Journal of Ovonic Research Vol. 1, No. 2, April 2005, p. 25 – 30

MODEL OF CONDUCTIVITY TRANSITION IN AMORPHOUS CHALCOGENIDES INDUCED BY AUGER RECOMBINATION

S. D. Savransky

The TRIZ Experts, 6015 Pepper Tree Court, Newark, CA 94560, USA

It is shown that Auger recombination destroys U^- centers in amorphous chalcogenides (a-Ch). Released energy leads to overheating of nano-clusters in a-Ch and following dissipation of excess temperature to intercluster regions. The electron induced thermal transformation between high (OFF) and low (ON) resistivity states in amorphous chalcogenides (e.g., $Ge_2Sb_2Te_5$ films) is discussed.

1. Introduction

Development and implementation of non-volatile phase change memory technology [1,2] require deep understanding of processes in electron and atom subsystems of amorphous chalcogenides (a-Ch) first of all switching and memory phenomena [2-10]. These phenomena became one of major topics of Ovonic research after widely accepted announcement of these phenomena in 1968 [3]. The physics of a-Ch has gained new knowledge [10-20] after the main initial achievements for switching and memory processes in first generation of these materials were obtained [3-10]. Some of these accomplishments applicable to the current second generation of non-volatile memory utilizing $Ge_2Sb_2Te_5$ (GST) active films [1].

The microscopic description of OFF-ON transition in active a-Ch films is reported on the qualitative basis in this paper. It is based on recently recognized features of electron and atom subsystems of a-Ch, such as U^- centers [10-17] and nano-clusters [18-21].

The following two aspects of a-Ch behavior are principal for understanding and description of switching and memory phenomena:

a) Holes (h) are dominant charge carriers in high resistivity (OFF) state while electrons (e) play more prominent role in dynamic low resistivity (ON) state [4,9,10]. Both charge carriers spend most of their lifetime in localized states and their mobility in the extended states is quite low. The charge carriers free path L is only about $10^{-9\pm0.5}$ m and their lifetime in the extended states is very short. Hence, a-Ch is rather relaxation than lifetime semiconductors in OFF state [22] because the dielectric relaxation time can be longer than diffusion-length lifetime or recombination time.

b) The photo-crystallization of GST (used in DVD-RAM [23]) as well as non-electrode electrical switching in high vacuum [24] indicate insignificant role of contact phenomena in generation and recombination of the charge carriers for physics of ON-OFF transition in GST films[1]. In this work electrodes are considered as a passive source of electrons and holes.

These aspects, high stability and relatively small threshold field in GST allow to disregard some of previous OFF-ON transition ideas and keep alive only group of models dealing with electronically driven non-equilibrium transformations in the atomic subsystem accompanying with energy dissipation. These selected ideas should take into account that both electronic and thermal processes are important for memory cells on GST base. There is certain consensus about the second part of this conclusion, but some researches ignore importance of electronic processes. We would like to stress that the direct experiments [1c] show that some charge should be injected in active volume of GST in order to initiate ON-OFF transition, moreover this charge (or impulse width at the same current) is independent on temperature wide range. For the reader convenience the Czubatyj-

[1] Of course, the electrodes, adhesives, heaters and other elements of memory chip that interact with an active a-Ch cell as well as technological processes strongly affect parameters, reliability, stability, and life-cycle of the memory cells.

Kostylev data for GST [1c] are presented in the Fig. 1. The two-ways behaviour (a capacitor under an electrical charge in OFF state and a fast switch to dynamic ON state) of a-Ch is clearly represented in this experiment. The dynamic ON state can exist (without crystallization) only until the holding voltage is applied to GST. Experiments show very weak dependence of this holding voltage on inter-electrode distance in contrast with threshold voltage that increases with the inter-electrode distance [1a, 1b]. The mentioned facts allow us to conclude that the electronic processes are very important during the GST transition from high to low resistivity state.

