THRESHOLD SWITCHING IN THE AMORPHOUS SEMICONDUCTOR
 $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$ AND IN THE ORGANIC SEMICONDUCTOR MELANIN

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Ph.D. Thesis Submitted to Iowa State University

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Threshold switching in the amorphous semiconductor $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$ and
in the organic semiconductor melanin

by

Charles Henry Culp III

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LIST OF SYMBOLS AND ABBREVIATIONS

t_d	Delay time
V_{th}	Threshold Voltage
DNR	Differential Negative Resistance
$\mathcal{E}$	Electric Field
$\mathcal{E}_0$	Constant in the Electric Field Dependence on Conductivity ($\mathcal{E}_0$ is equal to the field for which the resistivity is equal to 1/e of its low electric field value)
C	Heat Capacity
λ	Thermal Conductivity
T	Temperature
T_0	Ambient Temperature
σ	Electrical Conductivity
σ_0	Electrical Conductivity at $1/T = 0$
ΔE	Activation Energy
d	Sample Thickness
A	Electrode Area
V_{appl}	Applied Voltage
V_s	Sample Voltage
E	Energy
R_L	Load Resistor
R_0	Sample Resistance at $1/T = 0$
$\langle \frac{1}{R} \rangle^{-1}$	Inverse of the Average Inverse Resistance

ABSTRACT

The threshold switching properties of the amorphous semiconductor $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$ and the organic semiconductor melanin have been examined with threshold switching experiments. Measurements of delay time, energy and average resistance as functions of applied voltage were made by a computer controlled data acquisition system. These measurements were made on $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$ at 243 K, 273 K and 298 K. A time dependent electrothermal model was solved numerically. The material parameters that were measured for this model are activation energy, sample thickness, conductivity at T equal to infinity and area of the electrodes. With these measured parameters the calculation was compared to the experimental values of delay time, energy and average resistance as functions of applied voltage. The measured data and the calculations are in good agreement. Melanin was prepared from a lyophilized powder into a hydrated pellet. The melanin pellets were studied at 298 K, 190 K and 77 K with a double pulse apparatus. Time dependent current versus voltage characteristics were also measured. Melanin exhibits threshold switching at low electric fields (about 10^2 V/cm). The results from the melanin experiments show that threshold switching in melanin can be explained by a thermal runaway model. A pseudo-memory effect was also found in melanin.

CHAPTER I. INTRODUCTION

Amorphous Semiconductors

Interest in threshold switching in amorphous semiconductors developed from a paper by S. R. Ovshinsky.¹ Ovshinsky defined reversible switching to be a non-destructive change from a high resistance to a low resistance state. Several new concepts were introduced. Delay time, t_d , was defined to be the time interval between the application of a voltage greater than the threshold voltage and the attainment of low resistance in the sample. The threshold voltage was defined to be the minimum voltage required to make the sample switch. Ovshinsky showed that the current versus voltage curves were symmetrical with respect to the reversal of the applied voltage and current, as shown on Fig. 1. His samples were sputtered or hot pressed thin films of composition $\text{Te}_{48}\text{As}_{30}\text{Si}_{12}\text{Ge}_{10}$. Figure 1 shows the current-vs-voltage curves for a typical threshold switch. Ovshinsky found the holding voltage, V_h , to be almost constant as the current was varied when the sample was in the low resistance state. Current filaments were observed with diameters of about 5×10^{-3} cm. A functional form for the decrease in the delay time with increased voltage was given as $t_d = (\text{constant}) \times e^{-V/V_1}$. V_1 was found to be approximately 10% of the threshold voltage.

Many publications appeared soon after Ovshinsky's paper. They can be grouped into switching studies and material studies. Some investigators studied the properties of amorphous semiconductors to explain the material properties. Only the general properties of amorphous semiconductors needed to explain the various switching models will be

Fig. 1. Current versus voltage for a threshold switch. V_{th} is the threshold voltage. I_h and V_h are the minimum holding current and holding voltage attainable in the low resistance state. If the voltage is lowered below V_h , the threshold switch reverts back to a high resistance state.

discussed in this dissertation. Good reviews^{2,3} of the material properties of amorphous semiconductors are available. Other researchers studied switching and tried to explain the switching phenomenon with various models. Several reviews⁴⁻⁹ of switching have been published.

The thermal model was one of the earliest models¹⁰⁻¹⁹ to be proposed. This model requires a temperature rise due to Joule heating to lower the resistance of the sample. Since semiconductors have an exponentially decreasing resistance with reciprocal temperature, heating will cause the resistance to decrease. B. K. Ridley²⁰ originally predicted that high current filaments would exist if a current controlled negative resistance occurred. A filament is that part of the sample through which most of the current passes after the sample has been switched to a low resistance state. Many of the early thermal calculations assumed that the electrodes were infinite heat sinks. They still obtained a differential negative resistance (DNR). Kaplan and Adler²¹ showed that these calculations cannot predict DNR if an external series resistor is not present. Their more advanced time independent calculation has shown that a DNR segment on the current versus voltage curves will exist if a virtual electrode assumption is made. The virtual electrode model (VEM) removes the infinite heat sink assumption by displacing the equipotential plane for each electrode a small distance into the material. They also showed that a DNR segment exists if double injection is employed to overcome the high resistance material near each electrode or if the electric field dependent term (e^{E/E_0}) is added to the electrical conductivity. A complete time dependent solution

of the heat flow differential equation to explain threshold switching would be extremely difficult and has not been done. Many authors have circumvented this problem by adding an electronic effect to assist the thermal process. Such models lead to electrothermal calculations.

The bulk of these electrothermal calculations have been performed since 1969.²¹⁻³¹ Most of the early calculations were used to show trends that would be expected in the switching data. Although these models were qualitative, they did introduce new mechanisms by which switching could be initiated. A recent calculation by Kroll³¹ is very thorough in its treatment of an electrothermal theory.

Several authors have suggested various electronic effects to explain threshold switching. A double injection model was described by Barnett and Milnes.³² Double injection was applied to threshold switching in amorphous semiconductors by Henisch,³³ Fritzsche,³⁴ and other authors.³⁵⁻⁴³ Shousha et al.⁴⁴ and Hindley⁴⁵ developed avalanching models to explain switching. A polaron model was proposed as a possible explanation of switching by Frederichs.⁴⁶

Many models have been proposed to explain threshold switching in amorphous chalcogenide semiconductors. The purpose of this research is to attempt to isolate the model that best explains threshold switching in bulk amorphous semiconductors. The glass chosen to be investigated was $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$ since it exhibits the properties of many amorphous chalcogenides. The properties to be studied are delay time, energy, and average resistance as functions of applied voltage for a parallel plate sample configuration.

Melanin

Melanin is a polymer of indole 5,6 quinone and has a black powder appearance. The structure varies for different types of melanin. Thathachari and Blois⁴⁷ found differences in the x-ray diffraction patterns of plant and animal melanins. They found that synthetic melanin prepared by alkaline auto-oxidation of catechol or oxidation of DOPA (dihydroxyphenylalanine) with mushroom tyrosinase gave the same Bragg spacing as the animal melanins of natural origin.

The synthesis of melanin, which was published by Lerner,⁴⁸ is shown in Fig. 2. As in most biological compounds, the purity of the melanin produced by this path is somewhat uncertain. There can be remnants of the previous preparation step still present in the final product. The degree of polymerization of the indole 5,6 quinone is indeterminate. Also, a dimer can be created by linking two monomers of indole melanin. Very little is known about the variations of melanin and this is an area of ongoing research in biophysics.

Some work was done by Rosenberg and Postow⁴⁹ on the activation energy of synthetic melanin. They found dry melanin to have an activation energy (ΔE) of 1.5 eV, while partially hydrated melanin has a ΔE of 1.2 eV.

Threshold switching in animal and indole melanin was recently reported by McGinness, Corry and Proctor.⁵⁰ They also found that equine cytochrome c has threshold electric field properties of about 4×10^5 V/cm, which is comparable with thin film amorphous semiconductors.

Fig. 2. Pathway of melanin synthesis (Lerner).⁴⁸ The final product, melanin, is a polymer of indole 5,6 quinone.

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TYROSINE

DOPA

DOPAQUINONE

LEUCODOPACHROME

DOPACHROME

5,6 DIHYDROXYINDOLE

INDOLE 5,6 QUINONE

MELANIN

Melanin is unique because it switches at a very low electric field, about 10^2 V/cm.

Another interesting aspect of melanin is that it is found in some human organs where information transfer occurs. The mid-brain, inner ear, retina and skin contain melanin. Some recent evidence indicates that melanin has a role in such disorders as schizophrenia,⁵¹ deafness,⁵² and parkinsonism.⁵³ Since the electronic properties of melanin persist in intact melanosomes, McGinness suggested that the role of melanin in these disorders may be related to its ability to function as an electronic device.

The purpose of this research was to repeat the work done by McGinness, Corry and Proctor⁵⁰ and to explore the possible mechanisms involved with threshold switching in bulk melanin. McGinness et al. did not attempt to find the mechanism of threshold switching in melanin. It should be possible to isolate a model for threshold switching in melanin by double pulse experiments and time dependent current versus voltage experiments.

CHAPTER II. THEORY REVIEW

Thermal Model

The original papers deriving the thermal model usually started with the standard heat flow equation (Eq. 1) simplified by several assumptions.

$$C \frac{\partial T}{\partial t} = \nabla \cdot \lambda(T, \mathcal{E}) \nabla T + \sigma(T, \mathcal{E}) \mathcal{E} \cdot \mathcal{E}. \quad (1)$$

The first term on the right side of Eq. (1) is the heat loss, and the second term is the heat gain. In this equation, C is the heat capacity per unit volume, T is the temperature, t is the time, $\lambda(T, \mathcal{E})$ is the thermal conductivity, $\sigma(T, \mathcal{E})$ is the electrical conductivity, and $\mathcal{E}$ is the electric field. Typically, one assumes an infinite slab in two dimensions with a finite thickness in the third dimension. The electric field is assumed to be linear in the direction of the thickness.

A. C. Warren^{10,14} published an early thermal calculation in which he showed that switching occurs very rapidly, with a switching time between 0.25 μsec and 0.25 nsec for activation energies between 1.0 eV and 1.5 eV. This fast switching occurred after a long delay time of about 2.8 msec. Warren used the classical form for the activated conductivity and did not include any high electric field effects in the expression for the conductivity. He calculated the temperature and current density in the filament as a function of time. His calculation showed that the maximum current density was $2.7 \times 10^8 \text{ A/m}^2$, and the maximum temperature of the filament was about 1000K. The width of the conducting filament was calculated to be 1 micron. This calculation was

totally thermal and the electrodes were held at a fixed temperature. Warren did not publish the details of his calculation so it is difficult to see how he obtained DNR. According to Kaplan and Adler,²¹ Warren's assumptions would make DNR unattainable if he did not use an external series resistor in his calculation. Warren did not mention a series resistor in his papers or that switching could not occur in a thermal calculation in which the electrodes were held at a fixed temperature.

