Temperature dependence of Ge$_2$Sb$_2$Te$_5$ conductivity and its change during aging

Y V Vorobyov$^{1, *}$, A O Yakubov$^{1,2}$ and A V Ermachikhin$^{1}$

$^1$ Ryazan State Radio Engineering University, Ryazan 390005, Russia
$^2$ National Research University of Electronic Technology, Zelenograd 124498, Russia

* vorobjov.y.v@rsreu.ru

Abstract. Results of studies of conductivity activation energy and its evolution during the aging process are presented for the common phase change material Ge$_2$Sb$_2$Te$_5$. The evolution of temperature dependence of conductivity during quasi-isothermal annealing are interpreted in the framework of simple Arrhenius model as the change of two corresponding parameters: activation energy and pre-exponential factor. It is shown, that the change in resistivity of the Ge$_2$Sb$_2$Te$_5$ during aging is attributed to the simultaneous change of both parameters of the Arrhenius equation, that is, activation energy and pre-exponential factor. Temperature dependencies of those parameters are shown as well, and the Meyer-Neldel rule for conductivity of Ge$_2$Sb$_2$Te$_5$ is tested on the basis of the obtained data.

1. Introduction

The modern Phase Change Memory (PCM) technology [1] relies on use of the phase state of an active material for information storage. Two states of the material, crystalline and non-crystalline (amorphous), possess strikingly different physical properties. The phase transition between them is a reversible process, which could be induced by either optical or electrical disturbance. Crystalline state, being thermodynamically preferable, virtually does not change over time. Amorphous state could also last many years provided that temperature is not sufficiently high [2].

Partial crystallization of a memory cell volume is achievable, offering opportunities for multilevel storage of information [3]. Because of great difference between electrical conductivities of both phases, resistance of a memory cell is sensitive to the fraction of crystalline phase inside the active volume. The number of different levels of resistance is limited in the first instance by the signal-to-noise ratio necessary for reliable detection. However, in practice this is not the only limitation [4]. Due to the metastable nature of amorphous materials, they are prone to the process of aging. During this process, variety of material properties is changing, and this is of great concern for the developers of PCM devices [5]. Regarding electrical PCM, the main characteristic property of the material is resistivity, and its value of the material in amorphous phase tends to gradually increase over time. This phenomenon is called “resistance drift” in the literature.

Different approaches to the study of resistance drift in phase change materials, in particular Ge$_2$Sb$_2$Te$_5$, are reported. Atomistic simulations [6] show that the predominant process happening during aging of such compound is the transformation from a structure with mainly fourfold Ge and twofold Te into the one with the majority of Ge and Te atoms in the threefold coordination. It is
commonly accepted that this relaxation increases the activation energy for conduction [7]. Measurements show that thermal annealing leads to an increase of the band gap value [8,9], testifying in favour of this theory. On the other side, the modelling approach proposed in [10] suggests that the distance between trapping centres in GST decreases with increasing temperature, lowering the value of activation energy. Therefore, both time- and temperature dependence of activation energy take place in GST.

Our current study focuses on the experimental observation of how the activation energy changes with both time and temperature. Relation between those two processes could provide valuable insights on the resistance drift effect in PCM devices.

2. Methods

2.1. Measurement technique

The qualitative behaviour of the temperature dependence of conductivity in phase change materials obeys the well-known Arrhenius equation:

\[ \sigma = \sigma_0 \exp\left(\frac{-E_A}{k_B T}\right), \]

(1)

where \(k_B\) is the Boltzmann constant, \(E_A\) is the activation energy of conductivity and \(\sigma_0\) is called pre-exponential factor. Below we refer to the latter as the prefactor, for brevity.

During the process of aging, the value of conductivity gradually changes towards lower values. The obvious way to monitor these changes is the measurement of device resistance [11,12], which is inversely proportional to the conductivity value. However, (1) suggests that at a given temperature the value of conductivity is determined by two parameters, \(\sigma_0\) and \(E_A\). To study the process of resistance drift in greater detail than it is provided by resistance measurement, it is necessary to obtain temporal evolution of \(\sigma_0\) and \(E_A\) during this process.

