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The changing of initial state in a strong electric field and memory effect in chalcogenides

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Our preliminary investigations have shown that information recording based on glass-crystal phase transition, which is induced by pulse of electric field in the chalcogenide glassy semiconductors, has the following interesting peculiarity. Memory state arises not from semiconductors but from metal type state. This state is due to switching effect in thin films, which have strong non-linear current-voltage characteristics and inside which the phase transition from semiconductor to metal type conductivity takes place. The abovementioned effect very strong influences on a current filament characteristics, i.e. on the area where memory state arises. In the present paper it is shown that thermo-stimulated tunnel ionization of negative-U centers in a strong electric field may be the mechanism, which is responsible for appearance of metal like state.

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1. Introduction

A new class of materials – chalcogenide glassy semiconductors – was discovered in the mid-1950s [1-2]. In chalcogenide glassy semiconductors (CGS) a wide range of unique phenomena has been detected. These phenomena have been described in details by authors of the several monographs [3-7]. Among these phenomena, a special place is occupied by the phenomenon of the electric instability, discovered in the course of a study of thin films of CGS in a strong electric field [8,9].

The phenomenon consists in an abrupt and rapid transition of a small volume of the CGS from semiconducting high-resistance state (HS) to the metal-like low- resistance state (LS). The transition takes place locally at site of enhanced current density – current filament. Depending on the composition of CGS, as a result of development of the electric instability different final states can result. If the reverse transition to the HS takes place after removal of the applied voltage the phenomenon is frequently called the reversible switching effect (SE) and it is generally considered not to be connected with the structural transformations. The opposite case when the LS is remembered and exists without the applied voltage, one calls a memory effect. The later is associated with the appearance at the current filament of a crystallized channel and by a noticeable change in the LS resistance due to crystallization. In this case one speaks of reversible structural phase transitions since having chosen definite voltage pulse parameters it is possible to return the crystalline channel to its original glassy state. In nowadays papers this case is known as electric field induced Phase Change Memory (PCM) or Ovonic Unified Memory (OUM).

It is assumed that the initial stage in the development of SE and electric field induced PCM is fundamentally the same, and differences arise only at later stages. These differences are due mainly to differences in composition. In the PCM devices chalcogenide glassy semiconductors with an enhanced tendency to crystallize are generally used. Despite the large number of studies addressing the nature of the low-resistance, metal-like state (ON state) arising as a result of a SE and the initial stage of electric field induced PCM, its nature is still unclear. There are two points of view. According to the first one the mechanism of the switching effect and ON state nature are pure electronic [10-13]. According to the second point of view the switching effect and ON state have electronic-thermal nature [3, 14-19]. The later approach has taken into account the direct dependence of conductivity on electric field and allows to explain many experimental facts, which have been obtain for example for such compounds as $Si_{12}Te_{48}As_{30}Ge_{10}$ (STAG) and As_2Se_3-$4As_2Te_3$ [3, 14-19]. In this paper I would like to demonstrate that electronic-thermal mechanism can explain qualitatively the data apply to famous $Ge_2Sb_2Te_5$ compound.

The paper is organized as following. After a detail analysis of data obtained for STAG we have used these results and calculate in the frame of electronic-thermal model the current-voltage characteristic which is similar to that one for $Ge_2Sb_2Te_5$ compound (GST).

2. Non-linear current-voltage characteristics

It is very well known that in a weak electric field a Fermi level position in the CGS is governed by intrinsic defects with negative effective correlation energy (negative-U centers). Then one can consider the non-linear current-voltage characteristic in the CGS, which is due to specific behavior of the negative-U centers in a strong electric field. According to the book [20] after rather small electric field region of the Poole-Frenkel effect there is extensive region of electric field where the non-linear current-voltage characteristic is due to thermo-stimulated tunnel electron ionization from deep levels. In our case one need to consider the thermo-stimulated tunnel electron ionization from D^- and D^0, i.e. the first and second ionization of the negative-U centers. Fig. 1 shows the band diagram of the CGS with the first and second ionization energies of electron from negative-U center. The thermo-stimulated tunnel electron ionization for process D$^-$ → D^0 with energy ε_1 and for process D^0 → D$^+$ with energy ε_2 in the electric field are different. This difference arises due to different potentials, which act on removing electron. For the first ionization D$^-$ → D^0 electron is in the very narrow non-coulombic potential. Fig. 2 shows this potential together with the electric field.

