Phase Change Properties in Chalcogenide Semiconductors

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Since the discovery of chalcogenide semiconductors in 1955 at Ioffe Institute, it had passed half a century. During this time the unique properties of chalcogenide semiconductors were extensively studied, which had found many technical applications. In the past decades has seen an explosion of new interest to the chalcogenide semiconductors, due to their use as media for optical and electrical recording information based on "glass-crystal" phase transition. The properties of a high-resistance state ("OFF" state) and low-resistance state ("ON" state), which is resulting from the switching effect, i.e. phase change and nonlinearity of the current-voltage characteristics are studied intensively in recent year. In this research work, we studied the properties of phase change in chalcongenide semiconductors. Calculations was made by using Matlab.

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I. INTRODUCTION

Since the discovery of chalcogenide semiconductors in 1955 at Ioffe Institute, it had passed half a century. During this time the unique properties of chalcogenide semiconductors were extensively studied, which had found many technical applications. In the past decades has seen an explosion of new interest to the chalcogenide semiconductors, due to their use as media for optical and electrical recording information based on "glass-crystal" phase transition. Several firms such as Intel, Samsung and others are working on flash memory devices based on phase-change memory (PCM) cells, which is a promising device for nonvolatile technology. The properties of a high-resistance state ("OFF" state) and low-resistance state, which is resulting from the switching effect, i.e. phase change and nonlinearity of the current-voltage characteristics are studied intensively in recent year. In this research work, we studied the properties of phase change in chalcongenide semiconductors.

II. ELECTRONIC-THERMAL BREAKDOWN

Thermal breakdown or thermal instability is the explosive increase in current and temperature of the sample, which occurs to the exponential dependence of conductivity on temperature. In this case electrons, receiving energy from the electric field, give it to the atomic lattice. Heating the lattice increases the concentration of electrons. The breakdown that occurs in the presence of an explicit dependence of the conductivity on the voltage of electric field is called "electronic-thermal breakdown". It is known, that in semiconductors with conductivity of form

$$\sigma = \sigma_0 e^{-\frac{\Delta E}{kT}}$$

breakdown heat can't be more than:

$$\Delta T = T - T_0 \approx \frac{kT_0^2}{\Delta E} \text{ for } \Delta E >> kT_0$$

where T_0 is ambient temperature and ΔE is the activation energy of conduction. Thus maximum increase in conductivity, associated with Joule mechanism, can't be greater than:

$$\frac{\sigma(T)}{\sigma(T_0)} \approx \exp(1) \approx 3$$

But in subsequent studies show, that the increase in conductivity due to nonlinearity reaches the greater value. This implies, that nonlinearity observed in fields $F < F_{th}$ can't be explained not only by the Joule mechanism.

It was shown, that the dependence of conductivity on the field with good accuracy obeys:

$$\sigma \sim e^{v}$$

For composition $Si_3Te_{49}As_{33}Ge_6Ga_9$ conductivity was presented as:

$$\sigma = \sigma_0 e^{-\frac{\Delta E_a}{kT_0} + \frac{V}{V_0}}$$

The most significant conclusion made in these studies can be considered as the assumption of an existence of phase-change "semiconductor-metal", which occurs at temperature, close to the temperature T_2, at which linear dependence of $\frac{V_0}{T_0}$ on T_0 approaches to zero.

Also decreases linearly the value of V_{th} with increasing T_0. Extrapolation to zero the dependence $V_{th}(T_0)$ gives the value of temperature, up to tens of

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degrees, which matches with the values of T_2. The temperature T_2 is called “temperature of switch”.

The most probable view of explicit dependence of conductivity on the field is:

$$\sigma = \sigma_0 e^{\frac{F}{F_0}}$$

Namely this dependence for single thin films and volumetric samples, taking into account the presence of a phase transition from the conductivity of

$$\frac{F_0}{T} = a(T^* - T)$$

at the temperature T^* is the most consistent with some experimental facts:

$$\sigma \sim e^{\frac{F}{F_0 T (T - T^s)}} \sim e^{\frac{F}{F(1 - \frac{T}{T_s})}}$$

III. MODELS FOR ELECTRONIC-THERMAL BREAKDOWN

Thermal breakdown in a sample plate with a thickness of L occurs in the “weak” place with a few more conductive than the rest of the material, and having a kind of thin filaments, with cross sectional q. Neglecting the release of heat in the material out of the thread, we form the heat balance equation, that determines the temperature of thread:

$$qL\sigma_0 F^2 e^{-\frac{\Delta E}{kT}} = \lambda L(T - T_0)$$

on the left the total power Q, which distinguishes the entire volume of the thread qL and on the right is the term describing the heat Q_2. Since the thread with a small cross section, the heat occurs throughout the length of the sample L and the λ is a heat transfer coefficient. Let’s expand in Taylor’s series around the T_0:

$$T = T_0 + \Delta T$$

$$\sigma = \sigma_0 e^{-\frac{\Delta E}{kT_0} + \frac{\Delta E \Delta T}{kT_0^2}}$$