2.1.1. Time dependence.

A forementioned quantities could be obtained from temperature dependence of conductivity. However, to assign them to the process of aging at constant temperature it is necessary to obtain corresponding time dependencies in the same condition, that is, isothermally. One way to achieve this is to separate the aging process, induced by isothermal annealing, from the measurement [13]. Thus, annealing is performed sequentially in order to capture the time evolution of the resistance drift process \textit{ex situ}. Time resolution achievable in such experiment is poor. In [14] a better technique is used allowing better time resolution by combining annealing and measurement stages in the same setup. However, initial stages of aging process still lack time resolution.

In this study we propose to measure both \(\sigma_0\) and \(E_A\) simultaneously and \textit{in situ} by means of complex temperature profile. The sample is held at \textit{quasi}-constant temperature, that is, the temporal temperature profile is the sum of constant base level and small oscillations. The amplitude of the latter was chosen to be ±5°C to (i) avoid its influence on the resistance drift process and (ii) to provide enough data to calculation of desired quantities. The collected data is therefore a set of temperature dependencies of conductivity in the 10°C range around the base temperature. On the basis of (1), it is straightforward to define the activation energy as the slope of linear dependence \(\ln \sigma = f((k_B T)^{-1})\):

\[ \frac{d \ln \sigma}{d(k_B T)^{-1}} = -E_A. \]

(2)
2.1.2. Temperature dependence.

Data regarding the measurement of the temperature dependence of Arrhenius equation parameters for phase change materials is scarce, and it is not common to analyse it with respect to the resistance drift phenomena. The work [15] should be mentioned, where the values of activation energy for Ge$_2$Sb$_2$Te$_5$ are reported from the room temperature up to the melting temperature. The authors use semi-analytical approach to extract the desired quantity from the high-speed measurements of resistance, assuming prefactor $\sigma_0$ temperature-independent.

It should be noted, that the very definition of the temperature dependence of $E_A$ and $\sigma_0$ is not straightforward. In [16] it is pointed out, that if one’s approach implies the use of (1) for the entire temperature range, taking into account temperature dependencies of parameters leads, instead of (2), to

$$\frac{d \ln \sigma}{d (k_B T)^{-1}} = \frac{d \ln \sigma_0}{d (k_B T)^{-1}} - \frac{d E_A}{d (k_B T)^{-1}} = E_A.$$  \hspace{1cm} (3)

Two additional terms in (3), in comparison with (2), are unknowns, and their presence does not allow deriving the $E_A(T)$ dependence from the $\sigma(T)$ dependence alone.

Because of this limitation we do not attempt to describe the full temperature range with (1) together with temperature dependent $\sigma_0$ and $E_A$. Instead, we assume (1) to be valid locally over a small range around the given temperature. This definition, therefore, (i) allows use of simple equation (2) to calculate the value of activation energy using an experimental $\sigma(T)$ dependence and (ii) is in line with our method of time-resolved measurements of $E_A$.

2.2. Preparation of experimental samples

Simple planar structures were used for the study. TiN/W electrodes were formed on the oxidized silicon substrates with the inter-electrode distance 1.3 mm. The Ge$_2$Sb$_2$Te$_5$ layer was deposited on the top of electrodes by means of magnetron sputtering (residual Ar pressure 0.57 Pa, power 25 W). Thickness of films was about 130 nm according to atomic-force microscope profiles.

2.3. Experimental details

Measurement of temporal dependencies was performed using Linkam HFS600E-PB4 heating stage. Resistance measurements were performed sourcing constant voltage of 10 V (Agilent E3647A) to the experimental structures and registering the current along Ge$_2$Sb$_2$Te$_5$ layer using Keithley 6485 picoammeter. Constant Ar flow was provided through the sample camera during measurements to prevent the oxidation of Ge$_2$Sb$_2$Te$_5$ at elevated temperature.

Temperature dependencies of activation energy were measured in the Janis CCS-400/204N close-cycled cryostat. The same constant voltage regime was used to measure the sample resistance; Keithley 6487 picoammeter/voltage source was used. Heating rate during measurements was limited to 2 K/min.