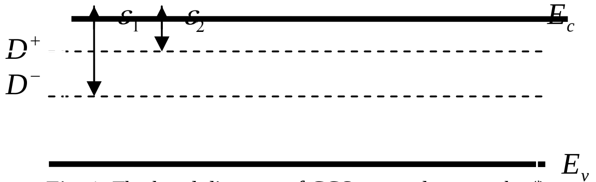

Fig. 1. The band diagram of CGS. ε_1 and ε_2 are the first and second ionization energies of electron from negative-U center.

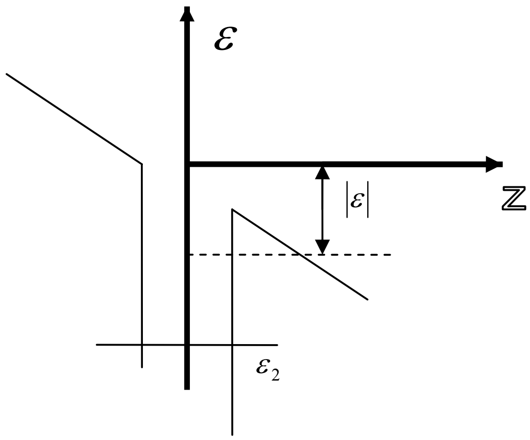

Fig. 2. The potential which acts on electron removing from negative U center in the D$^-$ state. ε - is the escaped electron energy [20].

For the second ionization D^0 → D$^+$ electron is in the coulombic potential (Fig. 3).

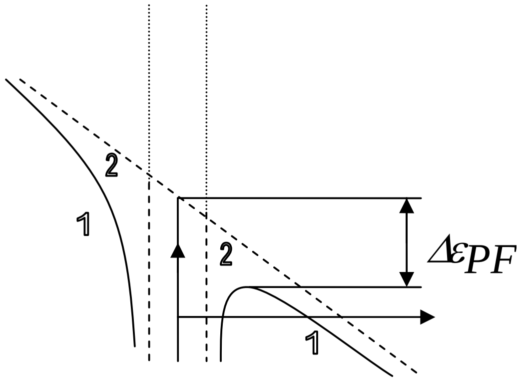

Fig. 3. Coulombic potential (1) for electron in the electic field (2). The case D^0 → D$^+$ ionization [20]. $\Delta\varepsilon_{PF}$ is the Pool- Frenkel energy barrier decreasing.

According to [20] ionization probability for thermo-stimulated tunnel electron ionization process D$^-$ → D^0 is equal to:

$$e(F) = e\exp(\frac{(qF)^2\tau_2^3}{3m\hbar}). \tag{1}$$

where e – zero field probability, m – electron mass, F – electric field intensity, q – electron charge and for characteristic time τ_2 one has expression

$$\frac{2\tau_2}{\hbar} = \frac{1}{kT} + \frac{2\tau_1}{\hbar}. \tag{2}$$

where τ_1 approximately equals to inverse phonon frequency ω^{-1}. In contrast to this case, ionization probability for the second ionization D^0 → D$^+$ is described by the following expression [20]:

$$e(F) = e\exp(\frac{(qF)^2\tau_2^3}{3\hbar m})\exp(\frac{2\sqrt{2m\varepsilon_2}}{qF\tau_2}\ln\frac{4(qF)^2\tau_2^3}{\hbar m}). \tag{3}$$

