Estimation of the activation energy in the Ag/SnSe/Ge$_2$Se$_3$/W self-directed channel memristor

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Abstract

In this study, we conducted an investigation into the Ag/SnSe/Ge$_2$Se$_3$/W ionic memristor, focusing on the determination of activation energies associated with its two primary operational processes: the formation of conductive filaments and memristor degradation. To ascertain the electrical conductivity of the memristor in both its basic electronic states, a low resistance state and a high resistance state, we constructed current-voltage characteristics. The estimation of activation energy values was carried out employing the Arrhenius law and the provisions of irreversible thermodynamics, with specific reference to Onsager’s second postulate. This fundamental concept posits that the growth rate of irreversible component of entropy can be expressed as the summation of products involving fluxes and thermodynamic forces when a system tends towards its equilibrium state. In the context of this study, the equilibrium state of the memristor is defined as the condition at which the memristor can no longer function as a resistive memory cell. Our experimentation involved the application of a flux of Ag$^+$ ions (electromigration). The calculated activation energy values were found to be 0.24 eV for the initial process and 1.16 eV for the latter. These divergent activation energy values indicate the differentiation between the agglomerative mechanism that governs the formation of conductive channels, prevalent in the Ag/SnSe/Ge$_2$Se$_3$/W memristor, and the “conventional” substance transfer mechanism based on a group of point defects that manifests itself during the memristor’s degradation.

Keywords
electrical conductivity, solid electrolyte, amorphous matrix, activation energy, agglomeration

1. Introduction

Memristors are dynamic electronic components whose electrical conductivity changes its value depending on the applied voltage. These devices exhibit a transition between their high resistance state (HRS) and low resistance state (LRS), accomplished through a resistive switching mechanism. Specifically, conductive filaments (CFs) are formed and disrupted within their solid body structure. These CFs can take the form of conductive phases, such as the Ti$_n$O$_{2n-1}$ Magnelli phases [1, 2] found in titanium oxide-based memristors or metallic filaments in solid electrolytes, such as As–S, Ge–Se, and Ge–S, when they function as electrolytic cells (EC) featuring active (Ag, Au, Cu) and inert (W, Pt) electrodes [3, 4]. Transition metal oxide-based memristors operate as vacancy mem-
ristor, with oxygen vacancies playing a pivotal role in CF formation, whereas EC memristors operate through ionic mechanisms. The current-voltage characteristic (I-V curve) of a bipolar memristor exhibits a distinctive hysteresis loop, which enables its utilization as a resistive memory cell. Two branches of I-V curve correspond to the two states of the memristor: HRS and LRS.

Karpov V. et al. [5] and Niraula D. et al. [6] have presented a thermodynamic model detailing the hafnium oxide-based memristor’s operation. This model revealed the relationships with the memristor turn-on voltage, the current flowing through it, and the thermodynamic properties of the CF system. It is valuable not only to utilize thermodynamic methods but also to determine the kinetic constants for the processes occurring within the memristor during its operation, with a particular focus on assessing the activation energy. The relationship between the thermodynamic properties of a memristor and the activation energy, or more specifically, the activation enthalpy, arises when describing the position of hopping atom at the vertex of energy barrier in terms of a transient state. This phenomenon, as elucidated by Glasstone S. et al. in their work on the theory of absolute reaction rates [7], serves as an illustrative example. In the transient state, positively charged oxygen vacancies (in the case of vacancy memristors) or the active electrode ions (in ion memristors), drifting within the electric field, overcome the energy barrier during diffusion elementary act. The activation energy for diffusion mass transfer in solids, induced by a thermally activated hopping mechanism (for example, electromigration), exhibits sensitivity to the material’s structure [8]. Precise activation energy values offer more comprehensive insights into the structural alterations occurring during the memristor operation. Consequently, activation energy serves as a crucial property characterizing CF formation and memristor degradation processes in both vacancy and ionic memristors.

