08.1

Degradation processes in a memristor based on germanium selenide with a self-forming conductive channel

A.N. Aleshin, O.A. Ruban

Institute of Ultra High Frequency Semiconductor Electronics of RAS, Moscow, Russia
E-mail: myx.05@mail.ru

Received November 10, 2022
Revised November 10, 2022
Accepted December 16, 2022

The effect of temperature on degradation processes in an $Ag/SnSe/Ge_2Se_3/W$ ionic memristor with a self-forming conductive channel in the temperature range of 22−65°C at a switching frequency of 100 Hz was studied based on determining the electrical conductivity of the memristor in low-resistance and high-resistance modes of operation. It has been established that at elevated temperatures, degradation processes occur faster and affect both the low-resistance and high-resistance modes of operation of the memristor. The degradation activation energy was determined to be 1.16 eV.

Keywords: electrical conductivity, solid electrolyte, degradation, conductive channel.

DOI: 10.21883/TPL.2023.02.55377.19423

Both memristors based on transition-metal oxides [1] and ion-type memristors, which are electrolytic cells based on a solid electrolyte with active and passive electrodes [2–4], currently attract great research attention. A complementary type of switching, which is important for passive memories [5], is among the advantages of ionic memristors. Featuring a hysteretic current–voltage curve (CVC), ionic memristors exhibit the resistive memory effect. Different CVC branches correspond to low-resistance (LRS) and high-resistance (HRS) states of a memristor. The concept of formation of conductive channels (CCs) in an ionic memristor plays a significant part in the theory of operation of an ionic memristor. A CC in an ionic memristor in LRS is a metallic filament that forms when a positive voltage is applied to the active memristor electrode. When a negative voltage is applied to the active electrode, a CC disintegrates, and a memristor switches to HRS. A CC cannot exist as a coherent structure in this state. The design of an ionic memristor (Fig. 1) discussed in [6] is characterized in chemical terms by formula $Ag/SnSe/Ge_2Se_3/W$ and does not require electroforming. This memristor was termed a self-directed channel (SDC) device by its creators. According to [6], the process of CC formation in an SDC memristor is underpinned by agglomeration (formation of aggregates) of Ag^+ ions that proceeds alongside the electromigration of these ions in a solid Ge_2Se_3 electrolyte. A CC in an SDC memristor forms when agglomeration regions overlap. The conductivity of this CC depends on the density of Ag^+ ions in agglomeration regions and the degree of their overlap. An SnSe layer between the active electrode and the Ge_2Se_3 solid electrolyte (amorphous chemical compound with a crystallization temperature of $\sim 350^\circ$C) ensures that Sn^{2+} ions, which act as catalysts of the process of agglomeration of Ag^+ ions [7], enter the active layer. The mechanism of Ag^+ agglomeration in the process of formation of a CC in an $Ag/SnSe/Ge_2Se_3/W$ SDC memristor was examined in more detail in [4]. An SDC memristor is a nanoscale electrical device in which a CC (a silver filament) forms within the bounds of a 15-nm-wide interelectrode space [8]. Such memristors are prone to degradation: their functional capabilities deteriorate gradually in the course of operation.

The aim of the present study is to examine the influence of temperature on the rate of degradation of an SDC memristor by plotting degradation curves (dependences of the memristor conductivity in LRS and HRS on the number of operation cycles). The conductivity value in each operating mode of an SDC memristor was calculated based on a series of CVCs, which integrated ten consecutive operation cycles, at a switching frequency of 100 Hz in a temperature range of 22−65°C. It should be noted that ionic memristors (SDC ones included) differ from memristors based on transition-metal oxides (see, e.g., [9]) in having no published data on degradation processes.

The studied SDC memristors were purchased from Knowm Inc. (United States), a small-batch producer of such devices. An automated measurement setup, which features a Tertroniks TDS 2042C oscilloscope, a Digilent Analog Discovery 2 waveform generator/oscilloscope, and a PC for control over measurement instruments and data processing, was used in experiments. This setup allows one to perform repeated and continuous measurements of memristor CVCs at different switching frequencies and temperatures. The effect of temperature on memristor operation was determined by introducing the studied devices into the chamber of an SM-60/150 80 TKh climatic test unit. A bipolar triangular voltage was applied to the top (active) electrode of a memristor in CVC measurements. The bottom (inert) electrode was grounded.

