermal loss lowers the sample's resistance during the application of voltage and thus, lowers the average resistance of the switching event.

From Fig. 27 there is the appearance that the data for two different samples is plotted, especially the data between 200 V and 500 V. During the two voltage sweeps between 200 V and 500 V, the sample must have changed in some manner. Also, the sample must have altered again for the voltage sweep between 500 V and 900 V. There was a considerable time difference of the order of a couple weeks between each voltage sweep. Generally, the scatter between various voltage sweeps decreases as the time elapsed between the voltage sweeps diminishes. Thus, the smallest amount of scatter in the data usually occurred when all of the data for a sample was collected within a few days.

A comparison can be made between the experimental data in Fig. 27 and the calculated points in Fig. 19. Although the numerical values of the average resistance for the calculated points do not agree with those of the data, the decrease of the average resistance for near threshold applied voltages and the asymptotic approach of the average

resistance to a constant value for larger voltages are the same in both figures.

The scatter in the data for the last series of figures (Fig. 23 through Fig. 27) is quite large, especially the low power supply voltage data. With each switching event the sample seems to change its electrical properties a little. Thus, the results of a particular switching event is to some extent dependent upon the history of the sample (i.e. the previous switching events). Therefore, the order in which the data was taken appears to have some importance. Generally, the power supply voltage was initially set to a value near the threshold voltage and a switching event measured. Then, the power supply voltage was incremented a little and the next event measured. This process continued until the maximum voltage (900 V) was reached. Next, the power supply was reset to a voltage near the threshold voltage and the voltage sweep from near threshold voltage to 900 V was repeated at least two times. For this series of figures (Fig. 23 - Fig. 27), the switching events above 500 V were measured after most of the data below 500 V was taken because originally the equipment could not generate pulses greater than 500 V. Thus, the data above 500 V was taken in one voltage sweep of the power supply. Also, some of the data from 100 V to 160 V was taken somewhat haphazardly. This data was not taken in a systematic way as part of a voltage sweep from 100

V to 500 V. Instead, smaller voltage sweeps from 100 V to 200 V and random applied voltages were employed. In addition, after each switching event several minutes elapsed before voltage was reapplied to the sample for the start of the next switching event. This time elapse of several minutes allowed the high-temperature filament to cool back to ambient temperature.

After each switching event one reason for the changing of the sample is the presence of the high-temperature filament during each event. The highest temperature in the filament is probably well above the first crystallization temperature (220 °C) of this glass. Also, although a signal was sent to the high voltage switch in order to stop the flow of current through the sample immediately after the sample switched, a delay, up to 0.1 ms, occurred in stopping the flow of current while the circuit containing the sample recharged itself. Since this composition of glass devitrifies if current is allowed to flow through it for several seconds (21), there is a good possibility that partial devitrification occurred immediately after the sample switched and before the current abated. Then, opposing the partial devitrification, partial revitrification could occur in some regions of the sample during each switching event. Thus, no net crystallization of the sample has to occur in order that the sample change its properties, only a

FIG. 28. Graph of the delay time for a switching event as a function of the applied power supply voltage. The results for various probe separations [psep] on the surface of the same glass sample are shown. Figures 28 - 32 are different plots of the same sets of data points.

FIG. 29. Graph of the energy input to the sample during the delay time as a function of the applied power supply voltage. The results for various probe separations [psep] on the surface of the same glass sample are shown. Figures 28 - 32 are different plots of the same sets of data points.

FIG. 30. Graph of the energy input to the sample during the delay time as a function of the delay time for a switching event. The results for various probe separations [psep] on the surface of the same glass sample are shown. Figures 28 - 32 are different plots of the same sets of data points.

FIG. 31. Graph of the average power input to the sample during the delay time as a function of the applied power supply voltage. The results for various probe separations [psep] on the surface of the same glass sample are shown. Figures 28 - 32 are different plots of the same sets of data points.

FIG. 32. Graph of the average resistance of the sample during the delay time as a function of the applied power supply voltage. The results for various probe separations [psep] on the surface of the same glass sample are shown. Figures 28 - 32 are different plots of the same sets of data points.

rearrangement of the devitrified regions.

The next series of figures (Fig. 28 through Fig. 32) shows the results of switching for four different probe separations [psep] in the same bulk sample of glass as before. One first notices that the scatter for two of the probe separations (AGB and AGD data) is considerably larger than the scatter for the other two separations (AGT and AGC data). Since all of the AGC data was collected within a couple of days, this data has a small amount of scatter. Whereas the AGT data was collected over many weeks and has a larger amount of scatter. The AGT data is the same set of data plotted in the previous series of figures (Fig. 23 - Fig. 27). The data was taken in the order of largest probe separation first and smallest separation last. Except for the AGT data three or four complete voltage sweeps from threshold voltage to 900 V were employed for each probe spacing in the collection of the data.