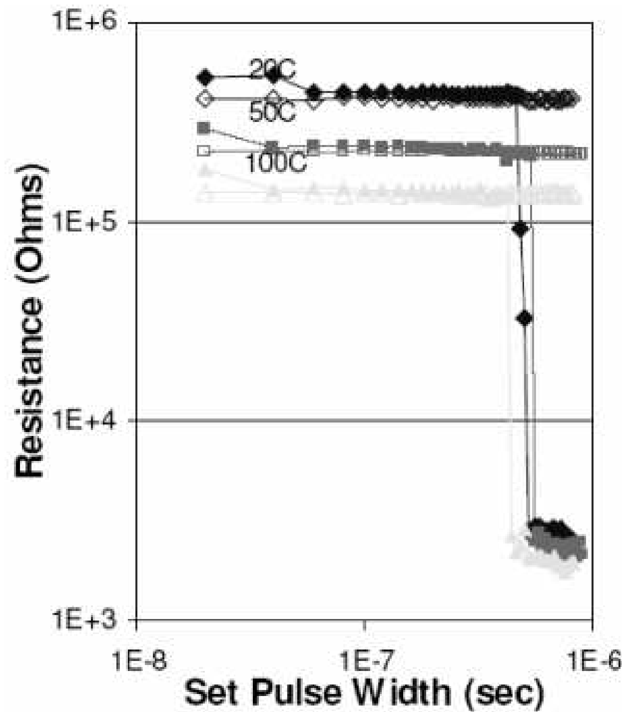

Fig. 1. Temperature independence of the set pulse (required for OFF-ON transition in GST) after W. Czubatyj and S. A. Kostylev "Properties of small pore Ovonic memory devices" [1c].

Additionally it is worth to mention that the behavior and characteristics of GST films used in modern technology [1,2] are to some extent different from parameters of the first generation of a-Ch initially used for Ovshinsky's memory devices [3]. Therefore, some re-examination of our understanding of switching and memory phenomena (especially ON-OFF transition) in GST is needed.

In the next section we summarize the concept of U^- centers proposed by P.W. Anderson for explanation contradictory properties of a-Ch [11] and outline importance of Auger recombination at U^- centers for this materials. Then we show that Auger recombination on U^- centers leads to selective overheating of local nano-clusters in GST and following transition from high to dynamic low resistivity state. In conclusion we outline the proposed scenario of switching from OFF to ON state in a-Ch.

2. U^- centers and Auger processes

It is well known that U^- centers [11-17] are main peculiarity of electronic sub-system in a-Ch that play important role in different phenomena including switching [2,5,7]. The main idea of U^- centers[2] is a possibility for a pair of similar charge carriers (electrons – e or holes – h) to overcome the Coulomb repulsion Uc (~ 0.5 eV) due to strong polaron interactions Ep (~ 1 eV) with the network of atoms in vitreous state [11,14-16]. Any change of a U^- center charge is accompanied by

[2] The existence of the U^- centers in amorphous $Ge_2Sb_2Te_5$ films was confirmed recently by J. K. Olson, P. C. Taylor and their co-workers in University of Utah in the direst ESR experiments (to be published).

a local rearrange of atoms positions at and around this U^- center due to the polaron interaction [11-17].

There are around $N_U=10^{18\pm1}$ cm^{-3} of the U^- centers with typical energy Uc-Ep in a-Ch. They are distributed in the mobility gap and pins the Fermi level F close to the middle of this gap [11-17]. Hence the average distance between U^- centers is about 50 nm and it is one or two orders of magnitude longer than L [3, 10, 19a]. Therefore, the processes at different U^- centers can be considered as mutually independent for the sake of simplicity. For the same purpose we will ignore hybridization between localized and extended states that can be quite important for U^- centers in GST.