3. Results and Discussion

Figure 1 shows the temporal evolution of $\sigma_0$ and $E_A$ for Ge$_2$Sb$_2$Te$_5$ thin films subjected to the annealing at 100°C. In [13] it is stated that the prefactor remains constant during aging process, suggesting that the change in activation energy alone drives the resistance drift phenomena. Authors [14], despite having identified the change of the prefactor for some compounds, also reported constant value of this quantity for Ge$_2$Sb$_2$Te$_5$. From the data in figure 1, however, it is evident, that change of $\sigma_0$ takes place in Ge$_2$Sb$_2$Te$_5$, though only at the very early stage of the process. That is, the drift of activation energy and prefactor are characterized by different time constants. Fundamentally, change of both $E_A$ and $\sigma_0$ during aging defines the resistance drift phenomenon in phase-change materials.

In figure 2 the temperature dependence of activation energy and prefactor are shown for the sample before and after annealing at 100°C for 5 hours. Both parameters exhibit significant temperature
dependence in the presented temperature range. In [15] the temperature dependence of activation energy is demonstrated for the wide temperature range and an increase of the activation energy value from 330 meV to 360 meV in 300–400 K range is reported. Our numbers are somewhat higher, but the relative difference, that is, the temperature coefficient of activation energy, is close. The difference, however, is that authors of [15] assumed the value of prefactor temperature-independent, while according to our results $\sigma_0$ increases with temperature, together with the increase of activation energy value.

The data for the initial sample show rapid increase of both $E_A$ and $\sigma_0$ for temperatures above 60°C. We believe that the source of this feature is again the aging process. The temperature scanning during the measurement is relatively slow, and as far as at elevated temperature the drift process becomes activated, the observed increase of $E_A$ could be attributed to time dependence of this quantity. It is not clear, if it is possible to decouple time- and temperature dependencies of $E_A$ and $\sigma_0$ when the drift process becomes activated. However, if several undrifted samples are available, the method described

Figure 1. Evolution of the Arrhenius equation parameters for the conductivity of Ge$_2$Sb$_2$Te$_5$ under isothermal annealing.

Figure 2. Temperature dependence of activation energy and pre-exponential factor before and after annealing at 100°C.
in [17] could be used utilizing different heating ramps.

The prefactor values before and after annealing practically coincide for temperatures below 60°C. From the first sight, it appears to contradict the detected change of the prefactor value during aging (figure 1). However, the figure 1 depicts values of prefactor that correspond to the elevated temperature 100°C, while the values for the same temperature in figure 2 appear to be distorted by the influence of drift process, which prevents direct comparison. Nevertheless, the fact that for lower temperatures the prefactor remains constant after annealing could still be described on the basis of the data in figure 1. It shows, that the value of prefactor saturates quickly during annealing, in comparison with the activation energy. After deposition, the samples were exposed to influence of room temperature for some time before measurements, which could already provoke the changes in $\sigma_0$ and $E_A$. Due to fast nature of those changes for $\sigma_0$, its value for lower temperatures could be already saturated.

The data in figure 2 clearly shows an increase of activation energy value in the whole range of temperatures after the annealing, which is in line with the results shown in figure 1. The difference $\Delta E_A$ is about 14 meV and it is spread uniformly across the whole temperature range. The drift phenomenon in the Ge$_2$Sb$_2$Te$_5$ is attributed to the band gap widening $\Delta E_g$ [8,18]. In [8] a 30 meV change after annealing at 80°C for 27 hours is detected, and it is indeed uniform from 80°C down to helium temperatures. Our results, therefore, support the theory of predominant influence of band gap widening on the resistance drift in Ge$_2$Sb$_2$Te$_5$.

Interesting to note, that the temperature dependence of $\sigma_0$ in semi-logarithmic scale clearly resembles the temperature dependence of $E_A$. This observation could be a manifestation of the Meyer-Neldel rule (MNR) [19] which states that the prefactor correlates with the activation energy as

$$\sigma_0 = \sigma_{00} \exp \left( \frac{E_A}{E_{MN}} \right),$$

where $E_{MN}$ is the characteristic energy of MNR. Since change of temperature provides means of changing the value of $E_A$, the data from figure 2 could be used to test the MNR in the case of Ge$_2$Sb$_2$Te$_5$ conductivity. Figure 3 shows the $\sigma_0(E_A)$ dependence in semi-logarithmic coordinates. The dependencies are sufficiently linear and straight lines provide fits to data according to (4). The estimated value of $E_{MN}$ is about 25 meV for both initial and annealed samples. This value is similar to those found for other chalcogenide systems [19]. Moreover, the obtained value is close to the

![Figure 3](image-url)
magnitude of optical phonons in amorphous Ge$_2$Sb$_2$Te$_5$, which is in the range 15–20 meV [20]. This correlates well with the multi-excitation theory of MNR, which states that in the systems where the potential barrier for a kinetic process is large in comparison with available excitations the activation is provided by means of multiple elemental excitations.

