

Multiphonon tunnel ionization of negative-U centers – the origin of switching and memory effects in chalcogenide glasses

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An electronic-thermal model of switching in chalcogenide glassy semiconductors is presented. Calculations show that multiphonon tunnel ionization of negative-U centers in strong electric field cause a strong nonlinearity of the current-voltage characteristic. Joule heating cause an electronic-thermal instability, that results in formation of an S-shaped current-voltage characteristic. The multiphonon tunnel ionization model is in good agreement with the experimental data on chalcogenide glassy semiconductors in strong electric field.

(Received November 1, 2011; accepted November 23, 2011)

Keywords: Switching, Memory effect, Chalcogenide glasses

1. Introduction

Phase change memory (PCM) technology, based on reversible phase transitions in chalcogenide glassy semiconductors (CGSs), is a promising candidate for next-generation non-volatile memory. As compared with flash-memory, PCM provides larger endurance, considerably faster read and write speeds and lower power consumption [1]. These desirable properties are based on the unique features of chalcogenide glasses. At room temperature these materials may exist in one of two phases, amorphous or crystalline. However, at higher temperatures, the amorphous phase crystallizes rapidly. Nowadays this effect is widely used in rewritable optical data storage and prototypes of non-volatile electronic memory.

Semiconductor properties of chalcogenide glasses were revealed by Kolomiets and Gorunova in 1955 [2]. In 1963 Kolomiets and Lebedev observed electrical switching from a highly-resistive state to a low-resistive one [3]. This effect was investigated by Ovshinsky in the 1960s, who also revealed memory switching [4].

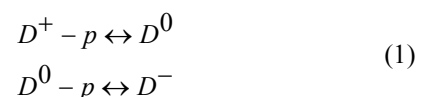
The S-shaped nonlinearity of the current-voltage characteristic (CVC) and the switching effect are extremely important for the PCM operation, since these effects decrease the resistivity of the CGS film and consequently recording voltage by several orders of magnitude [1]. Switching in CGSs has been investigated both experimentally and theoretically for about fifty years; nevertheless, the origin of switching is still not clear. There are various models interpreting the S-shaped CVC of CGSs [5-7] that fall into two classes, electronic and thermal. However, many scientists share the opinion that both factors should be taken into account [5,6].

Besides switching and memory effects, CGSs have a number of unique features, such as large Stokes shift and Fermi level pinning. These features correspond to the negative correlation energy approach, first applied by Anderson to show the possibility of electron coupling in amorphous materials [8] and later developed to explain a numerous experimental data on CGSs [9,10].

Nowadays it is widely believed that chalcogenide glasses have a high density of defects with negative correlation energy, referred to as negative-U centers. In our opinion, the most convincing evidence of negative-U centers existence in GeSbTe is the fact that different samples, obtained by different teams, have an equal value of the conductivity activation energy. Negative-U centers pin the Fermi level and thereby determine the conductivity in a weak field.

In a strong electric field a field-induced ionization of negative-U centers would occur, therefore, we believe that the tunnel ionization of negative-U centers could be the cause of the strong nonlinearity of the CVC in strong electric field. In the present paper we will use the theory of multiphonon tunnel ionization of deep centers, presented in [11-13].

Negative-U centers are not neutral in the ground state, since the total energy of a pair of charged states D^+ and D^- appears lower than the double energy of the neutral state D^0 [5, 6, 8-10]. Equilibrium in a system of negative-U centers is reached by transitions between different states of the centers. Since p-type conduction dominates in amorphous chalcogenides, in the calculations we will neglect electron transitions for the sake of simplicity.



2. Theory

2.1. Multiphonon tunnel ionization of a center

In this section, we will consider a center with a bound hole. Lattice oscillations change the binding energy, similarly to [11] we assume that the major role in the hole energy change is introduced by a single oscillation mode, which implies that the binding energy depends on a single coordinate x .

We will describe the center in the Huang and Rhys model [11]. In this model (Fig. 1) adiabatic terms U_1 (center with a bound hole) and U_2 (ionized center) are parabolic and the binding energy U_2-U_1 depends on x linearly and vanishes at $x = x_c$.