The investigation of these processes in the ionic memristor, which utilizes a Ge$_2$Se$_3$ solid electrolyte in its amorphous state with a glass transition temperature of 340 °C (it was documented by Feltz A. [9]) is summarized below. The chemical composition of the memristor is denoted as Ag/SnSe/Ge$_2$Se$_3$/W, where Ag and W represent the active and inert electrodes, respectively. It is noteworthy that, as pointed out by Campbell K. [10], the formation of CFs in such memristors occurs spontaneously, obviating the need for electroforming. Campbell K. [10] refers this specific type of memristor as a "self-directed channel" or SDC memristor. The primary objective of this study is to ascertain the activation energy associated with the formation of silver filaments and the degradation of SDC memristors. To achieve this, we conducted experiments where we obtained I-V curves and measured the conductivity of the SDC memristor in both its LRS and HRS operation modes at various temperatures. It is worth highlighting that both CF formation and the degradation of SDC memristors are fundamentally underpinned by the electromigration of Ag$^+$ ions, a pivotal and common process in ionic memristors. Our examination of electromigration was instrumental in determining the activation energy of degradation, employing the principles of thermodynamics of irreversible processes.

2. Materials and methods

The study focused on SDC memristors produced by Knowm Inc. (USA). These memristors are bipolar devices housed within ceramic packages. Detailed information about their design can be found in references [10] and [11], and a visual representation is provided in Fig. 1. The distance between the electrodes in these devices measures 15 nm [11]. The SnSe film within the memristor serves as the source of Sn$^{2+}$ ions. These ions play a crucial role in the Ge$_2$Se$_3$ solid electrolyte, as they migrate into the electrolyte via electromigration, thereby expediting the consolidation of CF [12, 13]. In accordance with the findings in reference [10], CF formation within SDC memristor based on the development of Ag$^+$ ion agglomeration sites during electromigration. These sites expand and overlap progressively, culminating in the formation of a monolithic, consolidated silver filament.

Figure 2 illustrates the CF formation through the overlapping of agglomeration sites. The driving force behind the creation of these agglomeration sites is the presence of elastic stress fields within minuscule volumes, stemming from the substitution of smaller Ge atoms with larger Ag atoms during the electromigration process within Ge–Ge dimers. These Ge–Ge dimers represent the primary units of short-range order within the amorphous matrix of Ge$_2$Se$_3$ (the crystalline structure of thin Ge$_2$Se$_3$ films was simulated by Edwards A. et al. [13]).

![Figure 1. Sequence of layers in an Ag/SnSe/Ge$_2$Se$_3$/WSDC memristor and their functional purposes: (1) active silver electrode, (2) spacer, (3) Sn$^{2+}$ ion source, (4) Ge$_2$Se$_3$ solid electrolyte (active layer), (5) inert tungsten electrode. Inter electrode space is 15 nm](image-url)
Figure 2. Initial stages of Ag⁺ ion agglomeration within the Ge₂Se₃ amorphous matrix: (a) unperturbed short-range order of the amorphous matrix; (b) formation of a microcavity when an Au atom substitutes a Ge atom in one of the Ge–Ge dimers; (c) accumulation of Ag⁺ ions around the microcavity. Arrows indicate the directions of movement of Ag⁺ ions near the microcavity from neighboring (parallel) regions of the amorphous matrix. The figure was generated by the authors using data sourced from [10].

As an Ag atom replaces a Ge atom, microcavities emerge within the amorphous matrix (see Fig. 2 b). These microcavities function as nucleation centers for the subsequent formation of agglomeration sites. As the electromigration proceeds, Ag⁺ ions from adjacent ("parallel") regions of the amorphous matrix are drawn towards these microcavities (see Fig. 2 c) due to elastic stresses. Consequently, in SDS memristors there is no the final stage of filament formation as it is in a “standard” ionic memristor when the growth of electrolytic depositions formed on an inert W electrode occurs into the direction of active Ag electrode [3, 4]. In SDC memristors the CF formation is restricted by the stage of electromigration of Ag⁺ ions caused by applying a positive voltage to an active Ag electrode. The number of stages of CF formation is reduced in SDC memristors. This circumstance allows to realize a high rate of memristor’s operation.