For thin films, the heat balance equation would look like:

$$qL\sigma_0 F^2 e^{-\frac{\Delta E}{kT}} = \lambda L(T - T_0) \qquad (1)$$

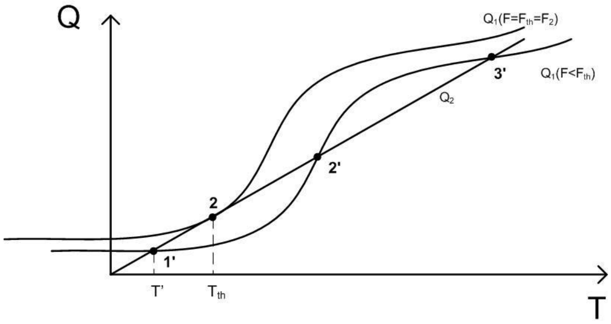

Figure 1: Heat Balance Equation

points 1’, 2’, 3’ are representing solutions of equation (1) in the case, where $F < F_{th}$ and the conductivity is a type

$$\sigma = \sigma_0 e^{-\frac{\Delta E}{kT}}$$

When temperature was expanded near T_0 just like $T = T_0 + \Delta T$, the heat Q with increasing the temperature T, increases without limit, and the equation (1) has a only two roots, corresponding to 1’, 2’.

Thus, for small values of F the equation (1) has only two solutions 1’, 2’ which are towards each other with increasing F and the temperature T’ (point 1’) corresponds to a slight heating in a fields smaller than the threshold value. The value of the field, when the solutions 1’ and 2’ merges, denote by F_{th}. Let’s find this value.

IV. CALCULATION AND MODELING

A. General Case

Mathematically, the merge of the two roots of the equation (1) is a equality of derivation by temperature from the left and right sides of the equation.

$$\begin{cases} qLF^2\sigma_0 \dfrac{\Delta E}{kT_0^2} e^{-\frac{\Delta E}{kT_0} + \frac{\Delta E}{kT_0^2}} = \lambda L \\ qLF^2\sigma_0 e^{-\frac{\Delta E}{kT_0} + \frac{\Delta E \Delta T}{kT_0^2}} = \lambda L(T - T_0) \end{cases}$$

and therefore

$$\begin{cases} T_{th} = T_0 + \Delta T_{th} = T_0 + \dfrac{kT_0^2}{\Delta E} \\ F_{th} = \sqrt{\dfrac{\lambda k T_0^2}{L\sigma \Delta E}} e^{\frac{\Delta E}{2kT_0} - \frac{1}{2}} \end{cases}$$

we obtain the roots of the systems of equation.

The meaning of T_{th} is the maximum temperature of the high-resistance state.

In further calculation, we will take

$\Delta E = 0.8 \cdot 10^{-19}$ J and

$$T_{th} = T_0 + \frac{kT_0^2}{\Delta E} = 316K$$

For convenience, let's make equation (1) dimensionless:

If we multiply by $\frac{k}{\Delta E}$, then

$$\frac{L\sigma_0}{\lambda}\frac{k}{\Delta E}F^2\sigma_0 e^{-\frac{\Delta E}{kT_0}} = (T - T_0)\frac{k}{\Delta E}$$

we introduce dimensionless values of field f, and use:

$$f = \sqrt{\frac{q\sigma_0}{\lambda}\frac{k}{\Delta E}}F$$

$$f = 4.2 \cdot 10^{-7} F$$

instead of F.

Do the same for the T, and use dimensionless t instead of T:

$$t = \frac{kT}{\Delta E} \text{ and } t = 1.75 \cdot 10^{-4} T.$$

Let's rewrite the equation (1) in this form:

$$f^2 e^{-\frac{1}{t}} = t - t_0.$$

and find the roots, through graphical method to the point where the curve will intersect with the line.

The scientist of the time, considered the thermal break, as a harmful effect, since in those days it was always about the electrical strength of insulating materials. The situation changed after the discovery of the switching effect in chalcogenide semiconductors.

There was done theoretical works from the point of view of its beneficial use. In contrast to the breakdown of insulation materials, breakdown in halcogenide semiconductors was reversible under certain condition, i.e. halcogenide thin film can withstand a large number of switches, each time restoring their properties, which is important for technical applications.