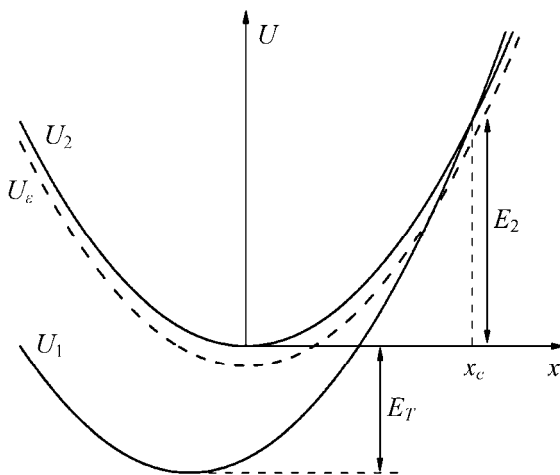


Fig. 1. Adiabatic terms of the negative- U center.

For the sake of simplicity, we can suppose that ionization occurs whenever the center achieves an intersection point of the adiabatic terms x_c while temperature oscillations in the U_1 potential. Therefore the ionization probability of the center is

$$P \propto \exp\left(-\frac{E_2 + E_T}{KT}\right). \tag{2}$$

Here $E_1 = E_2 + E_T$ means the activation energy of ionization. The principle of detailed balancing gives the hole capture cross section by an ionized center

$$\sigma \propto \exp\left(-\frac{E_2}{KT}\right). \tag{3}$$

Equations (2, 3) are valid in the case of sufficiently high temperatures. At room temperature, a center with lower energy can tunnel between the terms. Although the tunneling probability is small, it is compensated by the decrease of the activation energy. One can show that the following equation defines the optimal energy E_{opt} [11]:

$$\tau_2(E_{opt}) = \tau_1(E_{opt}) + \frac{\hbar}{2KT} \equiv \frac{\hbar}{2KT^*}. \tag{4}$$

here τ_1 means a characteristic time of tunneling under the U_1 potential. The temperature dependence of τ_1 is logarithmical and could be neglected [11].

The above refer to the case of zero electric field. According to the Poole-Frenkel effect, a relatively low electric field decreases the D^0 center ionization energy (Fig. 2), thus increasing the ionization probability. However, in a strong field, tunnel ionization of holes becomes most probable (Fig. 2). In this case, ionization process could be mentally divided into two steps. At a first step, the hole thermally excites; at the second step, the tunneling occurs. Since the excitation energy is much greater than the average phonon energy, it is multiphonon tunnel ionization (MTI).

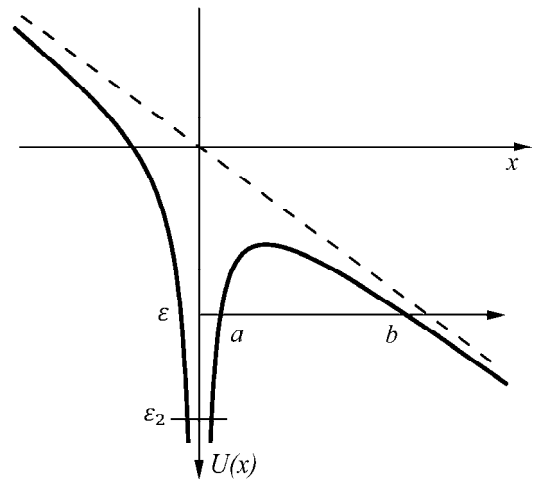


Fig. 2. Ionization in the coulomb attractive potential.

The first ionization of the positively charged D^+ center occurs in a short-range potential of the D^0 core (Fig. 3). Conversely, while the second ionization the hole appears to be under the influence of the negatively charged D^- core (Fig. 2).

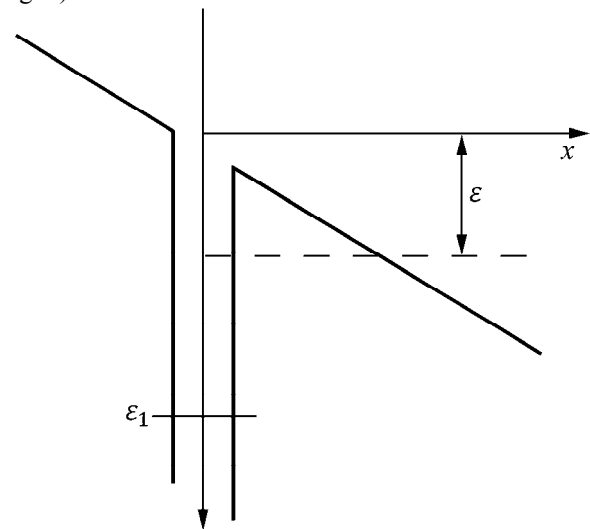


Fig. 3. Ionization in the short-range D^0 potential.

The center moves to the term U_e instead of U_2 while MTI (Fig. 1). In a first order by ϵ , the probability of the

core tunneling between the terms increases by the factor $\exp\left(\frac{\varepsilon}{KT^*}\right)$ [11], where T^* is the effective electron temperature, defined by (4).