We employed an automated measuring setup consisting of a Tertroniks TDS 2042C oscilloscope, a Digilent Analog Discovery 2 oscilloscope and analyzer, and a PC for instrument control and data processing. This configuration proved well-suited for the continuous and repeated recording of I-V curves of the memristor, conducted at various switching frequencies and temperatures. In order to investigate the influence of temperature on memristor performance, we utilized an SM-60/150 80 TX climatic chamber. For I-V curve recording, a time-variable bipolar triangular voltage was applied to the top electrode of the memristor, while the bottom electrode remained grounded. Our I-V curve recordings were conducted to determine the activation energy associated with CF formation at switching frequencies of 10, 100, and 1000 Hz, representing three distinct frequency values, across temperatures of 22 (room temperature), 50, and 75 °C. To determine the effects of degradation on the SDC memristor performance, we tested the device at 22, 35, 50, and 65 °C and a 100 Hz switching frequency. For generating I-V curves, we continuously recorded the applied electric potential at the top electrode and the resulting current. To determine the conductivity values of the SDC memristor, we aggregated a series of the I-V curves representing ten consecutive cycles.
3. Conductive filament formation

Aleshin A. et al. [14] conducted a frequency domain test with a switching frequency ranging from 1 to \(10^4\) Hz at room temperature. They observed a prominent linear correlation between the conductivity \(G\) of the Ag/SnSe/Ge\(_2\)Se\(_3\)/W memristor and the cycle period \(\tau\) (the reciprocal of the switching frequency) when the memristor operated. This relationship is expressed as follows in semi-logarithmic coordinates:

\[
\Delta G = \frac{\sigma}{l} \frac{dS}{dt} \Delta \lg \tau, \tag{1}
\]

where \(\sigma\) represents the specific electrical conductivity of silver, \(S\) denotes the cross-sectional area of the CF, \(\frac{dS}{dt}\) is the kinetic constant representing the rate of change in the CF’s cross-section area, \(t\) stands for time, and \(l\) represents the length of CF. The kinetic constant \(\frac{dS}{dt}\) can be determined as follow:

\[
\frac{dS}{dt} = \frac{l}{\sigma} \frac{dG}{d \lg \tau}, \tag{2}
\]

to achieve this, it is essential to have I-V curves registered at a minimum of three different switching frequencies. The kinetic constant \(\frac{dS}{dt}\) quantifies changes in the cross-sectional area of the CF over time, and consequently we can utilize the Arrhenius law (as it is described by Bokshtein B. et al. [15]) to determine the activation energy associated with the CF formation process by using an equation:

\[
\frac{d \ln(\frac{dS}{dt})}{dT} = \frac{Q}{kT^2}, \tag{3}
\]

where \(Q\) denotes the activation energy of the CF formation process, \(T\) represents the thermodynamic temperature, and \(k\) stands for the Boltzmann constant.

As mentioned previously, measurements of the kinetic constant \(\frac{dS}{dt}\) were conducted at switching frequencies of 10, 100, and 1000 Hz and temperatures of 22, 50, and 75 °C. Figure 3 illustrates the I-V curves of the Ag/SnSe/Ge\(_2\)Se\(_3\)/W SDC memristor for these frequencies and different temperatures. From Fig. 3, it is evident that at each temperature, as the switching frequency increases, the angle of slope of the I-V curve with respect to the \(X\)-axis decreases in the LRS, indicating a reduction in the memristor’s conductivity. Conversely, increasing the switching frequency has a minimal impact on the slope angle of the I-V curve in the HRS. Figure 4 presents the \(G(\tau)\) curves in semi-logarithmic coordinates for each temperature. This figure demonstrates that as the temperature increases, \(\frac{dG}{d \lg \tau}\) (and consequently, \(\frac{dS}{dt}\)) also increases. This observation implies that the kinetic constant \(\frac{dS}{dt}\), much like other similar constants such as diffusion coefficient, grain boundary mobility, and reaction rate constant, adheres to the Arrhenius law.