H. J. Stocker, C. A. Barlow Jr. and D. F. Weirauch¹⁶ have done a simplified thermal calculation and compared their calculation with data on evaporated $\text{Ge}_{20}\text{As}_{30}\text{Te}_{50}$. This author has attempted to evaporate a similar composition and found that most of the germanium remained in the evaporation boat. Stocker does not give an analysis of the composition of their film so their film may not be $\text{Ge}_{20}\text{As}_{30}\text{Te}_{50}$. The assumptions made by Stocker et al. are similar to Warren's,¹⁰ except Stocker et al. considered the external circuit. Both assumed the faces of the material remained at ambient temperature. Stocker's calculation started with a simple steady state calculation to derive the steady state current versus voltage characteristics. He used a form for the electrical conductivity ($\sigma = \sigma_0 e^{\alpha(T - T_0)}$) which is not commonly accepted, but may be a valid approximation over a small temperature range. This assumption, which is a Taylor series expansion to first order, enables one to solve the steady state ($\frac{\partial T}{\partial t} = 0$) heat flow equation analytically. Stocker obtains a threshold electric field and a threshold temperature dependence on the ambient temperature and some constants of the material. A threshold temperature is the temperature at which thermal runaway occurs.

Stocker also does an elementary calculation of the delay time by assuming a temperature distribution of the form $T(x) = T_m \cos\left(\frac{\pi x}{2L}\right)$. This leads to replacing the heat loss term by $-\frac{\pi}{2L}(T - T_0)$. The heat flow equation is now dimensionless and the delay time can be obtained by integrating the temperature from the ambient temperature to a final or threshold temperature. Stocker's results are shown in Eq. (2).

$$t_d \cong \frac{1.73 C L^2}{\lambda} \int_0^1 \frac{dx}{\left\{\left(\frac{V}{V_{th}}\right)^2 e^{\lambda} - e^x\right\}} \quad (2)$$

In Eq. (2) C is the heat capacity per unit volume, L is one half the width, λ is the thermal conductivity, V is the applied voltage, and x is a dummy variable. This equation is valid only for voltages above threshold voltage. K. H. Oh⁵⁴ has modified Stocker's calculation and obtained a better agreement with Stocker's data. Figure 3 shows Stocker's calculation and data and Oh's calculation.

Electrothermal Models

Kaplan and Adler²¹ showed that for a pure thermal model which does not allow for heating to occur in the electrodes, a negative differential resistance will not exist. The reason for this result is that the thermal model requires that the threshold material be thermally hot, and electrodes which have a very large heat capacity will keep the material very close to the electrode cool. Thus, the resistivity remains high and the material never switches. However, when virtual electrodes or an electronic initiation is introduced, a differential negative resistance

Fig. 3. Delay time versus applied voltage data for a 115 micron bulk sample of $\text{Si}_{10}\text{Ge}_7\text{As}_{43}\text{Te}_{37}\text{P}_3$ by Stocker *et al.*¹⁶ The calculation by Stocker *et al.* does not do as well as Oh's in predicting the data. Oh included a constant in place of the loss term in the heat balance equation and then solved for the delay time versus applied voltage.

exists. In the virtual electrode model the equipotential plane for each electrode is placed a small distance into the amorphous semiconductors. Figure 4 shows the results of Kaplan and Adler's calculation for the standard thermal model (STM) and the virtual electrode model (VEM). The STM uses the conductivity in the form $\sigma = \sigma_0 e^{-\Delta E/kT}$. If the conductivity is allowed an electric field dependent term, differential negative resistance will exist according to the calculation.

Boer and Ovshinsky²⁴ attacked the problem of explaining threshold switching by assuming an electric field dependence in the conductivity. They suggested that the rapid and reversible transition from the high to low resistance state can be thermal, but they require that the thermal runaway be limited by double tunneling. They require double tunneling because the temperature profile in the threshold switching material immediately after thermal runaway, causes high electric fields close to the electrodes. They obtained a temperature profile of the form $T_{\text{ambient}} + T_0(t) \cos(\frac{x}{d})$. It is obvious that in this model the temperature of the material touching the electrode is T_{ambient} . This type of model, which assumes high field effects near the electrodes is used by Fritzsche and Ovshinsky,⁴ Adler,⁷ O'Dwyer,²³ and Schmidlen.³⁷

Klein,²⁵ who began publishing papers on breakdown models in Insulators several years previous to his interest in reversible switching, compares thermal events with electronic events. He claims that to separate thermal from electronic switching events, one must first calculate the threshold voltage from a pure thermal model. If the

Fig. 4. Current versus voltage curves for the standard thermal model (STM) and the virtual electrode model (VEM) by Kaplan and Adler.²¹ The VEM curve has a negative resistance while the STM curve does not. These calculations were performed without consideration of an external circuit.

calculated value agrees with experimental data then a thermal process has occurred. If the calculated value of the threshold voltage is greater than the observed value, then an electronic event has occurred. His arguments assume that one can calculate the thermal threshold field accurately, which is typically not the case. Unfortunately, many authors do not feel that the problem is this simple.

Robertson and Owen²⁹ added a field dependence to the conductivity in their calculation of the threshold voltage for high resistivity films. They measured the constant V_1 in the field dependent term, e^{V/V_1} , and their calculation is in good agreement with experiment. Their calculation assumes a steady state, so they do not calculate any time dependent properties.

One of the most detailed and carefully done electrothermal calculation is by Kroll.³¹ He obtained the current versus voltage characteristics for two models. The first model is difficult to solve since the properties of the electrodes are retained in the calculation. The second model illustrates the physics, but it is an approximation of the first model. The heat loss term in the heat balance equation is approximated by $-\frac{8\lambda(T-T_0)}{d^2}$ in the second model. The coefficient $\frac{8\lambda}{d^2}$ was chosen so that the low current current versus voltage characteristics of the simplified model matched the low current current versus voltage characteristics of the complicated model. In the simplified model the steady state heat balance equation reduces to Eq. (3).

$$-\frac{8\lambda(T-T_0)}{d^2} + \sigma(T,e)e^2 = 0. \quad (3)$$

$$-\sigma(T) + \frac{\partial \sigma(T)}{\partial T} (T - T_0) = 0. \quad (4)$$

Kroll obtains Eq. (4) by solving for $\frac{\partial \mathcal{E}}{\partial I}$ and setting it equal to zero. $\frac{\partial \mathcal{E}}{\partial I}$ is zero at the breakback field, which is the point on the current versus voltage curves where the differential negative resistance segment begins. Kroll finds the temperature rise to be approximately 20 K above ambient for his parameters. Once T_{bb} , the breakback temperature, is known, I_{bb} may be substituted into Eq. (3) to obtain a relationship between the breakback field, ambient temperature and sample thickness. This is shown in Eq. (5).

$$-\frac{8\lambda(T_{bb} - T_0)}{d^2} + \sigma(T_{bb}) \mathcal{E}_{bb}^2 e^{\mathcal{E}_{bb}/\mathcal{E}_0} = 0. \quad (5)$$

Kroll does not continue and solve the time dependent heat balance equation for applied voltage versus time delay.

Electronic Models

Although double injection was first observed in crystalline materials this phenomenon has been applied to threshold switching in amorphous semiconductors. Henisch³³ and Fritzsche³⁴ suggested this mechanism. In this model, when a voltage is applied to the sample, electrons are injected into the negative electrode and holes into the positive electrode. At first a trapped negative space charge exists near the negative electrode, and a trapped positive space charge near the positive electrode. As time progresses the space charges extend into the

material until they overlap. In the overlap region, high electrical conductivity exists since all traps are filled. This overlap region then spreads until it fills most of the volume between the electrodes. Charges are injected at each end of the amorphous semiconductor.

Some evidence exists to support the conclusion that a double injection phenomenon is occurring in amorphous semiconductors threshold switches. Pryor and Henisch⁴⁰ and Henisch and Pryor³⁹ present double pulse data to support the double injection model. Balberg³⁵ and Shanks³⁸ have done a similar experiment using a double pulse technique, and they cannot find any evidence of a double injection effect. All authors have used Ovonic Threshold Switches (from Energy Conversion Devices, Troy, Michigan) and the controversy has not been resolved in the literature.

Electron avalanche has also been used to explain threshold switching in amorphous semiconductors. Shousha et al.⁴⁴ calculate the current and temperature profile as a function of radial distance away from the center of the filament. Electron avalanche becomes a viable model only when the electric field is very large, on the order of 10^6 V/cm. Shousha et al. assumed an electric field of 5×10^6 V/cm. Hindley⁴⁴ discussed avalanching when the threshold electric field is above 10^5 V/cm. For bulk samples and in most thin films these large fields are not required to initiate switching.

Fredericks⁴⁶ has given a possible explanation of the onset of threshold switching in terms of one phonon-assisted hopping of small polarons. Fredericks obtained a field of about 5×10^5 V/cm to create small

polarons from a phonon, and assumed that other mechanisms may predominate once the low resistance state is reached. Again this field is higher than normally needed in chalcogenide glasses.

CHAPTER III. SAMPLE PREPARATION

Chalcogenide Glasses

Several compositions in the Te-As-Ge chalcogenide glass system were prepared in the Ames Laboratory by Howard Shanks. The Te, As and Ge were mixed in the appropriate amounts and then sealed in an evacuated quartz tube. The purity of these elements was 99.999% or better. The quartz tubes were then placed in a rocking furnace. The furnace was heated to 950°C, and the chalcogenide glasses remained in the rocking furnace for 24 hours. The furnace also rotated the quartz tubes at 3 RPM to thoroughly mix the Te, As and Ge. After this the quartz tubes were quenched in liquid nitrogen cooled sand. This rapid cooling made the material amorphous. If the mixture had slow cooled, a mixed phase of crystals and glass would have resulted. On one inch or larger diameter tubes, a polycrystalline center would occasionally be observed on the sample. The most successful runs were made with quartz tubes of about 5 mm in diameter.

Once the ingot of amorphous chalcogenide was obtained, it had to be cut. If point probes were to be used, the chunk was placed in a mold which was filled with Quickmount self-setting resin. This was then lapped down such that a large area of the chalcogenide was exposed. The chalcogenide was then polished with 0.05 μ alumina powder. If rectangular blocks were needed for parallel plate electrodes or conductivity measurements, the chunk was cut on an abrasive wire saw. Originally, a diamond saw was tried but vibration or slight misalignments caused

the amorphous chalcogenide to crack and break up. The wire saw was successful. Chunks of the material were glued to a copper plate with Duco cement. This plate was bolted to the wire saw. A carborundum abrasive mixed with kerosene was used to cut the amorphous semiconductor. The wire saw cut rough sides so the samples had to be polished.