In the present paper the probability of the hole tunneling was calculated in the semi-classical approximation:

$$D(\varepsilon) = \exp\left(-\frac{2}{\hbar} \int_a^b \sqrt{2m|\varepsilon - U(x)|} dx\right), \quad (5)$$

where ε is the excited energy level, $U(x)$ is the total potential of the center and applied electric field, a and b are the classical turning points (Fig. 2), and m is the hole effective mass.

To calculate the total ionization probability one should multiply the probability of tunneling by the probability of thermal excitation and integrate over ε :

$$\tilde{\varepsilon}(E) \propto \int_{-\infty}^{\varepsilon_i} \exp\left(\frac{\varepsilon}{KT^*} - \frac{\varepsilon_i}{KT}\right) D(\varepsilon) d\varepsilon, \quad (6)$$

where ε_i is the ground energy level of the center.

2.2. S-shaped current-voltage characteristic

Now we will write down the expressions for the transition rates between different states of the centers (1) using the principle of detailed balancing:

$$\frac{D^0 p}{D^+} = N_V \cdot \exp\left(-\frac{\varepsilon_1}{KT} + \omega_1\right) \quad (7)$$

$$\frac{D^- p}{D^0} = N_V \cdot \exp\left(-\frac{\varepsilon_2}{KT} + \omega_2\right), \quad (8)$$

where N_V is the effective hole concentration at the valence band edge, p is the hole concentration, ε_1 and ε_2 are the ground energy levels of the D^+ and D^0 centers respectively, ω_1 and ω_2 give the increase of the ionization probability in the electric field calculated in the previous section. In accordance with [11] we suppose that the hole capture cross-section is loosely dependent on the applied field.

Equations (7-8) together with the neutrality equation give the dependence of the hole concentration on the applied field and temperature [14,15]. Further on, these results will be used to calculate the CVC. We neglect the dependence of the hole mobility on the applied field and temperature, therefore the conductivity is

$$\sigma(E, T) = ep(E, T)\mu. \quad (9)$$

Finally, the Joule heating of the film should be taken into consideration. For the sake of simplicity, we assume that the current distribution is uniform within the memory cell. We also suppose that the CGS film is thin enough to be heat homogeneous. Therefore, the following heat balance equation gives the steady-state temperature of the film:

$$E^2 \sigma(E, T)L = \lambda(T - T_0). \quad (10)$$

Here L is the film thickness, and λ is the heat exchange coefficient. Finally, we substitute the conductivity (9):

$$\frac{e\mu L}{\lambda} E^2 p(T) = (T - T_0). \quad (11)$$

A numerical solution of equation (11) gives the steady-state temperature of the CGS film and makes it possible to calculate the current density versus applied electric field:

$$j = ep(E, T(E))\mu E. \quad (12)$$

In order to calculate the CVC of the PCM cell, we should consider that the cell consists of a thin chalcogenide layer and a bottom electrode called heater [16]. The heater resistance R is usually smaller than the amorphous chalcogenide resistance but greater than the resistance of the crystalline CGS layer. Therefore, the chalcogenide layer determines the resistance of the cell in the amorphous state, while the heater determines the resistance of the crystalline cell. The following relation gives the current-voltage characteristic of the PCM cell:

$$I = \frac{ep(E, T)\mu}{ep(E, T)\mu R + L/S} U. \quad (13)$$

Here I is the total current, U is the applied voltage, S is the heater area and L is the film thickness.

3. Results

In the previous section we have calculated the current-voltage characteristic of the phase-change memory cell within the framework of the multiphonon tunnel ionization electronic-thermal model [15]; three possible solutions of equation (11) in strong electric field imply an S-shaped nonlinearity of the CVC.

In the calculations we have used the following values of parameters: the ground energy level of the D^+ center $\varepsilon_1 = 0.5$ eV; the ground energy level of the D^0 center $\varepsilon_2 = 0.3$ eV; the ambient temperature $T_0 = 300$ K; the hole mobility $\mu = 1$ cm²/V·sec; the heat exchange coefficient $\lambda = 10^4$ J/m²·sec·K; the film thickness $L = 50$ nm.

Fig. 4 shows the dependence of the subthreshold branch of the CVC calculated for a 1 μ m thick CGS film on the ambient temperature [15], compared with the experimental data for a 1 μ m thick Si₁₂Te₄₈As₃₀Ge₁₀ (STAG) film [17]. The corresponding value of the ambient temperature T_0 is shown near the curves.