It is well known that the Auger recombination (AR) is a three-particle process where one charge carrier recombines with a carrier having opposite charge and spin. The energy released in recombination is transferred by means of local interaction to another charge carrier which goes into a high excited state [25]. In the adiabatic approach AR and impact ionization (that is often considered as a foundation of threshold switching [5,2]) are related as inverse microscopic processes in conduction (valence) band of a crystal semiconductor through the principle of detailed balance in the same manner as photon emission and absorption[3]. On other hand, numerical femtosecond studies of crystal semiconductors [26] show that the timescale for AR is about 10^{-8} – 10^{-12} sec. while the impact ionization timescale is around 10^{-11} – 10^{-14} sec. AR probability $\sim pn^2$ is usually considered small to compare with other recombination processes in crystal semiconductors because of the second quadratic term.

The double positive ($-U_h$) /hole/ and double negative /electron/ ($-U_e$) centers are very favorable for AR because they already have two localized charge carriers with opposite spins, i.e., U^- centers provide n^2 term because $N_U=n^2$ [26]. Moreover, the probability of AR is relatively high[4] because the momentum is not a good quantum number in a-Ch [10, 27]. AR in contrast to the impact ionization doesn't require a long carrier free path in conduction (valence) band to collect electric field energy. Because the charge carriers free path L is small in a-Ch the impact ionization (even in lucky drift regime [28]) cannot lead alone to OFF-ON transition in observed threshold fields (compare Ref. [4,5,9,10]). Therefore, AR seems more reasonable driven force for memory and threshold switching in a-Ch than the impact ionization [2]. On the first glance it seems that a recombination cannot lead to lower resistivity because it decreases the number of free charge carriers. But it is not the case for AR through U^- centers as shown below, because e-h pair annihilation is accompanied by a third carrier excitation.

The four types of AR occur at the electron U^- centers in a-Ch: the extended AR is very similar to the same process in the crystalline materials ($p + -U_e \rightarrow e$) [24]; while three others (localized : $[p] +-U_e \rightarrow e$; trapped: $p + -U_e \rightarrow [e]$; hopping: $[p] + -U_e \rightarrow [e]$) ARs are quite unique for a-Ch [26]. For instance the hopping AR is a process where a hole from a localized state in the tail of valence band recombines with one electron of a $-U_e$ center and transfers its energy via the electron-electron and electron-network interactions to the other electron on same -Ue center, which jump into the conduction band tail. Evidently similar ARs[5] with typical cross-sections about $10^{-13.5\pm1.5}$ cm^2 occur also through the $-U_h$ centers. The U^- centers vary their state from double charged in the initial state to neutral (empty) in the final state for extended and localized ARs or metastable single appositively charged (half-occupied) in the final state for trapped and hopping ARs. Therefore the number of traps in mobility gap of a-Ch decreases due to first two ARs accompanied by

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[3] In the non-radiative (radiative) case, the e - h generation process is the impact ionization (optical or X-ray absorption), in which the initial object is the highly energetic impacting electron (photon); correspondingly their inverse recombination process is AR (photon emission), in which the final product is the Auger electron or hole (emitted photon). Hence, AR can be considered as complimentary mirror process to impact ionization [25] .

[4] AR probability in the amorphous semiconductors is higher at the $\exp(Tg/T)^2$ times than in crystalline semiconductors under the equal conditions at any temperature T, where Tg is the disordered parameter (probably coincide with the glass transition temperature for GST).

[5] It is worth to note that ARs are probably important for optical phase change memory processes in DVD-RAM [27b].

annihilation of a U^- center and also reduces due to last two ARs accompanied by thermalization of carrier from the metastable state after the destructive U^- center transformation from deep trap into shallow localized state. In all four ARs a commutative charge carrier is created that can explain change of dominant carriers type often observed at the OFF-ON transition [4,9].