To construct a sample with a parallel plate geometry, a wafer with a thickness of about 2 mm was cut on the abrasive wire saw. This wafer was then glued to a 1 1/4" aluminum disk with Duco cement and lapped flat. The lapped face was still rough so it was polished with 0.05 μ alumina powder. Molybdenum was sputtered onto the polished face. This face was glued to a small flat piece of brass to give the chalcogenide firm support. If a sample base was not used, the chalcogenide sample would crack. The rough surface facing away from the brass was then lapped and polished to the approximate thickness desired. A molybdenum mask with 0.9 mm diameter holes was placed over the top surface. Molybdenum was sputtered through the mask to form the top electrodes. The sputtering power was 100 watts. The sputtering was continued one to two hours for each side of the $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$ sample. All samples used in this study were from the ingot.

Melanin

Dehydrated melanin was purchased from Sigma Chemical Company (Sigma Chemical Co., P. O. Box 14508, Saint Louis, Missouri, 63178). Dehydrated melanin does not exhibit low electric field threshold switching. Melanin must be properly hydrated before threshold switching

will occur. In an early experiment, this dry melanin was wetted with distilled water and tightly packed into 1 mm inside diameter quartz tubes. This method proved unsatisfactory since internal arcing could be observed through the quartz tube when voltage was applied. In addition to this arcing, spikes in the current and voltage traces were observed on an oscilloscope. On one of these samples the arcing was allowed to continue. After 30 minutes, the arcing had completely decomposed the melanin.

A satisfactory method⁵⁵ for hydrating melanin was to suspend a dish of melanin in a beaker above the boiling water level. After two hours, the melanin was removed from the beaker. The color of the melanin changed to a darker black after hydration. The melanin was then dried at room temperature for at least 3 hours. In addition to this method, another satisfactory method of hydration was found. Steam was passed over a dish of dry melanin for approximately one minute, and then the melanin was allowed to dry in air at room temperature for 12 hours or more.

The melanin was formed into sample pellets by compressing it in a 1/4" (0.635 cm) diameter die to a pressure of 30,000 pounds per square inch ($2 \times 10^8 \text{ N/m}^2$). Pellet thickness varied from 1 mm to 7 mm. Each pellet was placed in a cylindrical synthane holder with electrodes at each end. Copper, molybdenum and carbon electrodes were used. Although the different electrodes did not seem to affect the switching characteristics of melanin, this point was not thoroughly studied. All measurements were made in air or helium gas. A vacuum environment ruined the

switching behavior of melanin.

Even though the hydration and pressing of the melanin was carefully done, some of the samples would not exhibit threshold switching. Most of these bad samples had resistances around $10\text{ k}\Omega$. It is quite probable that some water was still present on the surface of the melanin granules. Supporting evidence of this is that pellets made from wet melanin had resistances less than $1\text{ k}\Omega$. The good samples of melanin had resistance of about $1\text{ M}\Omega$.

CHAPTER IV. SAMPLE HOLDERS AND CRYOSTATS

Thermoelectric Cryostat

A thermoelectric cryostat was constructed to add a temperature variable to the switching and resistivity measurements. The cryostat which is a vacuum chamber with a thermoelectric cooler and sample holder was constructed with stainless steel and copper. The sample holder in the cryostat is shown in Fig. 5. The vacuum chamber has 14 glass-to-metal feed through pins, a four wire conax connector, a 3.8 cm viewing port, a 1.9 cm Cenco fitting for the vacuum pumps and a 14.6 cm removable lid. The base of this chamber is made of copper to give a stable ambient temperature reference to the hot side of the thermoelectric cooler. A probe assembly is attached to a copper disk with a 3.2 cm hole in the center so that it fits over the 3.2 cm disk holding the thermoelectric cooler. The probes are sharpened tungsten wires which are electrically isolated from the cryostat. The probe tips were sharpened with molten KNO_2 . The probe holders are spring loaded to provide adjustable probe tension. A standard roughing pump and diffusion pump set-up was used. Also, a temperature controller powered the thermoelectric cooler.

The temperature controller schematic is shown in Fig. 6. A Wheatstone bridge circuit sends voltages, which are related to the unbalance of two of the arms in the bridge, to two isolation operational amplifiers in the non-inverting configuration. These voltages are then fed into a high gain differential operational amplifier which drives

Fig. 5. Sample holder and probes in the thermoelectric cryostat. The sample has a parallel plate configuration. One side of the sample makes contact with the brass plate and the top side has molybdenum pads to provide good electrical contact between the probe and sample. The probe pressure can be adjusted.

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Fig. 6. Schematic of the thermoelectric cooler power supply and control circuitry. The reversing switch determines the direction of the current and enables the thermoelectric cooler to be used as a heater or a cooler. The range of temperatures attainable is -40°C to $+50^{\circ}\text{C}$.

the transistor output stage. The thermoelectric unit is used as the load resistor of the high current output transistor. The power supply for the controller is a standard full wave rectifier followed by a large inductor and capacitor. This controller held the temperature to better than 0.05°C once equilibrium was attained. The repeatability was not this good since the temperature of the sample depended on the magnitude of thermal load on the thermoelectric unit. The range of temperatures obtained with this system was from -40°C to $+50^{\circ}\text{C}$.

Dip Cryostat

The temperature range was extended to 77 K by constructing a dip cryostat. The dip cryostat has a removable copper base on which the sample can be mounted. The sample and top electrode are held on the base with three machine screws. The base is the bottom electrode. The top electrode is attached to a hollow glass-to-metal feed through. All pumping was done through this feed through. Two leads are available to apply voltages. This cryostat was used to hold melanin samples.

CHAPTER V. EXPERIMENTS

Double Pulse

A high voltage double pulser⁵⁶ was constructed to study the effect of polarity reversal upon the delay time. A block diagram of this apparatus is shown in Fig. 7. If a polarity dependence was found, a non-thermal threshold switching mechanism would be indicated. In the thermal model one would expect the delay time for the reversed polarity and the non-reversed polarity to be equal, since the Joule heating is proportional to the voltage squared.

Figure 8 shows the two types of double pulses. In the double pulse experiment a voltage V_1 is applied to the sample for a preselected length of time, t_1 , which is shorter than the time required for the sample to switch. At the end of this time interval, V_1 is turned off and V_2 is turned on. V_2 must be at or above the threshold voltage so that the sample will switch. The delay time is then measured for this switching event. If voltage V_1 is above threshold voltage, the delay time is the length of time for which both voltages were applied before the sample switched. If voltage V_1 is less than the threshold voltage, the delay time is the length of time voltage V_2 was applied before the sample switched. This procedure can be used to detect polarity effects by reversing the polarity of one of the voltages and looking for any changes in the delay times. If polarity effects are present, the delay time for the voltage sequence shown in Fig. 8b should be longer than the delay time for Fig. 8a. If the thermal effect is the dominant mechanism,

Fig. 7. System block diagram for the double pulser. Two consecutive voltage of either plus or minus polarity can be applied to the sample. The control and level dectector determines the pulse width of the two pulses.

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DOUBLE PULSER

Fig. 8. Timing diagram of the two consecutive pulses from the double pulses. If polarity effects are present, a difference in delay time will be observed as shown in Figs. 8a and 8b. If no polarity effects are present, the delay times should be equal as shown in Figs. 8c and 8d.

Fig. 9. Control timing diagram for the double pulser. The upper set of signals (a) shows the sequence of the timing signals when the current passing through the sample causes the high voltage across the sample to be turned off. The lower set of signals (b) shows the sequence of timing signals when the high voltage across the sample is manually turned off.

START

HVB 1
CONTROL

HVB 2
CONTROL

CURRENT

(a)

START

HVB 1
CONTROL

HVB 2
CONTROL

CURRENT

(b)

the delay times will be equal as is shown in Fig. 8c and 8d,

The block diagram for the double pulser is shown in Fig. 7, and a complete description has been reported.⁵⁶ To begin the sequence of pulses the START/STOP switch must be moved to START. This switch turns on voltage V_1 by turning on the high voltage switch 1. After a time determined by capacitor C_D , the control and level detector board turns off high voltage switch 1 and turns on high voltage switch 2. Both high voltage switches are isolated from ground by optical isolators. High voltage switch 2 will remain on until the START/STOP switch is returned to the STOP position or the current through the sample exceeds a predetermined value. The maximum current through the sample is set with $I_{\max} = \frac{4 \text{ volts}}{R_s}$. A timing diagram showing the control voltage levels and sample current is shown in Fig. 9. Figure 9a shows the levels when the sample switches, and Fig. 9b shows the levels when the sample does not switch. The arrows indicate which voltage level change causes another voltage level to change.

Computer Controlled Measurement of Switching Parameters

The computer controlled switching parameter apparatus⁵⁷ measures the energy, time delay if the sample switches or the voltage pulse duration if the sample did not switch, applied voltage, and charge input in an amorphous semiconductor during a switching event. The minicomputer sets the voltage from a high voltage power supply, the load resistor, the maximum pulse width and the integrator time constants upon command from the teletypewriter. A known applied voltage is put across the

sample and load resistor when the sample is in a high resistance state. If the sample does not switch within the maximum time allowed, the voltage is turned off by the minicomputer. If the sample current reaches a high value, usually defined as 10 mA, the sample has switched from a high resistance state to a low resistance state. After each event, whether switching or non-switching, the data and analysis are printed by the teletypewriter.

The simplified circuit without the minicomputer and control electronics is shown in Fig. 10. The loop and nodal circuit equations are shown in Eqs. (6) and (7).

$$V_{PS} = V_s(t) + V_L(t) + V_c(t) \quad (6)$$

$$I_{PS}(t) = I_s(t) = I_L(t) = I_c(t). \quad (7)$$

The energy input is the product of the sample voltage and the sample current integrated over the time that voltage is applied. After some mathematical manipulation the equation reduces to easily measured quantities. The steps are shown below.

$$E = \int_0^{t_f} I_s(t) V_s(t) dt$$

$$E = \int_0^{t_f} \frac{V_c(t)}{R_c} [V_{PS} - (\frac{R_L}{R_c} + 1) V_c(t)] dt$$

$$E = \frac{V_{PS}}{R_c} \int_0^{t_f} V_c(t) dt - \frac{R_L + R_c}{R_c^2} \int_0^{t_f} V_c^2(t) dt \quad (8)$$

Fig. 10. Simplified circuit for measuring delay time and energy as a function of applied voltage.

$$E = E_1 - E_2.$$

Equation (8) can be calculated by measuring the applied voltage V_0 , the current sensing resistor R_c , the load resistor R_L , and both of the integrals. The value of the integral can be obtained by electrically integrating V_c . The voltage output of the linear integrator is A_0 .

$$A_0 = \frac{1}{R_1 C_1} \int_0^{t_f} V_c(t) dt.$$

By knowing the time constant $R_1 C_1$, the value for the integral becomes $R_1 C_1 A_0$. Therefore, the energy E_1 is:

$$E_1 = \frac{V_0}{R_c} R_1 C_1 A_0.$$

The same procedure can be used to solve for E_2 . The energy E_2 becomes:

$$E_2 = \frac{R_L + R_c}{R_c^2} (10) R_2 C_2 B_0.$$

B_0 is the voltage output of the integrator and $R_2 C_2$ is the time constant for the squared integral. The factor of 10 is in the equation because the squaring unit produces $V_c^2/10$ for the output voltage.