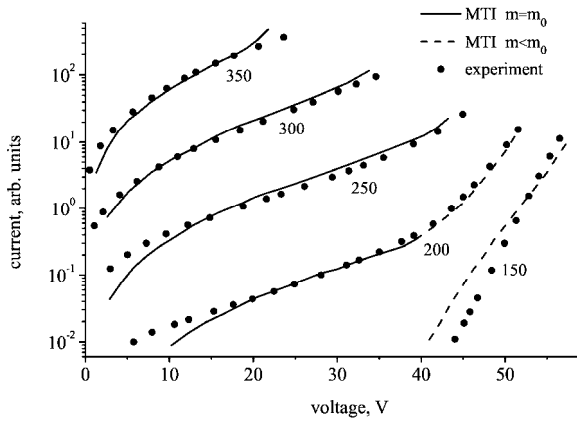


Fig. 4. Dependence of the subthreshold branch of the CVC on the ambient temperature in kelvin [15].

Fig. 5 shows the dependence of the calculated threshold voltage on the chalcogenide film thickness compared to the experimental data [18].

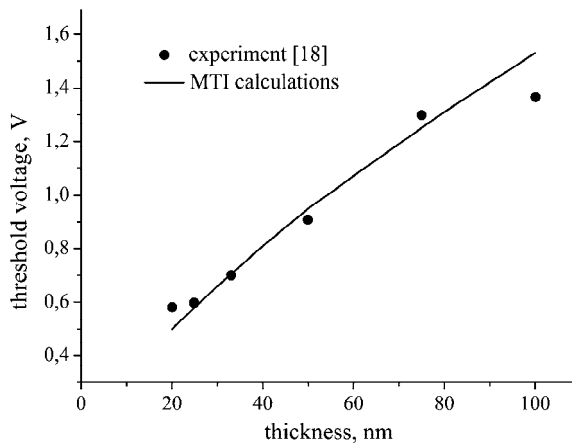


Fig. 5. Dependence of the threshold voltage on the film thickness.

Fig. 6 shows the calculated threshold current density versus film thickness.

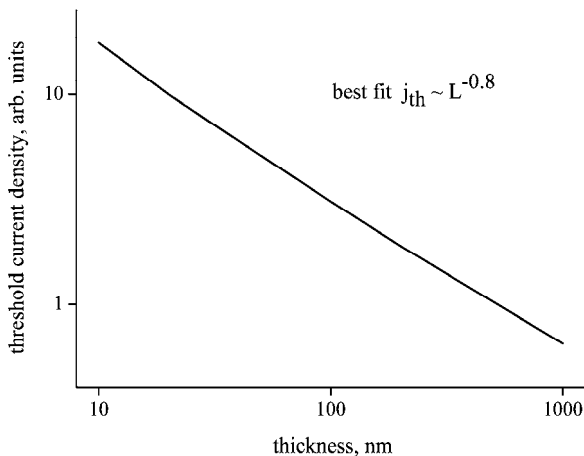


Fig. 6. Threshold current density versus film thickness

4. Discussion

One of the amorphous chalcogenides characteristic properties is the CVC nonlinearity, which could be approximated by a linear dependence of the current logarithm on the applied voltage in a wide range of voltages (Fig. 4). Experimental observations of such dependence in various CGS compounds gave rise to a phenomenological electronic-thermal model of switching [5,17]. However, none of the existing nonlinearity models could give such dependence. In the MTI model, the quasi-linear dependence is a result of the joint influence of the Poole-Frenkel effect (which yields a square root dependence) [11] and heating.

In Fig. 4 the dependence of the calculated CVC on the ambient temperature is compared with the experimental data [17]. In the low-voltage region, the results of the computation fit the experimental data well, however in the high-voltage region, the slope of the experimental curves increases rapidly. In the MTI model, a sharp increase of the CVC slope could be caused by a sharp decrease of the effective hole mass. In this case, the multiphonon tunnel ionization turns into direct tunnel ionization from the ground energy level. While computing, the effective hole mass in the low-voltage region was assumed to be equal to m_0 , where m_0 is the free-electron mass, while the required slope of the 150-K curve was achieved when the effective hole mass was assumed to be equal to $0.01 m_0$. The authors do not know the original cause of such sharp decrease of the hole effective mass.

As shown in Fig. 5, the dependence of the threshold voltage on the film thickness fit the experimental data well. The dependence of the threshold voltage on the ambient temperature also is of interest. According to [19] the threshold voltage in GST is weakly dependent on the ambient temperature, however the MTI model predicts a much stronger dependence, close to the experimental dependence in STAG [20].