4. Conclusions

Parameters of Arrhenius equation for conductivity are determined for the Ge$_2$Sb$_2$Te$_5$. Their evolution with both time and temperature are presented. Temporal measurements show considerable change of the activation energy and pre-exponential factor during isothermal annealing, which is attributed to the resistance drift phenomenon in phase-change materials. Temperature dependence of activation energy demonstrates a uniform shift toward higher values after annealing, which could be explained with corresponding increase of the band gap. The validity of Meyer-Neldel rule for conduction of Ge$_2$Sb$_2$Te$_5$ demonstrated leading to the value of an elemental excitation energy close to the phonon energy.

Acknowledgments

Authors acknowledge support of the Russian Science Foundation (project no. 19-73-00150).

References

[1] Noé P, Vallée C, Hippert F, Fillot F and Raty J-Y 2018 Semicond. Sci. Technol. 33 013002
[2] Kozyukhin S, Vorobyov Y, Sherchenkov A, Babich A, Vishnyakov N and Boytsova O 2016 Phys. status solidi 213 1831–8
[3] Stanisavljevic M, Pozidis H, Athmanathan A, Papandreou N, Mittelholzer T and Eleftheriou E 2016 IEEE 8th Int. Mem. Work. IMW 2016 4–7
[4] Athmanathan A, Stanisavljevic M, Cheon J, Kang S, Ahn C, Yoon J, Shin M, Kim T, Papandreou N, Pozidis H and Eleftheriou E 2015 Proc. - 2014 IEEE Asian Solid-State Circuits Conf. A-SSCC 2014 137–40
[5] Ielmini D, Sharma D, Lavizzari S and Lacaita A L 2009 IEEE Trans. Electron Devices 56 1070–7
[6] Raty J Y 2019 Phys. Status Solidi - Rapid Res. Lett. 13 1–10
[7] Le Gallo M, Krebs D, Zipoli F, Salinga M and Sebastian A 2018 Adv. Electron. Mater. 1700627
[8] Rütten M, Kaes M, Albert A, Wuttig M and Salinga M 2015 Sci. Rep. 5 1–11
[9] Krebs D, Schmidt R M, Klomfabetas J, Luckas J, Bruns G, Schlockermann C, Salinga M, Carius R and Wuttig M 2012 J. Non. Cryst. Solids 358 2412–5
[10] Kaes M and Salinga M 2016 Sci. Rep. 6 1–12
[11] Braga S, Cabrini A and Torelli G 2009 Appl. Phys. Lett. 94 1–3
[12] Pirovano A, Lacaita A L, Pellizzer F, Kostylev S A, Benvenuti A and Bez R 2004 IEEE Trans. Electron Devices 51 714–9
[13] Ielmini D, Fugazza D, Boniardi M, Montemurro G and Lacaita A L 2010 Epcos 7–8
[14] Wimmer M, Kaes M, Dellen C and Salinga M 2014 Front. Phys. 2 1–12
[15] Muneer S, Scoggin J, Dirisaglik F, Adnane L, Cywar A, Bakan G, Cil K, Lam C, Silva H and Gokirmak A 2018 AIP Adv. 8 065314
[16] Li J V., Johnston S W, Yan Y and Levi D H 2010 Rev. Sci. Instrum. 81 033910
[17] Oosthoek J L M, Krebs D, Salinga M, Gravesteijn D J, Hurkx G A M and Kooi B J 2012 J. Appl. Phys. 112
[18] Fantini P, Brazzelli S, Cazzini E and Mani A 2012 Appl. Phys. Lett. 100 013505
[19] Shimakawa K and Abdel-Wahab F 1997 Appl. Phys. Lett. 70 652–4
[20] Först M, Dekorsy T, Trappe C, Laurenzis M, Kurz H and Bèchevet B 2000 Appl. Phys. Lett. 77 1964–6