Other calculated quantities are the charge input and ratio of the linear integrator voltage to the squared integrator voltage. The charge input during the event is calculated by integrating the

current during the event, shown in Eq. (9).

$$Q = \frac{1}{R_c} \int_0^{t_f} V_c(t) dt. \quad (9)$$

The ratio is calculated by dividing E_2 by E_1 . This is converted to a percentage before being printed by the teletypewriter. This percentage is useful because if E_2 approaches the same magnitude as E_1 , then the experimental error for the energy increases.

The computer program to analyze and plot the data on the IBM 370 calculates some other quantities that the minicomputer does not. The data analysis is sent to a Cal. Comp. plotter which plots the various graphs. This program was written by D. Eckels.

A block diagram for switching parameter measurement system is shown in Fig. 11. The minicomputer controls the high voltage power supply through the D/A Converter Box, the load resistors through the reed relays, the scanner position, and the start and stop commands. The sequence for the primary timing signals is shown in Fig. 12. This control timing diagram shows the two ways by which a switching event can be terminated. The electronic circuitry has been completely described in a separate report.⁵⁷

Fig. 11. Block diagram for switching parameter measurement system.

Fig. 12. Control timing diagram of primary timing signals used in the switching parameter measurement system. The left group shows the timing sequence if the sample switches. The right group shows the timing sequence when the event is terminated by the minicomputer.

CHAPTER VI. CHALCOGENIDE DATA AND DISCUSSION

DC Conductivity

The DC conductivity of $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$ was measured with a four probe technique illustrated in Fig. 13. A rectangular sample was cut from the bulk ingot of $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$. The current source supplied the current which through the current measuring resistor, R_C , and the sample. After the current was turned on, potentiometer 1 was adjusted so that the voltage across electrometer 1 was 0.0 V. Potentiometer 2 was adjusted so that the voltage across electrometer 2 was 0.0 V. The voltage of potentiometer 2 was then equal to the voltage drop across the potential probes. Knowing the current, the voltage drop across the potential probes, the separation of the potential probes, and the cross-sectional area of the sample, one can calculate the resistivity. Another electrometer was placed across the entire sample so that the two probe resistance could be calculated. The measured activation energy for the two probe and the four probe measurements agree. Therefore, a two probe measurement is sufficient for measuring the activation energy of the $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$ samples. The extrapolated resistances at infinite temperature did not agree. Since these resistances did not agree, the voltage drop in the sample but near the current probes was greater than the voltage drop near the center of the sample. This indicates that there was detectable contact resistance at the indium current contacts. A decrease in resistance has been observed⁵⁸ by changing the contact material from indium to a liquid indium eutectic. This decrease in

Fig. 13. Four probe conductivity apparatus. The Keithley 601 electrometer measures the current through the sample. The voltage drop across the potential probes is read on potentiometer #2 after a null is obtained on each Victoreen electrometer.

resistance supports the conclusion that a noticeable contact resistance will occur when indium contacts are used. Figure 14 shows both measurements.

The expression for the conductivity of an intrinsic semiconductor is $\sigma = \sigma_0 e^{-\Delta E/kT}$. This expression assumes that an electric field dependence of the conductivity is either absent or is not important. The low electric field conductivity is shown in Fig. 14. The activation energy, ΔE , for $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$ is 0.3 eV. The value of σ_0 was calculated to be $5.3(\Omega\text{cm})^{-1}$, which is within the range of published values for σ_0 .

The parallel plate samples were polished and had molybdenum electrodes sputtered on each side. Figure 15 shows the low electric field resistance plotted as a function of reciprocal temperature. The activation energies are 0.35 eV for sample PA and 0.426 eV for sample PB. Since contact resistance problems may be present, an accurate value of σ_0 cannot be obtained from Fig. 15. A value for R_0 , the extrapolated resistance at reciprocal temperature equal to zero, can be obtained. The values of R_0 for PA and PB are 0.129Ω and $7.64 \times 10^{-3} \Omega$, respectively.

Since the activation energies are different for PA and PB and both samples were cut from the same ingot of $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$, the samples were probably annealed during the electrode sputtering process. K. Shimakawa *et al.*⁵⁹ have shown that annealing occurs at 378 K in a threshold amorphous chalcogenide. Brodsky⁶⁰ has shown that the activation energy for amorphous silicon increases as the sample is annealed. J. P. deNeufville⁶¹ demonstrated for several compositions

Fig. 14. Resistivity versus reciprocal temperature for $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$. Two probe and four probe measurements were made. The activation energy in both cases was 0.3 eV. The two probe measurement could not be used to determine the value of σ_0 . The value of σ_0 determined from the four probe measurement is $5.3 \text{ } 1/\Omega \text{ cm}$.

Fig. 15. Resistance versus reciprocal temperature for two parallel plate configurations of $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$. The activation energies for sample PA and sample PB are 0.35 eV and 0.426 eV, respectively. Molybdenum electrodes were sputtered on two sides of these samples. The difference in the activation energies can be explained by annealing.

Fig. 16. Resistance versus electric field at various ambient temperatures for $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$. The value of $\mathcal{E}_0$ is a constant within experimental error from 273 K to 297 K. The data points at 297 K start to deviate from the straight line at high electric fields because of sample heating.

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of GeTe_2 and GeSe_2 mixtures, the activation energy increased with annealing temperatures below the glass transition temperature. The preannealing activation energy was 0.3 eV. Sample PA has an activation energy of 0.35 eV and was in the sputtering plasma for a shorter time than sample PB. With the annealing arguments, PB is expected to have a larger activation energy than PA. Sample PB has a larger activation energy.

An estimate of the temperature rise on the side in the sputtering plasma can be made. The samples were mounted on a water cooled substrate holder. Mounting plates of brass and aluminum were between the sample and the stainless steel substrate holder. If a very good thermal contact between these materials is assumed, a temperature rise to 345 K is expected. Since the thermal junctions were not perfect, it is quite possible that the temperature on the face of the sample went above 373 K, which is close to the glass transition temperature. The glass transition temperature measurement of $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$ was made in the Ames Laboratory by Howard Shanks. The glass transition temperature is about 400 K for $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$.

Pulsed Resistance

A pulsed resistance measurement was made on a sample of $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$. The graph of $\ln \sigma$ versus $\mathcal{E}$ for 298 K, 273 K, and 243 K is shown on Fig. 16. The sampling voltage pulse was 1.0 msec since this pulse width gave the best results. If the pulse width were shorter, problems arose because of the initial current spike which charged the sample and line capacitances. If the pulse width were longer, Joule heating in the sample became a problem. For electric fields greater than 0.8×10^4

a decrease in resistivity below that predicted by $\sigma \propto e^{\mathcal{E}/\mathcal{E}_0}$ is conspicuous for the measurements at 297 K. This decrease is barely noticeable at 1.0×10^4 V/cm for the measurements at 273 K. This decrease in resistivity is not observed at all for fields up to 1.2×10^4 V/cm for measurements at 243 K. When the resistance begins to decrease at a faster rate than the term $e^{\mathcal{E}/\mathcal{E}_0}$ would predict, Joule heating in the sample is causing the resistance to change. An oscilloscope was connected to monitor the increase in current which caused the heating. This measurement confirmed that the current began increasing when deviation from the function $\sigma \propto e^{\mathcal{E}/\mathcal{E}_0}$ occurred.

The values obtained for $\mathcal{E}_0$ from the high field conductivity equation are around 4.2×10^4 V/cm. Values around 2 to 4×10^4 V/cm are commonly accepted in the literature.³¹

A physical interpretation of the electric field dependence in the conductivity has been given by Whitehead.⁶² If two traps are separated by a distance (a) and an electric field ($\mathcal{E}$) is applied, Whitehead shows that the conductivity is equal to

$$\sigma_0 \left(e^{-\frac{(\Delta E - 1/2 a e \mathcal{E})}{kT}} - e^{-\frac{(\Delta E + 1/2 a e \mathcal{E})}{kT}} \right).$$

The first term is the conductivity in the direction of the field and the second term is in the opposite direction. The first term dominates so the conductivity reduces to Eq. (10).

$$\sigma(T, \mathcal{E}) = \sigma_0 e^{-\frac{\Delta E}{kT}} e^{ae\mathcal{E}/2kT}. \quad (10)$$

Walsh, Vogel, and Evans⁶³ observed this electric field dependence of the conductivity in 0.6μ to 1.2μ films of $\text{Ga}_{12.5}\text{As}_{12.5}\text{Ge}_8\text{Te}_{67}$. Figure 14 shows our $\ln \sigma$ versus $\mathcal{E}$ plot for bulk $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$. If one equates $1/\epsilon_0$ with $1/2 a e/kT$, one can solve for a . The value obtained for a at 298 K is about 10^{-6} cm. The distance between traps can be converted into a density of traps in the material. The density of traps obtained is about $10^{18}/\text{cm}^3$. Trapping densities in the $10^{19}/\text{cm}^3$ range^{1,2} have been reported.

This model does predict a temperature dependence for ϵ_0 which is not observed. The temperature dependence only varies ϵ_0 by about 20% from 240 K to 300 K, and the measured values of ϵ_0 may be inaccurate to 20%. Thus this temperature dependence may not be seen in the data. With the exception of the temperature dependence which was not observed, this model gives a quantitative explanation of the electric field dependence in the conductivity.

An extension of this model could give it temperature independence. In amorphous semiconductors the trapping states are continuous below the conduction band edge. The applied field could lower the barriers that keep the charges trapped. In very shallow trapping states the barrier could be lowered to a value which is less than kT . The charges are then essentially free charges that can contribute to conduction. This extension of the model discussed by Whitehead⁶² effectively lowers the activation energy of the material, and the temperature dependence is removed from the electric field dependent part of the conductivity expression.

Double Pulse

An extensive study with the double pulser apparatus was done on melanin. A chalcogenide glass sample was also run on the double pulser. Sharpened tungsten probes were placed on a polished surface of the chalcogenide surface about 2 mm apart. By varying voltages V_1 and V_2 , considerable change would be seen in the delay time as would be expected. When the voltages V_1 and V_2 were held constant and a double pulse applied for V_2 positive and then a double pulse applied for V_2 negative, the delay times would be the same. This data was taken at room temperature. These findings support the conclusion that the threshold switching action is primarily a thermal mechanism in the bulk material.

Time Delay, Energy and Resistance

A time dependent electrothermal model to calculate time delay, energy and average resistance as functions of applied voltage is derived in Appendix A. This model was calculated for two parallel plate samples with different thicknesses. The experimental data were measured at 243 K, 273 K and 298 K for each of the two samples. The material parameters in the calculation are σ_0 , ΔE , d , A , λ , ϵ_0 and C . The values of ΔE , R_0 , d , ϵ_0 and A were measured for each sample. The values of λ and C were taken from commonly accepted values in the literature³⁰ for chalcogenide glasses. The temperature and applied voltage were selected to match the experimentally measured temperature and applied voltage. The value of σ_0 was an adjustable parameter, since

one cannot directly measure σ_0 in these samples and only a rough approximation could be calculated from R_0 , d and A . Nevertheless, the values of σ_0 used in the calculation for samples PA and PB were in reasonable agreement with the approximate values of σ_0 calculated from R_0 , d and A .