The commutative charge carrier (typically electron in GST) collects impulses from their predecessors (typically holes) and energy obtained from the polaron term of the annihilated U^- center. Assume that an $-U_e$ center had energy close to the Fermi level F and a free or localized hole was close to valence band mobility edge Ev before AR in A-CH [12-15,2]. Then the excess energy of a "commutated" electron can be estimated as

$$(Ep-2F-Ev) \sim 0.1 \div 0.5 \text{ eV}$$

because 2F is very close to the energy of mobility gap. Note that the excess energy is almost the same as the conductivity activation energy (F-Ev) ~ 0.33 eV in low electrical fields in OFF state of GST [1,2,23].

Due to the energy conservation the electron and atomic subsystems around the former U^- center are not in thermal equilibrium with the rest of A-CH immediately after AR[6]. This excess energy of the free "commutated" charge carrier can be released for carriers multiplication. The charge carrier in the mobility gap created due to the hopping and localized cannot disject the excess energy to other charge carriers, but can create rearrangement of atoms in the place of charge carrier localization. The excess energy of the localized "commutated" charge carrier can be released as a heat and used for re-direction of chemical bonds or creation new chemical bonds during GST crystallization that occurs in the course of the ON-OFF transition.

3. Heating in amorphous chalcogenides

Direct combined nanobeam diffraction and high resolution electron microscopy experiments [21] show that more and less disordered nano-regions[7] exist in atomic structure of amorphous GST films, that can be named as nano-crystallites and nano-clusters. Unfortunately the typical size of the more disordered nano-clusters in the glass structure is not known. Experiments [21,20] indicate that this size is comparable to the size of medium-range order correlations (nano-crystallites) in amorphous GST. We assume that nano-cluster size is about 2nm in a-Ch and that a U^- center forms a nano-cluster' nucleus in a-Ch films[8].

A short-living "shake-up effect" of atoms of the former U^- center can occur just after annihilation of electron-hole pair during AR (probably within $10^{-13.5\pm0.5}$ sec) [25,27]. On other hand, the structural relaxation due to minimization of energy [11,14,15] occurs at time scale about $10^{11\pm1}$ sec. Between these two events the few stages of energy transfer occurs in a-Ch [29] that we shall consider in this section. Practically the whole process can be labeled as heat production due to the transfer of the excess polaron energy from the atom(s) at the former U^- center to the surrounding atoms in the form of vibration energy. It should be stressed that this heating is very effective due to localization of vibrations within nano-clusters in a-Ch. Indeed the destruction of a U^- center is

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[6] On the first glance the situation reminiscent hot charge carriers and thermal spikes well known for various crystal semiconductors but we have to remember that any glass (as well as amorphous $Ge_2Sb_2Te_5$ films) exists itself in a thermodynamically non-equilibrium state.

[7] Direct experiments show that some kind(s) of less disordered regions known as 1-3 nm medium-range order nano-crystallites or correlations exist in various amorphous and even liquid (supercooled) chalcogenides including GST [16a, 19, 21]. The existence of more ordered regions means the more disordered regions should also exist.

[8] Another possibility that a U^- center exists at a nano-cluster / nano-crystallite boundary. The following results are not sensitive to the exact atomic structure at and around a U^- center, hence, this situation is not considered here. The "boundary" case can be quite important respect to the dynamics of polycrystals grow versus ration of crystal embrio creation in GST.

accompanied by the generation of high-frequency vibrations within the nano-cluster during the first stage. Due to the Ioffe-Regel localization criteria (see e.g., [10, 19a, 29]) these initial high-frequency vibrations exist only inside a nano-cluster. These vibrations have non-equilibrium spectrum and their wave numbers are limited by characteristic size of the nano-cluster. During the life-time of the localized vibrations (that exceed characteristic phonon frequency in 1-2 orders) within the nano-cluster its temperature T increases strongly and can be much higher than that obtained on a basis of elementary evaluation with a heat capacity. The increase of temperature can be estimated as

$$(Ep-2F-Ev)/bN^{1/3} \geq \Delta T \geq (Ep-2F-Ev)/aN \sim 30 \div 200K,$$

where $N \sim 10^{2.5\pm0.5}$ is number of atoms in the nano-cluster, a = 3k is heat capacity per atom for Planck distribution of phonons at T above the Debye temperature and b ~ 10 for non-Planck distribution of localized vibrations in overheated nano-clusters.