CVC measurements were performed at 22 (room temperature), 35, 50, and 65°C within 30, 7, 1, and 0.142

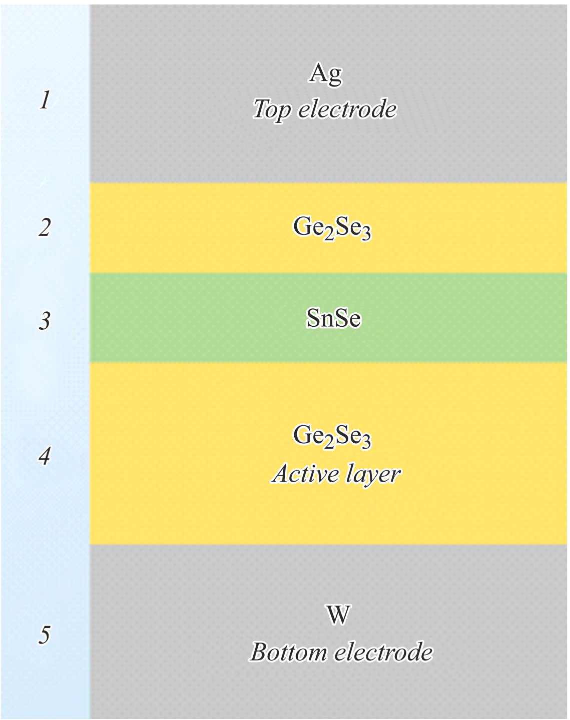

Figure 1. Sequence of layers and their functionality in an Ag/SnSe/Ge_2Se_3/W SDC memristor. *1* — active silver electrode, *2* — spacer, *3* — Sn ion source, *4* — solid Ge_2Se_3 electrolyte (active layer), *5* — inert tungsten electrode. The interelectrode space is 15 nm.

h, respectively. These measurements were stopped when CVCs degenerated (i.e., when different branches, which initially formed a hysteretic configuration, got very close to each other or even merged completely). The corresponding time (τ) was set as the end time for degradation curves. The transition from a classical CVC (such CVCs for an Ag/SnSe/Ge_2Se_3/W memristor are provided in [4]) to a degenerate one occurred in a short (compared to the entire CVC measurement time) time interval that varied from 1 h at 22°C to 30 s at 65°C. It was assumed that CVC degeneration is a marker of loss of the capacity of an SDC memristor to function as a cell with resistive memory.

Degradation curves for LRS and HRS are shown in Fig. 2. The SDC memristor degradation consists in gradual convergence of conductivity values in LRS and HRS with an increase in the number of operation cycles; the ratio of these two values, which characterizes the quality of resistive memory, decreases with increasing temperature. It can be seen from Fig. 2 that the degradation of an SDC memristor is driven by changes in LRS conductivity at 22 and 35°C (Figs. 2, *a* and *b*) and by the variation of HRS conductivity at higher temperature of 50 and 65°C (Figs. 2, *c* and *d*). The degradation curves for 35°C and 22°C were similar, and the curves for 65°C and 50°C also behaved in a similar fashion. The LRS degradation curve in Cartesian coordinates may be represented by linear dependence $\ln G = Ax + B$, where G is conductivity and x is the number of operation cycles of a memristor. At temperatures of 22 and 35°C, $A < 0$; at 50 and 65°C, $A \approx 0$. In other words, the degradation process in an SDC memristor „switches" from LRS to HRS at a temperature on the order of 50°C. The $\ln G = Ax + B$ representation of the LRS degradation curve at 22 and 35°C (with $A < 0$) characterizes conductivity G that decreases with time in accordance with exponential decay law $G(t) = G_0 \exp(-t/t_0)$ (t and t_0 are the current time and the characteristic process time and G_0 is a pre-exponential factor) that is ubiquitous in nature. This dependence may be interpreted as a CC cross-section area reduction in the process of memristor operation.

It appears important to determine the activation energy of the degradation process, because this parameter is a structurally sensitive one. Since the CC formation in an SDC memristor is underpinned by the process of electromigration of Ag^+ ions, one may derive relation

$$T^2(\partial s/\partial t)_{irrev} \propto \exp(-Q/kT) \qquad (1)$$

for the irreversible part of the entropy of a system, where s is the entropy per unit volume, Q is the activation energy for electromigration of Ag^+ ions, k is the Boltzmann constant, and T is thermodynamic temperature, relying on the Nernst law [10] and concepts of thermodynamics of irreversible processes (specifically, the second Onsager postulate [11]). It follows from expression (1) that growth rate $(\partial s/\partial t)_{irrev}$ of the irreversible part of the entropy of a system in electromigration increases with temperature. Since the initial and end (CVC degeneration) states of an SDC memristor are the same at all the studied temperatures, this conclusion may be extended to growth rate $(\partial s/\partial t)_{irrew}$ of the irreversible part of the entropy of a system in transition of an SDC memristor from the initial state to a degenerate one. The behavior of experimental quantity τ^{-1} is similar. Assuming that $(\partial s/\partial t)_{irrev}$ is directly proportional to τ^{-1} and substituting the first quantity in (1) with the second one, we find

$$T^2\tau^{-1} \propto \exp(-U/kT), \qquad (2)$$

where U is the degradation activation energy. The dependence of product $T^2\tau^{-1}$ on reciprocal thermodynamic temperature (i.e., the Arrhenius law for degradation of an SDC memristor) is presented in Fig. 3. The value of U is 1.16 eV.