The width of the applied voltage pulse was 1 sec. Two minutes were allowed between voltage pulses to allow the sample to return to thermal equilibrium. Longer waiting times were tried but the results were the same as if a two minute time between switching events was allowed.

This electrothermal model uses the temperature dependent heat loss term which Kroll³¹ derived. Kroll obtained this heat loss term by matching the low field current versus voltage characteristics of this simplified model with the current versus voltage characteristics of a more advanced calculation which included the spatial dependence of the heat loss term. This simplified model removes the spatial dependence of the calculation. The calculation can then be solved using numeric integration techniques. Since a single temperature dependent loss term is used, one would expect the calculation to be inaccurate in the voltage region near the threshold voltage, because the loss term is large.

By removing the spatial dependence of the loss term, an approximation for the final switching temperature must be made. In the experiment, the switching phenomenon was defined to occur when 10 mA passed through the sample. Observations of a current versus time trace on an oscilloscope confirmed that the current was rising very rapidly when 10 mA

was flowing through the sample. The final temperature was calculated from the expression for the electrical conductivity. The expression for the final temperature is shown in Eq. (11).

$$T_F = \frac{\Delta E}{k} \left[\ln \frac{A\sigma_0}{I_f d} (V_{\text{appl.}} - I_f R_L) e^{\frac{(V_{\text{appl.}} - I_f R_L)}{d \epsilon_0}} \right]^{-1}. \quad (11)$$

T_F is an average temperature for the sample at the time when threshold switching occurs. The calculation of T_F does not contain any spatial temperature information.

The delay time versus applied voltage for sample PA is shown in Fig. 17. The parameters used in the electrothermal calculation (solid lines) are listed on Table 1. The sequence that the data were taken was 298 K, 273 K, 243 K and 298 K. The last set of measurements at 298 K was to check and make sure that the switching properties of the sample did not change during the first three runs at 298 K, 273 K and 243 K. The experimental data and theory are in good agreement for voltages above $2 V_{th}$, but the agreement is not good for the region near the threshold voltage. This electrothermal model was not expected to give close agreement with data for voltages near V_{th} .

The theory predicts a shorter delay time for a given voltage than is observed on the data at 243 K. The calculation is very sensitive to small changes in temperature around 243 K. A 1K temperature rise will shift the 243 K plot almost 0.5 cm to the left on the scale shown in Fig. 17. The calculation is less sensitive to small changes in temperature in the 273 K to 298 K range. The calculations at 273 K and

Table 1. Parameters for sample PA and PB.

Sample	PA	PB
ΔE	.346 eV	.426 eV
σ_0	$60.0 \frac{1}{\Omega \text{cm}}$	$920.0 \frac{1}{\Omega \text{cm}}$
d	0.0392 cm	0.063 cm
A	0.0078 cm^2	0.0078 cm^2
λ	$0.002 \frac{\text{W}}{\text{cm K}}$	$0.002 \frac{\text{W}}{\text{cm K}}$
C	$1.25 \frac{\text{J}}{\text{cm}^3 \text{ K}}$	$1.25 \frac{\text{J}}{\text{cm}^3 \text{ K}}$
F_0	$4.0 \times 10^4 \frac{\text{V}}{\text{cm}}$	$4.0 \times 10^4 \frac{\text{V}}{\text{cm}}$

Fig. 17. Delay time versus applied voltage for sample PA. The experimental data and the electrothermal theory are in fairly good agreement.

298 K predict the data with errors occurring only near V_{th} .

Ovshinsky¹ gave a functional form ($t_d \propto e^{-V/V_1}$) for the decrease in delay time as a function of overvoltages. Our data and electrothermal calculations do not agree with Ovshinsky's findings. For voltages slightly above V_{th} , the delay time falls off very rapidly with increasing voltage. Only for very large overvoltages does the delay time as a function of voltage begin to approach $t_d \propto e^{-V/V_1}$. Stocker et al.¹⁶ also found that the delay time as a function of voltage approached $t_d \propto e^{-V/V_1}$ for large overvoltages.

The energy versus applied voltage for sample PA is shown in Fig. 18. The energy calculation is in reasonable agreement with experimental data for applied voltages greater than 200 V for 298 K and 273 K. Since the delay time versus applied voltage at 243 K is different from the measured values, the energy calculation also differs from the energy data at 243 K. Any disagreement with data in the delay time versus applied voltage calculation magnifies the disagreement between data and calculations in the energy versus applied voltage plot.

The calculation can only be expected to give an approximate fit to data in the energy versus applied voltage plot. A feature that the calculation and the energy data share is the energy starting to become independent of the applied voltage for very large overvoltages. This constant value of energy is the minimum energy required to make the sample switch.

The data for the energy versus applied voltage for voltages less than the threshold voltages at 298 K, 273 K and 243 K are shown in

Fig. 13. Energy versus applied voltage for voltages greater than threshold voltage for sample PA. The agreement of data and theory is fairly good for applied voltages greater than 200V for 298K and 273K. Agreement is poor for 243K.

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Fig. 19. These data were plotted with logarithmic scales to show the voltage at which sample heating becomes important. If sample heating did not change the resistance, the slopes of the curves would be two since the energy input would be equal to the voltage squared divided by the resistance. The slope for the lowest voltages is approximately two and begins to increase slowly as sample heating becomes more important. As the voltage is increased to the threshold voltage the slope increases more dramatically, indicating that thermal runaway is about to occur.

The inverse of the average inverse resistance versus voltage is shown in Fig. 20. The data and the calculated values agree at 298 K. The calculation gives lower values for 273 K and 243 K, because the energy calculated for each voltage is greater than the measured energy values. The calculation does predict an almost constant $\langle \frac{1}{R} \rangle^{-1}$ for a large range of applied voltage. The experimental data also exhibit values of $\langle \frac{1}{R} \rangle^{-1}$ which are almost constant.

The field dependent term in the conductivity is responsible for the curvature of $\langle \frac{1}{R} \rangle^{-1}$ at voltages much greater than the threshold voltage. The field dependent term was removed from the calculation, and $\langle \frac{1}{R} \rangle^{-1}$ was recalculated. The curvature at high voltages disappeared. This result is reasonable. If the heat loss term and field dependent term are excluded from the calculation, $\langle \frac{1}{R} \rangle^{-1}$ is constant with applied voltage. Since the heat loss term becomes less important at high applied voltages, the field dependent term has the most noticeable effect at high voltages. Incorporating the heat loss and field dependent conductivity in the calculation of $\langle \frac{1}{R} \rangle^{-1}$ gives the small

Fig. 19. Energy versus applied voltage for voltages less than V_{th} for sample PA. The slope of these curves at the lower voltages is approximately two, indicating that sample heating is not important. As heating becomes important, a change in slope is noticeable.

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Fig. 20. Reciprocal of the average inverse resistance versus applied voltage. An essentially constant value of $\langle 1/R \rangle^{-1}$ is observed in the data and predicted by the electrothermal theory. The magnitude of $\langle 1/R \rangle^{-1}$ observed in the data differs from the predicted value at 273K and 243K.

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curvature in the plots of $\langle \frac{1}{R} \rangle^{-1}$ versus applied voltage.

The delay time versus applied voltage for sample PB is shown in Fig. 21. Table 1 lists the calculations that were used in the electrothermal calculations. The agreement between the electrothermal calculation and the delay time data is excellent. The sequence that the data were taken is the same as sample PA. The first and fourth runs at 298 K are essentially the same, so the switching properties of the sample did not change during these measurements.

The agreement of theory with data is much better than that obtained with sample PA. The calculation does dip slightly lower than the data for the 298 K and 273 K plots. The 243 K data exhibits a slight offset in the 420 V region. Occasionally, during the course of a series of measurements the data would show an offset. These offsets were generally small, but a clear explanation was not obvious. It is possible that the material parameters changed slightly or that the contacts changed during a switching event. Considering the complete set of data, the switching events were very repeatable.

The energy versus applied voltage data and theory is shown in Fig. 22. The energy data for all samples measured was never as stable or repeatable as the time delay versus applied voltage. One reason for this is the offset and noise problems associated with the analog integrators in the equipment. Another reason is that the calculation has shown that the energy is much more sensitive to any changes in the delay time or sample parameters than the delay time versus voltage. The overall agreement between theory and energy data is reasonably good.

Fig. 21- Time delay versus applied voltage at three ambient temperatures for sample PB. The agreement between data and the theoretical calculations is excellent for all three ambient temperatures.

Fig. 22. Energy versus applied voltage above threshold voltage. The agreement between the data and theory is within about 30%.

The 243 K plot shows very good agreement between data and theory with the exception of the data that appears to be unstable around 400 V. The calculations for the 298 K and 273 K temperatures are lower in energy than the measured data. The errors are around 20% to 30% for the 298 K and 273 K calculations.

The preswitching energy versus applied voltage is shown in Fig. 23. As with sample PA, the preswitching energy data has a slope of about 2 at low voltages when plotted on a logarithmic scale. The data at 243 K has an offset problem in the 150 V range. The energy data at 298 K and 273 K are smoothly varying functions of voltage. A strong indication that sample runaway is about to occur is shown by the rapidly increasing slope of the data near the threshold voltage.

The inverse of the average inverse resistance, $\langle \frac{1}{R} \rangle^{-1}$, versus applied voltage is shown in Fig. 24. The agreement is reasonable. At 243 K the theory and data agree. At 273 K and 298 K the value of $\langle \frac{1}{R} \rangle^{-1}$ is higher than the data, but the calculations still give the trend that the data follows. The slope of the calculations at 298 K very closely approximate the slope of the data. The same comparison of slopes hold true for the 273 K and 243 K plots. The calculations predict the approximate values of the data and predict a different slope at each temperature which closely follows the data.

The calculated electrothermal model can predict the delay time versus applied voltage reasonably well for values larger than the threshold voltage if the material parameters are known. The energy and inverse of the average inverse resistance versus applied voltage calculations

Fig. 23. Energy versus applied voltage below threshold voltage for sample PB. The increase in slope on each curve indicates sample heating is becoming important.

Fig. 24. Reciprocal of the average inverse resistance versus voltage for sample PB. The agreement is best at 243K. The predicted values are close to the experimental values.

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predict the data qualitatively. Trends are shown to agree, but errors arise when one tries to predict the energy and $\langle \frac{1}{R} \rangle^{-1}$ versus voltage data. The $\langle \frac{1}{R} \rangle^{-1}$ calculations had their values above the data for sample PB and below the data for sample PA.

The electrothermal model described also scaled well for the different temperatures and sample thickness. The model exhibits the correct temperature dependences of the switching properties as is illustrated in samples PA and PB. Also, the model scales the correct amount for changes in sample thickness. These two features make this electrothermal model very attractive in predicting the threshold switching behavior of amorphous semiconductors.