The AGB data at higher voltages does not follow the same trends as the other three sets. As was mentioned, the scatter in the AGB data, all of which was collected within several days, is also larger than either the AGT or AGC data which was taken before and after the AGB data. After the first few switching events at a new electrode spacing, tens of switching events are measured for a constant power supply voltage which is slightly greater than the threshold voltage.

These early measurements assure that the electrodes become firmly embedded into the sample and check the stability of the switching of the sample. The AGB data was not very stable during these early measurements. For a constant power supply voltage both the delay time and the energy input would sometimes vary by at least a factor of two for successive switching events. Possible explanations for the unusual behavior of the AGB data are that the electrodes were never properly embedded into the sample or that there was some sample defect or inhomogeneity at or between the electrodes.

For the AGD data the sample definitely was different for each complete voltage sweep. The data points for the first voltage sweep are the ones with the largest delay time or energy input for a given power supply voltage. For the second voltage sweep the electrodes had moved closer together. From the graphs of the AGD data, the electrodes apparently started to move closer together during the first voltage sweep at approximately 300 V. At the end of the three voltage sweeps, the discovery was made that the electrodes had decreased the distance between them to approximately 0.1 mm. Also, during the third voltage sweep at approximately 140 V, arcing between the electrodes in the air across the sample's surface started to occur. The effect of the arcing on the AGD data is clearly seen in Fig. 28. The delay times for the arcing data are all less than 0.2 ms in the voltage range from 140 V

to 300 V. Thus, for the arcing data the breakdown of the air occurred more quickly than the switching of the sample.

One of the most puzzling observations about the data is the upturn in the average resistance curves at low power supply voltages for the AGB and AGC data in Fig. 32. From the theory of the thermal switching mechanism, the average resistance of a sample would curve downward for low power supply voltages (Fig. 19). The downward turn is due to the thermal loss of the sample during the application of voltage.

The AGB and AGC data were taken more systematically than the AGT data. Complete voltage sweeps from 100 V to 900 V were made for the AGE and AGC data. For the AGT data most of the data from 90 V to 200 V was taken somewhat haphazardly and not part of complete voltage sweeps. For the AGB and AGC data the sample along the filamentary region could be structurally different for near threshold applied voltages compared to higher applied voltages. The systematic manner of the data taking for the AGE and AGC data could have caused a partial devitrification in the filamentary region of the sample for the higher applied voltages which was not present for the near threshold voltages. The quenching rates of the filamentary region after the switching of the sample are probably quite different for higher applied voltages compared to near threshold voltages. The slower the quenching rate, the more devitrification occurs.

FIG. 33. Graph of the energy input to the sample during a delay time of 1.00 s as a function of the distance between the electrodes [psep] on the surface of the glass sample. The bars on the plotted points indicate the scatter of the experimental data for that point. The slope of the plotted points is approximately 1.6.

Figure 33 is a graph of the energy input to a sample as a function of the distance on the sample's surface between the electrodes [psep]. The energy input to a sample can be divided into two parts, the thermal loss from the high-temperature filament and the formation of the high-temperature filament. For a first approximation switching events, which occur with equal delay times but have different probe separations, should have equal thermal losses or at least thermal losses which are directly proportional to the probe separation. In addition, the energy which is required for the formation of the high-temperature filament should also be directly proportional to the probe separation since the high-temperature filament is much more one dimensional than two or three dimensional. Thus, a log-log plot of the energy input versus the probe separation for a constant delay time should be a straight line with a slope of one. The slope of the four points in Fig. 33 is not 1.0 but is approximately 1.6. The energy required for the formation of the high-temperature filament including the high-temperature regions around the sharpened electrodes might not be directly proportional to the probe spacing. Also, the assumption about the linear relationship between the thermal loss and the probe separation might be invalid.

VII. CONCLUSION

Switching in bulk samples of 0.15As-0.12Ge-0.73Te glass has been verified to be caused predominantly by a thermal switching mechanism for near threshold applied voltages. Also, switching in this bulk sample of glass occurred by a thermal mechanism even for applied voltages an order of magnitude above the threshold voltage of the sample. Although the switching data in this glass sample does not agree with the numerical values of the one dimensional calculation of the thermal switching mechanism, the data does follow the same trends as the calculation. The numerical values of a two dimensional calculation of the thermal mechanism would certainly agree much more closely with the experimental switching data.

The delay time and the energy input of a particular switching event are to some extent dependent upon the switching history of the sample. Possibly, microscopic structural changes occurring during each switching event are responsible for the history dependence of the switching. In addition, the large scatter in some of the data and the upward turn of the average resistance for near threshold voltages in parts of the data are probably also due to microscopic structural changes within the glass sample during each switching event. The extent of the dependence of the switching history on the scatter in the data and the upward

turn in the average resistance could be investigated more thoroughly by varying the order in which the data is taken and by measuring the resistance of the sample before each switching event. Also, to further study the switching history dependence of the data, samples which do not crystallize as easily as this composition of glass should be measured. Finally, if the filamentary region of a bulk glass sample could be well heat sunk by putting a thick film of glass on a substrate with a high thermal conductivity, the effect on the switching of that sample would be interesting.

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