B. S-Shaped Current-Voltage Characteristics of the Halcogenide Semiconductor.

An importance reason for the disappearance of S-shaped current-voltage characteristics was pointed out in a 1966 by Chirkin L.K., Lototskii B.Yu. [2]. According them:

$$\begin{cases} qLF_{1.2}^2\sigma_0 e^{-\frac{\Delta E}{kT_{1.2}}} = \lambda L(T_{1.2} - T_0) \\ qLF^2{}_{1.2}\sigma_0 \frac{\Delta E}{kT_{1.2}^2} e^{-\frac{\Delta E}{kT_{1.2}}} = \lambda L \end{cases} \quad (2)$$

Expanding near temperature T_0, we get:

$$\lambda L(T_{1.2} - T_0)\frac{\Delta E}{kT_{1.2}^2} = \lambda L$$

And this leads as to a quadratic equation for temperature:

$$T_{1.2}^2 - \frac{\Delta E}{k}T_{1.2} + \frac{\Delta E T_0}{k} = 0$$

The solutions are:

$$T_{1.2} = \frac{\Delta E}{2k}(1 \pm \sqrt{1 - \frac{4kT_0}{\Delta E}}) \approx T_0 \pm \frac{kT_0^2}{\Delta E}$$

(at condition $\frac{\Delta E}{kT_0} > 4$). In our case T_2 is a T_{th}.

Let's find a differential conductivity. We can write a current by the product of conductivity and voltage.

$$I = \sigma F = F\sigma_0 e^{-\frac{\Delta E}{kT}}$$

then the differential conductivity is a first order differential from current by voltage. By substituting above expression, gives:

$$\frac{dI}{dF} = \sigma_{differ} = \sigma_0 e^{-\frac{\Delta E}{kT}} + F\sigma_0 e^{-\frac{\Delta E}{kT}}\frac{\Delta E}{kT^2}\frac{dT}{dF}$$

Let's consider an implicit function Φ(T(F), F):

$$\Phi(T(F), F) = qLF^2\sigma_0 e^{-\frac{\Delta E}{kT}} - \lambda L(T(F) - T_0) = 0$$

$$\begin{cases} \frac{d\Phi}{dT} = qLF^2\sigma_0\frac{\Delta E}{kT^2}e^{-\frac{\Delta E}{kT}} - \lambda L = 0 \\ \frac{d\Phi}{dF} = 2qLF\sigma_0 e^{-\frac{\Delta E}{kT}} \end{cases}$$

From this we get a differential form of conductivity

$$\sigma_{\partial u\phi\phi} = \frac{dI}{dF} = \sigma_0 e^{-\frac{\Delta E}{kT}} + F\sigma_0 e^{-\frac{\Delta E}{kT}}\frac{\Delta E}{kT^2}\frac{2qLF\sigma_0 e^{-\frac{\Delta E}{kT}}}{qLF^2\sigma_0 e^{-\frac{\Delta E}{kT}}\frac{\Delta E}{kT^2} - \lambda L}$$

$$= \frac{-qLF^2\sigma_0^2 e^{-\frac{\Delta E}{kT}}\frac{\Delta E}{kT^2} - \lambda L\sigma_0 e^{-\frac{\Delta E}{kT}}}{qLF^2\sigma_0 \exp(-\frac{\Delta E}{kT})\frac{\Delta E}{kT^2} - \lambda L}$$

From the expression of differential conductivity, we can we see current-voltage characteristics has two vertical sections, at value of the field F_2=F_{th} and F_1. For these values of field $\sigma_{differ} = \infty$, and in the interval between F_1 and F_2, for one value of field correspond three value of current. In other words at the values of F_1 and F_2 the differential conductivity goes to infinity, and between them three values of current is located. Thus we can assume, that current-voltage characteristics has a S-shape.

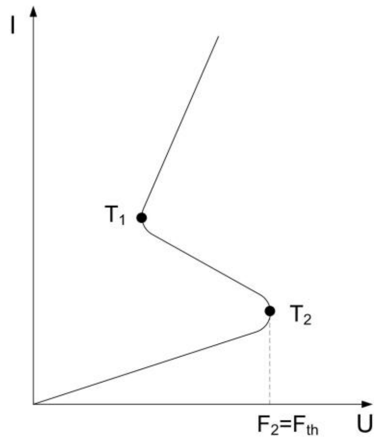

Figure 2: Current-Voltage Characteristics

C. Explicit Form of Conductivity

But later it turned out, that some of the features of the electrical transmission can be explained, if we take into account in the calculation of the explicit dependence of the conductivity in the form $e^{-\frac{F}{F_0}}$. Thus conductivity in the case of electronic-thermal breakdown has a form:

$$\sigma = \sigma_0 e^{-\frac{\Delta E}{kT}+\frac{F}{F_0}} \text{, where } F=aT\ (a=const)$$