CHAPTER VII. MELANIN DATA AND DISCUSSION

Time Dependent Current Versus Voltage

After the melanin was properly hydrated, and pressed, the samples were placed in a sample holder. Time dependent current versus voltage curves were measured using the double pulser to generate a single high voltage pulse. Each melanin sample was placed in series with an 11K load resistor, a power supply and one transistor switch in the double pulser. When voltage was applied, current versus voltage traces were photographed on an oscilloscope. A level detector was used to sense the current flowing through the sample by monitoring the voltage drop across a current sensing resistor. When this current exceeded a preselected value, usually between 2 mA and 10 mA, the transistor switch was turned off. The time variable was added to the oscilloscope trace by modulating the z-axis of the oscilloscope with 1 kHz pulses. The electron beam in the oscilloscope tube was turned on for about 100 μ sec of each 1 msec time period. As the beam moved in the x and y directions on the tube face, dots appeared which were separated in time by 1 msec.

Figure 25 shows a typical time dependent current versus voltage trace obtained. The rise-time of the voltage pulse was about 1 μ sec, so dots are not present on the initial segment of this curve. The closeness of the time marker dots on the differential negative resistance (DNR) segment illustrates the slow switching characteristics of melanin. If switching is due to a thermal mechanism, one would

Fig. 25. Time dependent current versus voltage characteristics for a pellet of melanin 4 mm thick at room temperature. The time between the marker dots is 1 msec. The inset shows the oscilloscope photograph with 2 mA/div. on the vertical axis and 50 V/div. on the horizontal axis.

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expect the current to start slowly up the DNR segment and then speed up as thermal runaway occurs. At the very beginning of this segment the time marker dots overlap and then spread out as the current increases. Because the dots overlap, it is impossible to determine the delay time from this curve. At the largest value of the current, the level detector turned off the voltage in a few microseconds so dots are not present on the return-to-zero segment. If a level detector was not used larger currents would flow through the sample when switching occurred and cause a degradation of the switching characteristics.

Since one would expect a much faster traversal of the DNR segment for an electronic model, this data indicated that a thermal model should be used to explain threshold switching in bulk melanin.

Double Pulse

After observing the relatively slow traversal of the DNR segment on the time dependent current-vs-voltage curves, a high voltage double pulser was used to determine if any polarity dependence occurred in the switching event. If no polarity effects were found then this would give further evidence that switching was primarily thermal effect.^{35, 38, 39, 40}

In the double pulse method a voltage V_1 is applied to the sample for a preselected length of time. If V_1 is above threshold voltage the time selected must be shorter than the delay time associated with the applied voltage. The sample must not be allowed to switch during the V_1 voltage pulse. At the end of this time period, V_1 is turned off

and V_2 is turned on. V_2 must be at or above the threshold voltage so that the sample will switch. This method can be used to detect polarity of one of the applied voltage pulses and look for changes in the delay time. If polarity effects are present,^{39, 40} the delay time for the voltage sequence shown in Fig. 26a should be shorter than the delay time for Fig. 26b. If the thermal effect is the dominant mechanism, the delay times should be nearly equal.

In Figs. 26a and 26b, voltage V_1 (140 volts) was applied for 330 msec. Voltage V_2 (230 volts) was then applied and switching occurred with a delay time of 60 msec. The delay time was about 60 msec for both positive and negative V_2 . This experiment was repeated again for several different V_1 voltages including some which were slightly above the threshold voltage for this sample, and again no polarity effects were found. To be certain that V_1 had a large effect on the delay time, V_1 was set to zero and V_2 was left at 230 volts. In this case the delay time increased to 110 msec. This is definitely longer than the 60 msec delay time observed with V_1 at 140 volts. From these results one can conclude that the Joule heating which occurred during the V_1 voltage pulse effectively shortened the delay time.

Lowering the ambient temperature of a threshold switching sample is expected to enhance electronic effects which may be present.⁴⁰ A melanin pellet was placed in a dipping chamber which was backfilled with helium gas. This chamber was then immersed in liquid nitrogen, and the sample was switched many times by the double pulser apparatus. Figure 27 shows the measured delay time for each threshold switching event.

Fig. 26. Double pulse oscilloscope trace showing voltage V_1 (140 V) applied for 330 msec. Then voltage V_2 (230 V) was applied and the melanin switched 60 msec later. This data was taken at room temperature on a melanin pellet about 4 mm thick. The (a) trace is for positive V_2 and the (b) trace is for negative V_2 . The delay time for each pulse sequence is approximately 60 msec.

Fig. 27. Results of a number of double pulse switching events. The $\circ$ symbols represent double pulses with one voltage positive and one negative. The $+$ symbols represent double pulses with both voltages positive. The delay time, t_d , is the total delay time for both pulses since both V_1 and V_2 were above the threshold voltage. Switching occurred during the second pulse. The averages of the delay times for the two types of double pulses are essentially the same. This 3 mm thick pellet was immersed in liquid nitrogen, and 1 mm was allowed for the pellet to come to equilibrium between the applications of voltage. Longer waiting times did not change the average delay times.

The + symbol denotes double pulses for which each voltage had the same polarity, and the 0 symbol denotes double pulses for which one voltage was positive and one voltage was negative. The average values for the two types of double pulses are shown and are essentially the same.

The scatter in the data show that melanin does not have a stable delay time if the applied voltage is near threshold voltage. This amount of scatter was observed in all double pulse measurements that were done at room temperature, dry ice temperature, and liquid nitrogen temperature. At each temperature the average values of the delay times for the two types of double pulses were approximately the same. All of these results support the conclusion that threshold switching in melanin can be explained using a thermal model.

Pulsed Resistance

A pulsed resistance measurement was made on samples of melanin. If the conductivity of melanin exhibited a strong dependence upon applied voltage, then this would be a polarity independent electronic effect which would enhance thermal runaway. Voltage pulses with 0.1 msec and 1.0 msec duration were applied. Very short pulses (<0.1 msec) could not be used because the initial charging of the sample and line capacitances caused a current spike which masked the steady state current through the sample. Long pulses (>1.0 msec) created problems with sample heating so that the temperature of the sample became uncertain. Pulses in the range from 0.1 to 1.0 msec were found to minimize the capacitance and heating effects. The pulsed voltage was

varied from zero to 900 volts which was over twice the threshold voltage for the melanin samples. The resistance was essentially independent of voltage over this voltage range. Therefore, a voltage dependent conductivity has a negligible effect on switching in melanin.

Pseudo-Memory Effect

Several samples of melanin were switched to the low resistance state and then a current of about 20 mA was allowed to flow through these samples for several seconds. After the voltage was removed, the melanin samples remained in the low resistance state. A memory effect in chalcogenide glasses is a well-known effect, and a commercial memory using this effect is produced by Energy Conversion Devices. In the chalcogenide memory materials, the material can be returned to the high resistance state by applying a short high current pulse to the material. The melanin samples would not return to the high resistance state by applying a short high current pulse. This memory effect in melanin can be called a pseudo-memory effect since the melanin samples returned slowly to a high resistance state only after several days or weeks.

One possible explanation of this effect is that when a melanin sample switches and the current remains on, the hot filament in the material boils out the water of hydration away from the center of the filament to cooler areas surrounding the hot filament. The water of hydration could then condense around the outside of the filament to become excess surface water on the melanin molecules. When melanin was prepared with excess water the samples possessed a low resistance after

being pressed into a pellet. The excess water around the filament could produce a conducting ring surrounding the filament after the current is removed. The sample would be expected to return to the high resistance state as the excess water diffused back into the original filament. This should occur slowly. McGinness and collaborators⁵⁵ have found dopants which allow water to pass in and out of hydration states with much less difficulty than with undoped melanin.

Delay Time and Energy

Samples of melanin were placed in the thermoelectric cryostat which was flushed and filled with nitrogen gas. The samples were then connected to the energy measurement apparatus. Figure 28 shows the delay time versus applied voltage. The load resistor in series with the sample and high voltage switch was 10 k Ω . The sample pellets were about 0.5 cm thick and were hydrated and pressed as previously described. Sample MHD12 was exceptionally well behaved. Sample MHD11 was more typical of the samples measured. Almost all of the melanin samples had a significant amount of scatter in the data obtained.

One of the interesting features of this curve is that the delay time decreases very rapidly with increasing voltages above threshold. This was consistent with most of the data taken on melanin pellets.

The energy input versus applied voltage graph is very similar to the chalcogenide data, except that the melanin energy input decreases faster than the chalcogenide energy input with increasing applied voltage. Also, the maximum energy input, which occurs at the threshold

Fig. 28. Delay time versus applied voltage for two samples of melanin. The unique part of these data is the very rapid decrease in delay time with increasing voltage. A large amount of scatter was observed in most of the other samples that were measured.

Fig. 29. Energy versus applied voltage for two samples of melanin. The rapid decrease in energy with increasing voltage is more rapid than observed in the chalcogenide glasses.

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voltage, was 250 mJ for the melanin data. This energy is more than an order of magnitude higher than the energy input to the parallel plate chalcogenide glass samples. Since the melanin volume is larger, this result is reasonable. The data are shown in Fig. 29.

The DC resistance was measured for samples of melanin in the thermoelectric cryostat which was filled with nitrogen gas. Several problems were encountered. The thermal contact of the melanin pellet to the thermoelectric unit was not very satisfactory, since the pellet could only be attached at one side. The top of the pellet was at a different temperature than the bottom. This problem was magnified since the samples could not be placed in vacuum environment. The nitrogen gas provided a thermal transfer from the cryostat walls to the parts of the samples which were not in direct contact with the thermoelectric unit. Another problem was to be certain that the hydration level, which very dramatically affects the resistance, remained constant as the temperature was varied. The heat transfer problem lowered the measured activation energy from the value one should have. Rosenberg and Postow⁴⁹ found that partial hydrated melanin had an activation energy of 1.2 eV. The measured value for the activation energy at points close to room temperature was about 0.8 eV for partially hydrated melanin. It is difficult to say whether these values agree or do not agree since the degree of hydration in each is an unknown factor. Rosenberg and Postow show that the activation energy for melanin drops from 1.5 eV to 1.2 eV as the hydration level goes from dry to partially hydrated.

Since the melanin samples made in this laboratory were completely hydrated (water of hydration seems to slowly leave a sample as it ages) at the time of preparation. The hydration level is probably higher in our samples, which makes the 0.8 eV activation energy seem reasonable.

CHAPTER VIII. CONCLUSIONS

The activation energy of $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$ was measured on a sample which was cut from the bulk ingot. The activation energy was also measured on other samples from the same ingot which had molybdenum electrodes sputtered on each side of the thin plates. The activation energy was larger for the samples which were in a sputtering environment. The sputtering environment probably annealed these samples since the exposed side of the amorphous semiconductor could be heated to temperatures near the glass transition temperature by the sputtering plasma. Other authors^{59, 60} have observed increases in the activation energy of amorphous semiconductors from annealing these materials with temperatures close to the glass transition temperature.