The energy of activation of CC formation in an Ag/SnSe/Ge_2Se_3/W SDC memristor was estimated at 0.19 eV in [4]. This is in line with the capacity of this memristor to operate at high switching frequencies (up to 10^5 Hz) [6]. An activation energy this low corresponds to Ag^+ electromigration along the interfaces of structural units (structured within the first coordination sphere) of an amorphous matrix (it is a known fact that the activation energy of grain- and phase-boundary diffusion decreases relative to the one of bulk diffusion). The value of U is almost an order of magnitude higher than the activation energy of CC

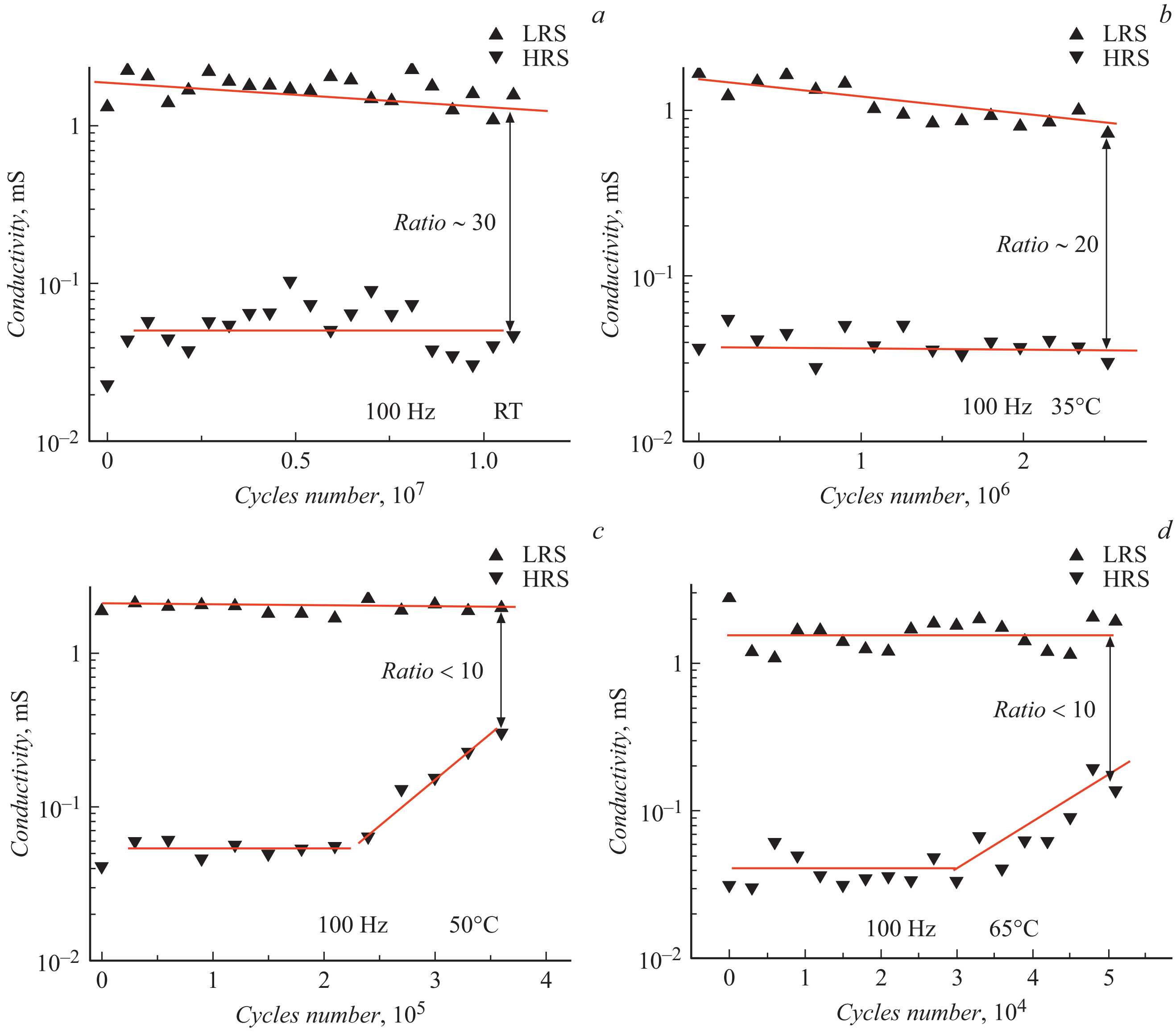

Figure 2. Degradation curves for LRS and HRS at temperatures of 22 (*a*), 35 (*b*), 50 (*c*), and 65°C (*d*) measured within 30, 7, 1, and 0.142 h, respectively.

formation in an SDC memristor and apparently corresponds to the process of electromigration of Ag^+ ions directly in the bulk of the amorphous matrix of solid electrolyte Ge_2Se_3 (in circumvention of fast diffusion routes). Owing to the stochastic nature of the electromigration process or under the influence of temperature, electromigration of this kind may occur spontaneously at times, disrupting the agglomeration mechanism of CC formation. This is what causes the degradation of an SDC memristor.