Then, after some delay time (about ~ 10^{-12} sec.), there is the swapping of energy into long-wave phonons that transfer energy from the nano-cluster to the rest of a-Ch film. The transfer superfluous energy, connected to overheated nano-cluster, leads to increase of temperature (less than ΔT) of the rest of film due to the standard phonon-phonon interactions. As the result the resistivity of a-Ch decreases at moderate electrical fields and more charge carriers are generated. We emphasize that Auger recombination and following heating occurs selectively in more disordered nano-clusters in the a-Ch structure, i.e., exactly there structural transformations are needed for amorphous-crystal conversions in the non-volatile memory chips. Probably the space between nano-clusters with simultaneously destroyed U^- centers is squeezed in relatively high electrical fields due to the thermal expansion of these overheated nano-clusters. This pressure leads to decrease of activation energy for electrical conductivity in case of high charge carriers concentration in OFF state of a-CH films. Therefore, such positive feedback mechanisms control effective Joule heating of a-Ch due to activation nature of electrical conductivity that increase with pressure and, as the result, they lead to a thermal breakdown in high electrical fields about $10^{5.5\pm0.5}$ V/cm.

Even more important for GST is process of local rearrangement of atoms inside the overheated nano-cluster that transforms it (whole or part) into more ordered nano-crystallite if $T + \Delta T < Tg$. Two factors are favorable creation of new chemical bonds during GST crystallization: strong mean square displacements of atoms from their positions due to high T and existence of excess charge carrier(s) probably related to the chalcogen's lone-pair electrons inside the nano-cluster. Such weak chemical bonds in crystal GST film were recently discovered [30]. From another hand, a weak possibility of intrinsic nanoscale phase separation [31] in amorphous GST should not affect the described scenario of selective heating at least on qualitative level[9]. Finishing this section we would like to note again that several steps occur behind the simple phenomenology of ON-OFF transition as crystallization of an amorphous GST film. These steps described on qualitative level here should be studied deeply for further progress in memory.

4. Conclusion

We have analyzed of the following scenario:
Auger recombinations at U^- centers → change of atoms positions due to shake-up effect → release of polaron energy → generation of localized high frequency vibrations → local over-heating and expansion of nano-clusters → delayed heat transfer to compressed intercluster regions → decrease of the activation energy for conductivity → increase of carriers concentrations and mobility → the OFF-ON transition

[9] Technological processes such as sputtering, etch, etc. can lead to the contaminative doping of $Ge_2Sb_2Te_5$ by Oxygen, Chlorine, Argon, Nitrogen, etc. and, hence, to shift in nanoscale phase separation [31a] occurrence with moving away from ($2GeTe-Sb_2Te_3$) mixture.

as the major stages of the electron induced thermal transformation between high (OFF) and dynamic low (ON) resistivity states in a-Ch. This scenario allows us to explain various observed features of the OFF-ON transition in GST films used for active cells of modern non-volatile memory chips[10]. This scenario refines and unifies many initial ill-compatible ideas proposed for explanation OFF to ON transition and replaces them with one rigorous approach. The scenario not only covers the early clarified features of the switching and memory phenomena but also gives explanations to the reversal of dominate conductivity carriers (from holes to electrons), sounds created during the switching from the OFF state to the ON state [6], mechanical stresses in active films [8], abnormal temperature rates for crystal embrios nucleation and other attributes of the transition in a-Ch [2-5]. The description of transitions between OFF and ON states of a-Ch was only presented here on qualitative base. Nevertheless it is possible to conclude that probably the second generation of a-Ch films (namely GST) has quite favorable set of parameters for all described steps of the transition. The further optimization of a-Ch films in memory structure to the mentioned steps and to probably different microscopic stages of transit from OFF to ON state as well as stability of both states should lead to better devices.

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