Samples of $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$ were found to have an electric field dependence in the electrical conductivity. The value of $\mathcal{E}_0$ was found to be 4.2×10^4 V/cm, which is consistent with other published values of $\mathcal{E}_0$ for chalcogenide glasses. A possible explanation for the electric field dependence of the conductivity ($\sigma = \sigma(T)e^{\mathcal{E}/\mathcal{E}_0}$) was proposed by Whitehead.⁶² By incorporating the field dependence into the theory, the theory became an electrothermal model.

The electrothermal model, which was an extension of Kroll's³¹ work, fit the data reasonably well. Delay time versus applied voltage data is in reasonable agreement with calculations for sample PA and very good agreement with calculations done for sample PB. If the parameters in this model are known for a sample, the theory should be able to predict the time delay versus voltage data reasonably well. The energy versus

applied voltage calculations for samples PA and PB do not do as well as the time delay calculations. The theory followed the data qualitatively but had errors as much as a factor of two in predicting the energy as a function of applied voltage. The energy data and calculations showed that the energy began approaching a constant value for large overvoltages. The preswitching energy data for both samples shows the voltage range in which sample heating begins to occur. The $\langle \frac{1}{R} \rangle^{-1}$ calculation also had quantitative errors. The theory does predict that the value of $\langle \frac{1}{R} \rangle^{-1}$ data is approximately constant also. The calculations for sample PB qualitatively show some of the slight deviations from a constant value seen in the data for $\langle \frac{1}{R} \rangle^{-1}$ versus applied voltage.

Although it is not possible to definitely say that this electrothermal model is the threshold switching mechanism, many electronic mechanisms can be eliminated. Avalanching and polaron models of threshold switching can be eliminated as the predominant mechanism since they require much larger electric fields than were used in this investigation. Double injection can be eliminated as being a dominant mechanism since the double pulse data did not exhibit a polarity dependence. It is possible that one or more of these electronic models occur during threshold switching in a minor role.

The electrothermal model scales properly with ambient temperature and sample thickness. Although other mechanisms may be occurring to a limited extent, this electrothermal model predicts for the observed threshold switching properties of bulk $\text{As}_{15}\text{Te}_{70}\text{Ge}_{15}$ reasonable well.

Melanin was studied using several techniques. The time-dependent current versus voltage characteristics illustrated the relatively long time required to traverse the DNR segment. Most chalcogenides switched much faster than the melanin. This is a strong indication that the switching effect is primarily thermal. The double pulse experiments came next and showed that melanin did not exhibit any polarity effects even at 77 K. This experiment ruled out any electronic model which would require a polarity dependence on the double pulse experiment. Double injection requires a polarity dependence. A field dependent term in the conductivity would be an electronic effect which would not exhibit a polarity dependence. The high field conductivity was measured for melanin and no effect was found. Electron avalanching does not require a polarity dependence, but is ruled out as a mechanism since it requires a high field of about 10^5 V/cm to occur and the switching would be much faster than the switching speed observed on the time dependent current versus voltage curves. Melanin switched at a field of about 4×10^2 V/cm which is a very low threshold field. Polaron switching can also be ruled out with the same arguments given for electron avalanching. From the results obtained, threshold switching in bulk melanin can be explained using a thermal model.

The next logical step for melanin research would be to perfect a way of preparing melanin granules of approximately the same size as is found in the human body. A method of attaching very small electrodes would have to be developed. Once this was accomplished, a study could be made that would approximate the natural conditions of melanin.

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APPENDIX A. TIME DEPENDENT ELECTROTHERMAL MODEL

Kroll³¹ derived a time independent model and predicted the break-back field versus sample thickness. He also calculated the temperature for which thermal runaway began to occur in a sample, the slope of the current versus voltage curve is infinite. His calculation has been extended to calculate the time delay versus applied voltage. By putting the time dependence back into the heat balance equation and using Kroll's loss term, one obtains Eq. (12).

$$C \frac{\partial T}{\partial t} = \frac{-8\lambda(T - T_0)}{d^2} + \sigma \mathcal{E}^2. \quad (12)$$

C is the heat capacity per volume, λ is the thermal conductivity, d is the sample thickness, T_0 is the ambient temperature, σ is the field dependent conductivity ($\sigma = \sigma_0 e^{-\Delta E/kT} \mathcal{E}/\mathcal{E}_0$), and $\mathcal{E}$ is the electric field in the sample. The electric field is dependent on temperature, so this dependence must be found before proceeding to solve Eq. (12). A constant electric field is assumed to exist in the sample.

By writing the loop equation for the circuit with a power supply, series load resistor and sample, one obtains Eq. (13).

$$\begin{aligned} V_{ps} &= IR_L + \mathcal{E}d \\ &= j \cdot A \cdot R_L + \mathcal{E}d \\ &= A\sigma R_L \mathcal{E} + \mathcal{E}d \end{aligned}$$

$$V_{ps} = (A\sigma R_L + d) \mathcal{E} \quad (13)$$

$$\therefore \mathcal{E} = \frac{V_{ps}}{A\sigma R_L + d} \quad (14)$$

In Eq. (14), R_L is the load resistor and A is the area of the electrodes. The temperature dependence is contained in σ . One can also use Eq. (13) to determine the temperature of the sample when the current is 10 mA. Starting with Eq. (13) and solving for the final temperature of the sample, one obtains Eq. (15).

$$T_f = \frac{\Delta E}{k_B} \frac{1}{\ln \left[\frac{A\sigma_0 (V_{ps} - I_f R_L)}{I_f d e^{\mathcal{E}/\mathcal{E}_0}} \right]} \quad (15)$$

I_f is the final current, 10 mA in this case.

Going back to Eq. (12) and integrating, one obtains Eq. (16).

$$t_d = \int_{T_0}^{T_f} \frac{C dT}{\frac{-8\lambda (T - T_0)}{d^2} + \sigma \mathcal{E}^2} \quad (16)$$

In Eq. (16), t_d is the delay time. This equation was solved numerically on a computer and gave reasonable results for applied voltages above threshold. The integrand is not a continuous well-behaved function for applied voltages near or below the threshold voltage. Figure 30

shows typical values of the integrand with various applied voltages. The ambient temperature is 303 K. Since for voltages above 100 volts the function is well behaved in the interval $300 \text{ K} < T < 450 \text{ K}$, the integration can be performed. The + sign means the points on the line are positive and the - signs mean the points on those lines are negative.

The experiment also measures the energy as a function of voltage. One can change the integration variable from time to an integral over temperature using the heat flow equation. Equation (17) shows the energy integral with the parameters used in this model.

$$\text{Energy} = d A C \int_{T_0}^{T_f} \frac{dT}{T_0 \left[1 - \frac{8 \lambda (T - T_0)}{\sigma \epsilon^2} \right]} \quad (17)$$

The average resistance was calculated. Since the analysis of the energy and time delay data yields the average of $\langle \frac{1}{R} \rangle^{-1}$, the calculation was done for $\langle \frac{1}{R} \rangle^{-1}$. The quadratic used to give $\langle \frac{1}{R} \rangle^{-1}$ from the experimental data can be calculated from Eqs. (18) and (19).

$$\frac{\text{Energy}}{t_d} = \frac{V_s^2}{R_s} \quad (18)$$

$$\frac{V_s}{R_s} = \frac{V_{ps}}{R_L + R_s} \quad (19)$$

In these equations, V_s is the voltage across the sample, R_s is the average resistance of the sample, t_d is the delay time, R_L is the

series load resistor. The result for $\langle \frac{1}{R} \rangle^{-1}$ is shown in Eq. (20).

$$\frac{1}{R_s}^{-1} = \frac{V_{PS}^2 t_d}{2 \text{ Energy}} \left(1 \pm \sqrt{1 - \frac{4R_L}{V_{PS}^2 t_d}} \right) - R_L. \quad (20)$$

The + sign is used when R_L greater than $\langle \frac{1}{R_s} \rangle^{-1}$, and the - sign when R_L less than $\langle \frac{1}{R_s} \rangle^{-1}$.

To calculate the value of $\langle \frac{1}{R} \rangle^{-1}$, one begins with Eq. (21).

$$\langle \frac{1}{R_s} \rangle^{-1} = \frac{\int_0^{t_d} dt}{\int_0^{t_d} \frac{1}{R_s} dt} \quad (21)$$

By changing the time variable to a temperature variable and putting in the equation for R_s [Eq. (22)], one obtains Eq. (23).

$$R_s = R_0 e^{\Delta E/kT} e^{-|e|/e_0} = \frac{d}{\sigma_0 A} e^{\Delta E/kT} e^{-e/e_0} \quad (22)$$

$$\langle \frac{1}{R_s} \rangle^{-1} = \frac{t_d d}{AC} \frac{1}{T_F \int_{T_0}^{\infty} \frac{[8\lambda(T - T_0) + \sigma e^2]}{d^2}} \quad (23)$$

Equation (23) can be solved by a numerical integration.

The assumptions used in this electrothermal model limit the expected accuracy of the calculation. Below and close to the threshold voltage, the integrand can and does have poles. The calculation can

Fig. 30. The calculated integrand of the delay time versus temperature. The temperature range of interest is from 303 K to approximately 450 K. For low applied voltages (less than and near the threshold voltage) the value of the integrand increases to infinity. The + symbols represent positive points of that segment of the curve. The - symbols represent negative values of the integrand. For voltages a little above the threshold voltage, the integrand become a smoothly decreasing function of temperature over the temperature range through which the integrand was integrated.

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only approximate real situations when the applied voltage is larger than the threshold voltage. This electrothermal model does have desirable features. The high field conductivity is incorporated into the expression for the conductivity, which enables one to obtain differential negative resistance without a load resistor. The external circuit is considered in the derivations for time delay, energy and average resistance. The loss term has been obtained from a model³¹ which takes the electrode properties into account in the theory.

APPENDIX B. DELAY TIME, ENERGY, AND RESISTANCE DATA

Data taken at 243 K on sample PB are listed in Table 2. The maximum pulse width is 1 second. If the time listed in the delay time column is 1 second, the sample did not switch. A time interval of 2 minutes elapsed between data points to allow the sample enough time to return to equilibrium. The load resistor in the external circuit was 1.4 k Ω for all measurements.

Table 2. Data for sample PB at 243 K.

V_{appl} (V)	t_d (msec)	Energy (mJ)	$\langle \frac{1}{R} \rangle^{-1}$ (M Ω)
9.81	1,000.0	0.0003	32.8
49.92	1,000.0	0.062	40.0
79.98	1,000.0	1.879	3.40
99.88	1,000.0	3.815	2.61
119.93	1,000.0	5.928	2.42
139.78	1,000.0	5.70	3.43
159.77	1,000.0	8.40	3.04
179.87	1,000.0	14.21	2.27
189.86	1,000.0	17.99	2.00
199.94	1,000.0	23.09	1.73
209.96	1,000.0	26.54	1.66
219.95	1,000.0	31.22	1.58
229.79	1,000.0	36.86	1.43
239.76	1,000.0	44.72	1.28

Table 2. (Con't.)