Degradation processes in ionic Ag/SnSe/Ge_2Se_3/W memristors with self-directed channels were examined by plotting degradation curves (dependences of conductivity on the number of operation cycles) in low-resistance and high-resistance modes of memristor operation within a temperature interval of 22–65°C. This degradation consists in gradual convergence of conductivity values in LRS and HRS with an increase in the number of operation cycles; the process of degradation is governed either by LRS (at temperatures of 22 and 35°C) or by HRS (at higher temperatures of 50 and 65°C). In the former case, degradation curves reveal a reduction in conductivity; in the latter case, the conductivity increases. As the temperature grows, the ratio of LRS and HRS conductivities, which characterizes the quality of the studied resistive memory, at the end sections of degradation curves decreases. The degradation activation energy is 1.16 eV, which is indicative of electromigration of Ag^+ ions in the bulk of an amorphous matrix, thus providing evidence of disruption of the agglomeration mechanism of CC formation. This is what causes the degradation of an SDC memristor.

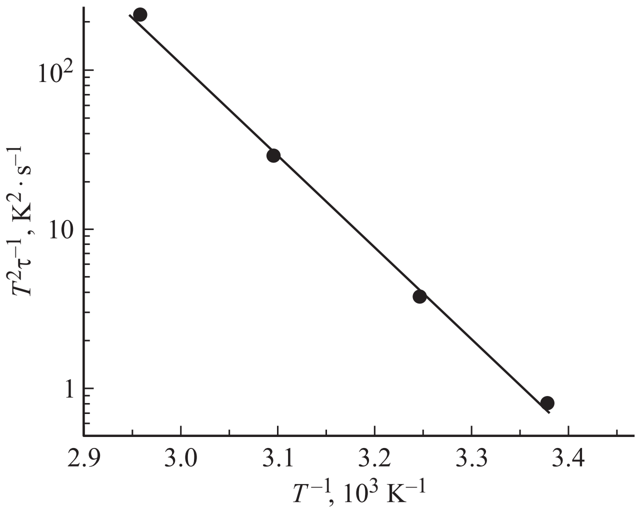

Figure 3. Arrhenius law for degradation of an Ag/SnSe/Ge_2Se_3/W SDC memristor in the 22−65°C temperature interval. The activation energy is 1.16 eV.

Funding

This study was supported financially by the Russian Foundation for Basic Research (grant No. 19-29-03003 MK).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] K.M. Kim, D.S. Jeong, C.S. Hwang, Nanotechnology, **22**, 254002 (2011). DOI: 10.1088/0957-4484/22/25/254002
[2] R. Waser, R. Dittmann, G. Staikov, K. Szot, Adv. Mater., **21**, 2632 (2009). DOI: 10.1002/adma.200900375
[3] I. Valov, R. Waser, J.R. Jameson, M.N. Kozicki, Nanotechnology, **22**, 254003 (2011). DOI: 10.1088/0957-4484/22/25/254003
[4] A.N. Aleshin, O.A. Ruban, Russ. Microelectron., **51** (2), 59 (2022). DOI: 10.1134/S1063739722020020.
[5] E. Linn, R. Rosezin, C. Kuegeler, R. Waser, Nat. Mater., **9**, 403 (2010). DOI: 10.1038/NMAT2748
[6] K.A. Campbell, Microelectron. J., **59**, 10 (2017). DOI: 10.1016/j.mejo.2016.11.006
[7] A. Devasia, S. Kurinec, K.A. Campbell, S. Raoux, Appl. Phys. Lett., **96**, 141908 (2010). DOI: 10.1063/1.3385781
[8] K.A. Campbell, J.T. Moore, US Patent 7,151,273 (issued December 19, 2006).
[9] L. Wu, H. Liu, J. Li, S. Wang, X. Wang, Nanoscale Res. Lett., **14**, 177 (2019). DOI: 10.1186/s11671-019-3015-x
[10] A.K. Ivanov-Shits, I.V. Murin, *Ionika tverdogo tela* (Izd. S.-Peterb. Gos. Univ., SPb., 2000), Vol. 1 (in Russian).
[11] B.S. Bokshtein, M.I. Mendelev, Yu.V. Pokhvisnev, *Fizicheskaya khimiya: termodinamika i kinetika* (Izd. Dom MISiS, M., 2012) (in Russian).