Experimentally, in some range of temperature and voltage we can write the explicit form of conductivity:

$$\sigma = \sigma_0 e^{-\frac{\Delta E}{kT}+\frac{F}{F_0(1-\frac{T}{T_s})}}$$

This can lead us to apparently phase change. In the exponent, two terms

$$-\frac{\Delta E}{kT} + \frac{F}{F_0(1-\frac{T}{T_s})} = 0$$

are a cancelling each other and we get the constant conductivity $\sigma = \sigma_0$, as in metal. This phase change is meant not on the structure of semiconductors, but the conductivity, which depends on temperature and voltage is constant and we consider impact of such a phase transition to the electronic-thermal instability.

And so we have the equation, which changes:

$$qLF^2\sigma_0 e^{-\frac{\Delta E}{kT}+\frac{F}{F_0(1-\frac{T}{T_s})}} = \lambda q(T - T_0) \quad (3)$$

To make the equation above dimensionless, let's make substitution as before:

$f = \sqrt{\frac{L\sigma_0 k}{\lambda \Delta E}}F$ for field, and $t = \frac{kT}{\Delta E}$ for temperature and we get the dimensionless form of the equation (3):

$$f^2 e^{-\frac{1}{t}+\frac{F}{aT_s(T_s-T)}} = t - t_0$$

so therefore:

$$\frac{F}{a(1-\frac{T}{T_s})} = \frac{fF_0}{a(1-\frac{t}{t_s})} = \frac{f}{f_0(1-\frac{t}{t_s})}$$

Where $f_0 = a\sqrt{\frac{L\Delta E}{\lambda k}}$, $a = 6\cdot 10^8$ V/m, and t is a dimensionless temperature, f is a dimensionless field.

Considering this, we get:

$$f^2 e^{-\frac{1}{t}+\frac{f}{f_0(1-\frac{t}{t_s})}} = t - t_0 \qquad (4)$$

V. RESULTS OF CALCULATION

A. Dependence of Heat from the Thickness of Sample

Let's solve the equation (4) graphically. We take three values of T_s: T_s=1000K, 500K, 400K. For each value of T_s, vary the f_o until the straight line $t - t_0$ will be tangent to curve:

$$f^2 e^{-\frac{1}{t}+\frac{f}{f_0(1-\frac{t}{t_s})}}$$

The intersection point F_{th}, T_{th} is a switching temperature and field. The thickness of sample depends from f parameter as below:

$$L = \frac{\lambda k f_0^2}{a^2 \Delta E}$$

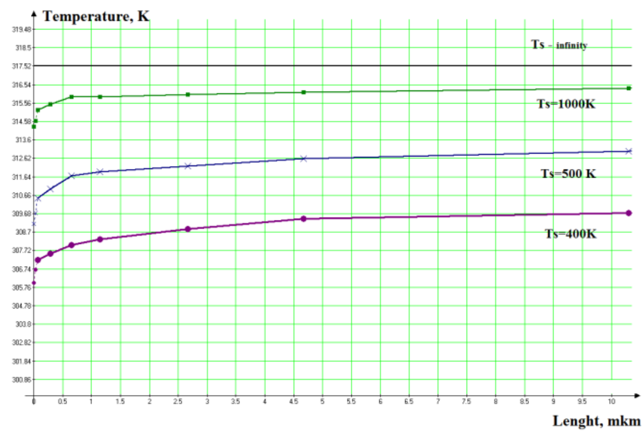

Figure 3. Dependence of heat ΔT, required for electronic-thermal switch, at different values of T_s

As can be seen from the Figure 3, for T_s=1000 K, dependence of heating temperature ΔT, from thickness of sample is weaker. This weak dependence due to the fact that the phase change transition temperature is far from the phase change. With a decrease of T_s to room temperature, dependence is increasing.

As a result, accounting phase change semiconductor-metal transition occurring in a strong electric field, reduces this heating ΔT, required for electronic-thermal switch.

This reduction is expressed more strongly, if the thickness of sample is smaller. This means that the electron thermal switch in thin films, in a strong electric field occurs at much lower temperature than the bulk samples

B. Conclusion

The main goal achieved in this work is the fact, that inclusion of the phase change semiconductor-metal transition, occurring in a strong electric field reduces that heating is required for electronic – thermal switch. This reduction is expressed more strongly, if the thickness of sample is smaller. This calculation takes into account, that conductivity has a nonlinearity form of $\sigma \sim e^{\frac{F}{F_0}}$, and effect of this nonlinearity on the characteristics of electron thermal instability.

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