V_{appl} (V)	t_d (msec)	Energy (mJ)	$\langle \frac{1}{R} \rangle^{-1}$ (M Ω)
249.85	1,000.0	54.32	1.15
259.81	1,000.0	65.93	1.02
269.83	1,000.0	82.82	0.876
279.92	1,000.0	86.45	0.903
281.81	982.0	91.72	0.848
285.77	895.5	85.62	0.851
289.92	872.0	93.89	0.778
299.94	781.5	78.19	0.896
319.80	624.7	70.25	0.907
339.81	497.1	57.75	0.991
359.97	426.1	59.11	0.931
389.80	338.8	55.41	0.926
419.87	252.8	40.08	1.109
449.95	237.8	51.03	0.940
479.80	201.5	50.67	0.912
509.81	171.2	47.13	0.941
539.96	146.4	44.87	0.948
569.81	126.2	43.01	0.949
599.87	109.8	41.19	0.956
649.77	88.0	37.60	0.985
699.96	72.3	35.23	1.003
749.87	60.9	33.83	1.009

Table 3 contains data taken on sample PB at 273 K. Again, the maximum pulse width of the applied voltage was 1 second. The time between data points was 2 minutes. The load resistor was 1.4 k Ω .

Table 3. Data for sample PB at 273 K.

V_{appl} (V)	t_d (msec)	Energy (mJ)	$\langle \frac{1}{R} \rangle^{-1}$ (k Ω)
9.80	1,000.0	0.25	386.3
29.91	1,000.0	2.66	334.1
49.91	1,000.0	8.28	298.0
53.86	1,000.0	9.95	288.8
57.77	1,000.0	11.83	279.4
61.96	1,000.0	14.11	269.4
65.80	1,000.0	16.48	259.9
69.76	1,000.0	19.39	248.2
73.91	1,000.0	22.80	236.8
77.86	1,000.0	26.64	224.8
81.95	1,000.0	31.12	212.9
85.90	1,000.0	36.16	201.3
89.81	1,000.0	42.41	187.3
93.93	1,000.0	50.23	172.8
97.89	1,000.0	59.50	158.2
101.80	1,000.0	70.94	143.3
105.75	1,000.0	85.80	127.5
109.82	983.4	104.99	110.2

Table 3. (Con't.)

$V_{\text{appl}} \text{ (V)}$	$t_d \text{ (msec)}$	Energy (mJ)	$\langle \frac{1}{R} \rangle^{-1} \text{ (k}\Omega\text{)}$
111.81	894.4	93.88	116.3
113.78	843.8	90.75	117.6
115.76	806.7	90.69	116.4
119.92	725.0	86.35	117.9
126.00	645.6	86.21	116.1
131.93	565.1	83.23	115.3
137.80	535.2	86.98	114.0
143.84	449.6	76.28	119.1
149.89	397.0	73.33	119.0
159.76	342.1	72.04	118.4
169.85	287.9	68.32	118.8
189.85	213.6	60.40	124.6
209.96	173.5	61.90	120.7
229.78	137.4	56.96	124.5
249.85	111.7	53.94	126.5
269.83	92.1	50.85	128.9
289.92	79.0	50.80	127.9
309.78	67.0	47.84	131.6
329.97	56.8	45.50	133.1
349.88	49.78	44.70	133.3

Table 4 lists data taken for sample PB at 298 K. The maximum pulse width was 1 second, the time between pulses was 2 minutes, and the load resistor is 1.4 k Ω .

Table 4. Data for sample PB at 298 K.

V_{appl} (V)	t_d (msec)	Energy (mJ)	$\langle \frac{1}{R} \rangle^{-1}$ (k Ω)
1.96	1,000.0	0.03	117.0
5.91	1,000.0	0.29	116.7
9.81	1,000.0	0.86	108.8
13.77	1,000.0	1.85	99.9
17.86	1,000.0	3.34	92.8
21.81	1,000.0	5.32	86.7
25.97	1,000.0	8.05	80.9
29.92	1,000.0	11.45	75.3
33.79	1,000.0	15.52	70.8
37.99	1,000.0	21.47	64.4
41.89	1,000.0	28.83	58.0
47.93	1,000.0	45.17	48.0
51.89	1,000.0	61.18	41.2
55.79	1,000.0	84.13	34.1
59.99	1,000.0	122.42	26.5
61.97	923.0	126.35	25.2
63.83	785.5	106.31	27.2

Table 4. (Con't.)

V_{appl} (V)	t_d (msec)	Energy (mJ)	$\langle \frac{1}{R} \rangle^{-1}$ (k Ω)
65.81	713.1	101.68	27.5
69.76	602.1	95.92	27.6
73.92	515.5	92.42	27.6
75.89	481.3	90.96	27.6
79.98	418.9	87.62	27.6
89.81	311.1	81.88	27.7
99.87	237.5	76.61	27.8
119.93	153.3	70.80	28.2
139.78	105.9	65.03	29.0
159.77	75.4	57.91	30.3
179.87	54.9	50.86	32.0
199.94	41.1	44.96	33.7
219.95	31.3	39.75	35.3
239.77	34.4	35.23	36.9
259.81	19.1	31.24	83.4
279.92	15.2	24.72	40.0
299.95	12.1	24.51	41.7
319.80	9.8	21.81	43.1
339.82	8.0	19.34	44.6
359.97	6.5	17.06	46.3
379.97	5.3	15.10	47.6
399.77	4.3	13.29	49.1

APPENDIX C. DELAY TIME, ENERGY, AND RESISTANCE CALCULATIONS

Table 5 shows the results of the electrothermal calculation for sample PB at 243 K. Points below the threshold voltage are not shown, since the calculation was only intended to be used above the threshold voltage. The parameters of sample PB shown in Table 1 are incorporated in the calculation. Table 6 contains the calculated results for sample PB at 273 K and Table 7 contains the calculated results for sample PB at 298 K.

Table 5. Calculation for sample PB at 243 K.

$V_{\text{appl}} \text{ (V)}$	$t_d \text{ (sec)}$	Energy (mJ)	$\langle \frac{1}{R} \rangle^{-1} \text{ (k}\Omega\text{)}$
270.0	1.25	89.4	999
280.0	1.06	83.5	974
290.0	0.913	78.8	956
300.0	0.801	75.1	942
310.0	0.711	72.0	931
320.0	0.638	69.4	923
330.0	0.576	67.2	917
340.0	0.524	65.2	912
350.0	0.479	63.5	908
360.0	0.440	61.9	905
370.0	0.406	60.5	903
380.0	0.376	59.2	901

Table 5. (Con't.)

V_{appl} (V)	t_d (sec)	Energy (mJ)	$\langle \frac{1}{R} \rangle^{-1}$ (k Ω)
390.0	0.349	58.1	900
400.0	0.325	57.0	899
410.0	0.304	56.0	899
420.0	0.285	55.0	898
430.0	0.267	54.2	898
440.0	0.257	53.4	899
450.0	0.237	52.6	899
460.0	0.224	51.9	900
470.0	0.212	51.2	900
480.0	0.201	50.6	901
490.0	0.190	49.9	902
500.0	0.181	49.4	903

Table 6. Calculations for sample PB at 273 K.

$V_{\text{appl}} \text{ (V)}$	$t_d \text{ (sec)}$	Energy (mJ)	$\langle \frac{1}{R} \rangle^{-1} \text{ (k}\Omega\text{)}$
100.0	1.500	109.0	128
110.0	0.970	87.2	125
120.0	0.704	75.5	125
130.0	0.543	68.0	126
140.0	0.435	62.5	128
150.0	0.359	58.4	130
160.0	0.302	55.1	132
170.0	0.257	52.3	135
180.0	0.223	50.0	137
190.0	0.195	48.1	139
200.0	0.172	46.3	141
210.0	0.152	44.8	143
220.0	0.136	43.4	145
230.0	0.123	42.2	147
240.0	0.111	41.1	149
250.0	0.101	40.0	151
260.0	0.0919	39.1	153
270.0	0.0841	38.2	155
280.0	0.0773	37.4	156
290.0	0.0712	36.6	158
300.0	0.0659	35.9	160

Table 6. (Con.t.)

$V_{\text{appl}} \text{ (V)}$	$t_d \text{ (sec)}$	Energy (mJ)	$\langle \frac{1}{R} \rangle^{-1} \text{ (k}\Omega \text{)}$
310.0	0.0610	35.2	161
320.0	0.0567	34.5	163
330.0	0.0528	33.9	164
340.0	0.0492	33.3	166
350.0	0.0460	32.7	167
360.0	0.0431	32.2	168
370.0	0.0405	31.7	170
380.0	0.0380	31.2	171
390.0	0.0358	30.7	172
400.0	0.0337	30.2	174
410.0	0.0318	29.8	175
420.0	0.0301	29.3	176
430.0	0.0285	28.9	177
440.0	0.0270	28.5	178
450.0	0.0256	28.1	179
460.0	0.0243	27.7	181
470.0	0.0231	27.4	182
480.0	0.0219	27.0	183
490.0	0.0209	26.7	184
500.0	0.0199	26.3	185

Table 7. Calculations for sample PB at 298 K.

$V_{\text{appl}} \text{ (V)}$	$t_d \text{ (sec)}$	Energy (mJ)	$\langle \frac{1}{R} \rangle^{-1} \text{ (k}\Omega\text{)}$
50.0	2.250	167.0	26.5
60.0	0.890	92.5	27.9
70.0	0.524	70.0	30.4
80.0	0.354	58.4	32.9
90.0	0.257	51.2	35.2
100.0	0.196	46.1	37.3
110.0	0.154	42.2	39.2
120.0	0.124	39.2	41.0
130.0	0.103	36.7	42.6
140.0	0.0858	34.6	44.2
150.0	0.0727	32.8	45.6
160.0	0.0623	31.2	47.0
170.0	0.0540	29.7	48.3
180.0	0.0471	28.5	49.5
190.0	0.0414	27.3	50.7
200.0	0.0366	26.3	51.9
210.0	0.0325	25.3	53.0
220.0	0.0291	24.3	54.1
230.0	0.0261	23.5	55.1
240.0	0.0235	22.7	56.1
250.0	0.0213	21.9	57.0

Table 7. (Con't.)

V_{appl} (V)	t_d (sec)	Energy (mJ)	$\langle \frac{1}{R} \rangle^{-1}$ (k Ω)
260.0	0.0193	21.2	58.0
270.0	0.0176	20.5	58.9
280.0	0.0160	19.9	59.8
290.0	0.0147	19.3	60.6
300.0	0.0135	18.7	61.5
310.0	0.0124	18.1	62.3
320.0	0.0114	17.6	63.1
330.0	0.0105	17.1	63.8
340.0	0.00974	16.6	64.6
350.0	0.00902	16.1	65.4
360.0	0.00836	15.6	66.1
370.0	0.00777	15.2	66.8
380.0	0.00722	14.8	67.5
390.0	0.00673	14.3	68.2
400.0	0.00627	13.9	68.9
410.0	0.00585	13.5	69.5
420.0	0.00546	13.1	70.2
430.0	0.00511	12.8	70.8
440.0	0.00486	12.8	70.6