To use these expression for current-voltage characteristic calculation one can write equations for two abovementioned reactions

$$\frac{D^0 n}{D^-} = N_c\exp(-\frac{\varepsilon_1}{kT} + \frac{(qF)^2\tau_2^3}{3m\hbar}),$$

$$D^- - q \leftrightarrow D^0 \tag{4}$$

$$\frac{D^+ n}{D^0} = N_c\exp(-\frac{\varepsilon_2}{kT} + \frac{(qF)^2\tau_2^3}{3\hbar m} + \frac{2\sqrt{2m\varepsilon_2}}{qF\tau_2}\ln(\frac{4(qF)^2\tau_2^3}{\hbar m}));$$

$$D^0 - q \leftrightarrow D^+; \tag{5}$$

where D^+, D^0 and D^- are the concentrations of corresponding states of negative U centers. One has to add the neutrality equation

$$D^+ = D^- \tag{6}$$

and condition of constant concentration D of negative U centers

$$D = D^+ + D^- + D^0 \tag{7}$$

Solving the set equations (4)-(7) one obtains electron concentration

$$n = N_c\exp(-(\frac{\varepsilon_1+\varepsilon_2}{2kT}) + \frac{(qF)^2\tau_2^3}{3\hbar m} + \frac{\sqrt{2m\varepsilon_2}}{qF\tau_2}\ln(\frac{4(qF)^2\tau_2^3}{\hbar m})). \tag{8}$$

and conductivity:

$$\sigma = qn\mu, \tag{9}$$

Fig. 4 shows the calculated current-voltage characteristics together with experimental values for STAG compound from [21]. The following set of parameters has been used: $\varepsilon_2 = 0{,}4$ eV, $\varepsilon_1 + \varepsilon_2 = 1{,}2$ eV, the sample thickness $L = 1.2 \cdot 10^{-6}$ м, $m = 1{,}7 m_0$, $\tau_1 = 0.3 * 10^{-13}$ s

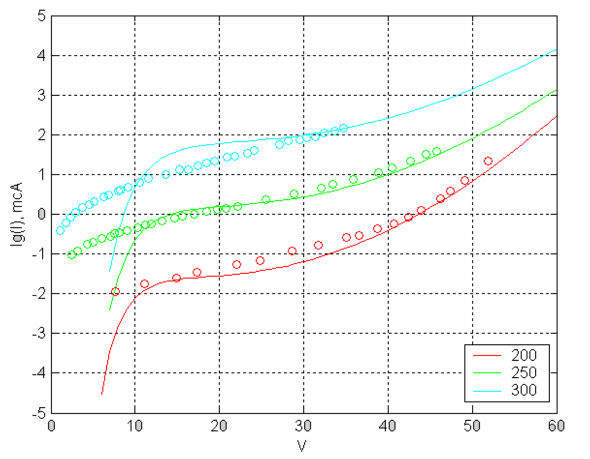

Fig. 4. Current-voltage characteristics for STAG. Dots – experimental data from [21]. Lines – theoretical values of this paper.

One can see that theoretical curves have two prominent features, which coincide in principle with the experimental data. Its have quasi-linear regions after Ohm law which followed by over-linear region (approximately V^2 law). This result allows us to assume that thermo-stimulated tunnel electron ionization of negative-U centers may be responsible for non-linear current-voltage characteristics (CVC) in CGS thin films.

3. Switching and memory effects in STAG and GST compound

Fig. 5 shows the schematic CVC for micron thickness film of STAG.

As we have said in the introduction, ON state consists of the current filament. According to the electronic-thermal mechanism of switching [3, 16, 17] the minimum radius of filament r_f is equal to $0.25(\kappa L/\lambda)^{1/2}$. For typical values heat transfer coefficient $\kappa \approx 0.4$ W/m K and coefficient of an external cooling $\lambda \approx 10^4$ W/m^2 K [3, 16, 17] one has $r_f \approx (L\ 10^{-6})^{1/2}$ or $r_f \approx 1$ μm for $L \approx 1$ μm and $r_f \approx 300$ nm for $L \approx 100$ nm. The cross section of OUM devices with $L \approx 100$ nm is less than this radius values $r_f \approx 300$ nm. To my opinion it is the main reason for differences between results which are depicted on Fig. 5 and current-voltage characteristics of nowadays OUM devices with nanometers dimensions which have not very fast switching (t_{sw}) accompanied by filament formation. If we have not the filament formation process, one can calculate the current-voltage characteristics without filament formation using the following set of equations:

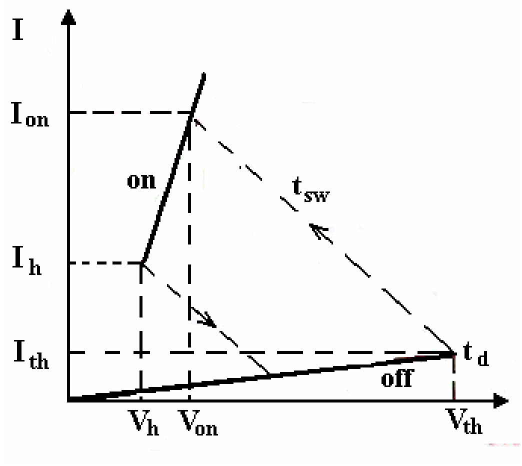

Fig. 5. Schematic picture of the switching effect for STAG compound. The switching time t_{sw} is less then 10^{-10}s [9].

$$\begin{cases} Q_1 = Q_2 \\ \dfrac{dQ_1}{dT} = \dfrac{dQ_2}{dT} \end{cases} \tag{10}$$

where $Q_1 = SL\sigma F^2$, $Q_2 = \lambda S(T - T_0)$, S – device square, L – film thickness, T_0 – device and room temperatures.

For the conductivity we have use the expression for electron concentration (9), then one has the following expression:

$\sigma = \sigma_0$

$$\exp\left(-\frac{\Delta E}{KT} + \frac{10^4 \cdot U^2}{T^3} + \frac{1 \cdot T}{U} \cdot \ln\left(\frac{12 \cdot 10^4 \cdot U^2}{T^3}\right)\right) \tag{11}$$

S- shaped CVC calculated according to (10), (11) is shown on Fig. 6.

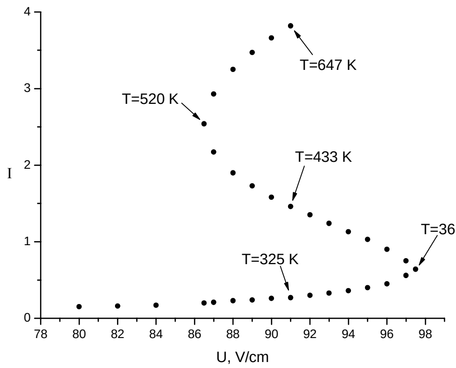

Fig. 6. S- shaped CVC calculated according to equations (10), (11).

This S- shaped CVC qualitatively is similar to that one which has been measured for $Ge_2Sb_2Te_5$ compound [13]. For quantitative analysis and comparison with experimental data we need several unknown parameters.

It is very well known that for pure thermal breakdown the extreme points of S- shaped CVC correspond to temperature $T_1 = \Delta E/k$ and $T_2 = T_0 + T_0^2/k\Delta E$. In our case with $\Delta E \sim 0.5$ eV and T_0=300 K value of T_1 is very large (~ 5000 K). T_2 is equal to 315 K. Taking into account the thermo-stimulated tunnel electron ionization of negative-U centers T_1 and T_2 become equal to 520 K and 363 K correspondingly (see Fig. 6). Then the first important result of our version of electronic-thermal mechanism is the strong decreasing of T_1 up to very reasonable value. The second result consist in the weak dependence of conductivity on a temperature. Estimations show that for all upper part of CVC, i.e for T_1> 520 K exponent in the conductivity expression (11) rather small. Then one may conclude that for temperature T > 520 the ON state is the metal type state. And structural phase transition from amorphous to crystalline phases which occurs at temperatures ~ 500 K [22-24] in OUM devices is the transition not from amorphous semiconductor but from metal type state.

4. Conclusion

It has been shown that taking into account the thermo-stimulated tunnel electron ionization of negative-U centers allows us in the frame of electronic-thermal theory to describe reasonable values of ON state temperature and crystallization not from semiconductor but from metal type state.

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