The dependence of the threshold current density on the film thickness has been investigated by Kostylev in various GCS compounds [21]. In a wide range of thicknesses, he revealed a superlinear dependence $j_{th} \propto L^{-1.4}$; therefore, the dependence of the threshold current density on the film thickness may be a useful assessment criterion for nonlinearity models. Fig. 6 shows the threshold current density versus thickness calculated in the MTI model. Although the MTI model gives a weaker dependence $j_{th} \propto L^{-0.8}$, predictions of this model are the closest to the experiment [21]; for example most electronic models predict that the threshold current is independent on the film thickness [21].

The role of heating has always been a subject of hot discussions. Though an isothermal MTI model can cause strong nonlinearity of the CVC, it does not display negative differential resistance [14]. However taking into account the Joule heating allows to obtain an S-shaped nonlinearity of the CVC [15]. A comparison between the two cases is shown on the fig. 7. Here the ambient

temperature $T_0 = 300\text{ K}$, the temperature of characteristic points is shown. One can see that within the framework of the MTI model heating in the high-resistive state does not exceed 40 degrees at the threshold point. Nevertheless, we cannot neglect heating, since it is important for the feedback.

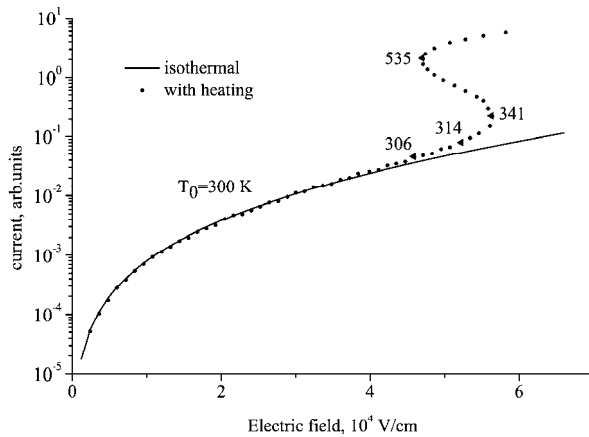


Fig. 7. Calculated CVC compared with an isothermal one [15]. The corresponding temperature in Kelvin is shown.

A rough estimate of the heat emission in a PCM cell gives that heating at the threshold point is about several tens of degrees centigrade. In addition, a characteristic thermal relaxation time of a 50-nm thick GST film is about several nanoseconds, which is substantially less than the set pulse width. The latter says much for electronic-thermal models of switching.

Undoubtedly, switching does not require heating up to the softening temperature. Nevertheless, heating up to the softening temperature and higher is required to crystallize the film. Therefore heating is extremely important for the PCM operation.

Finally, we want to speculate about the role of the intrinsic S-shapeness of the CGS film. Usually chalcogenide materials display a pronounced S-shaped CVC; however, the resistance of the heater is selected to make the S-shaped CVC of the memory cell weakly pronounced. Heater significantly increases the resistance of the memory cell in a set state and thus decreases the reset voltage. However, high resistance of the heater makes a considerable part of the reset pulse power expend within the heater. Since a large value of a reset current is known to be a big challenge of the PCM technology [1], we believe that utilizing materials with a less pronounced S-shaped CVC will make it possible to decrease the heater resistance and thus increase the efficiency of the heat emission and decrease the reset current.

In the MTI model, the S-shapeness vanishes at high temperatures equal to $\frac{\varepsilon_1 + \varepsilon_2}{8K}$, which is about 1000 K for GeSbTe materials; unfortunately, this is well over the melting temperature. However, the S-shapeness of the CVC decreases while the mobility μ , and the film thickness L decrease, and the heat exchange coefficient λ

increase. A detailed investigation of this question will be a subject of a further research. We believe it will help to find out materials, which can decrease the reset current in the PCM devices.

5. Conclusions

The multiphonon tunnel ionization model has been applied to negative-U centers in chalcogenide glassy semiconductors. Developed MTI electronic-thermal model of switching can account for various experimental data on CGSs behavior in strong electric field, namely the subthreshold branch of the CVC; the dependence of the threshold voltage on the film thickness and temperature.

Investigation of the role of heating has pointed out that the threshold temperature of the high-resistive state is about several tens of degrees, while the typical temperature of the low-resistive state is close to the softening temperature of CGSs, required for the crystallization and memory.

Potential applications of the MTI model are calculation of the PCM cell characteristics and selection of the most suitable CGSs compounds.

Acknowledgement

The research was supported by the Russian Foundation for Basic Research (project no. 10-03-00456a)

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