The application of the Arrhenius law to the kinetic constant \(\frac{dS}{dt}\), as estimated from Eq. (2) while considering the temperature correction for the specific conductivity...
of silver σ, is depicted in Fig. 5. The determined activation energy is 0.24 eV. The relatively low activation energy for CF formation aligns with the Ag/SnSe/Ge$_2$Se$_3$/WSDC memristor's capability to function effectively as a resistive memory cell even at high switching frequencies, extending up to $10^5$ Hz [10]. Moreover, this activation energy aligns with the assumption that the primary mechanism facilitating Ag$^+$ ion transport within the amorphous matrix of the Ge$_2$Se$_3$ solid electrolyte corresponds to their migration along boundaries dividing structural blocks of the amorphous matrix. These structural block boundaries within the amorphous matrix, akin to grain boundaries in metals, exhibit high misorientation angles [16] and, consequently, may possess some excess free volume [17]. The latter circumstance allows to realize a rapid mass transfer along structural block boundaries of the amorphous matrix. High diffusion rates, in turn, correspond to low activation energies, a factor that influences the activation energy associated with CF formation.

### 4. Self-directed channel memristor degradation

In our investigation of SDC memristor degradation, we subjected the device to continuous I-V curves registration at 100 Hz and temperatures of 22, 35, 50, and 65 °C. The I-V curves were recorded for durations of 30, 7, 1, and 0.142 h, respectively. Registration of the I-V curves was terminated when the curves exhibited significant degeneration, with I-V curves either strongly converging or, in some cases, completely merging. At this point, denoted as ξ, the I-V curve registration was halted. The transition of the I-V curve from its conventional shape (Fig. 3) to a degenerated shape occurred relatively quickly, constituting a small fraction of the overall I-V curve registration period. This transition time varied from 1 hour at 22 °C to 30 s at 65 °C. Therefore, the duration required to capture the I-V curve shape change is relatively short when compared to the total I-V curve registration time for the analysis of SDC memristor degradation. We assumed that the degeneration of the I-V curve indicates that the SDC memristor can no longer function as a resistive memory cell. The conductivity values in both the LRS and HRS, when converted into cycles versus time, form the degradation curve. Figure 6 presents the degradation curves at 22, 35, 50, and 65 °C. A common characteristic among these curves is that, at elevated temperatures, their shapes change in both the LRS and HRS states. Additionally, Fig. 6 illustrates that as the degradation of the memristor progresses, the degradation curves for both the LRS and HRS states tend to converge. For a more detailed analysis of SDC memristor degradation, Aleshin A. et al. [18] conducted an extensive study on this subject.

In order to determine the activation energy of degradation, we employed the principles of thermodynamics of irreversible processes, specifically, Onsager’s second postulate, expressed as follows [15]:

$$T \left( \frac{\partial s}{\partial j} \right)_{\text{irrev}} = jX, \quad (4)$$

where $j$ represents the particle flux, $X$ is the generalized thermodynamic force, and $s$ denotes the entropy of the system per unit volume. In the stationary state, the flux of positively charged silver ions $j_{Ag^+}$ is $cv$ (where $c$ is the concentration of silver ions; $v$ is the drift velocity). The generalized thermodynamic force in this context is the electric force $qE$ (where $q$ is the charge of the Ag$^+$ ion; $E$ is the electric field). As per the Nernst equation [19], the drift velocity $v$ of Ag$^+$ ions in an electric field (electromigration) is defined as:

$$v = \left( \frac{qD_{Ag^+}}{kT} \right)E, \quad (5)$$

where $D_{Ag^+}$ stands for the diffusion coefficient of Ag$^+$ ions in the Ge$_2$Se$_3$ amorphous electrolyte. If we assume that
electromigration is the dominant process governing structural changes during the operation of the SDC memristor, we can establish a relationship between the growth rate of the irreversible component of entropy (∂/∂t)_{irrev} of the system in which the electromigration occurs, and the activation energy of electromigration:

$$T^2 \left( \frac{\partial s}{\partial t} \right)_{irrev} \propto \exp \left( -\frac{W}{kT} \right),$$

where $W$ represents the activation energy of electromigration. Consequently, during electromigration in isothermal conditions, the growth rate of the irreversible component of the entropy (∂s/∂t)_{irrev} increases with temperature. This (∂s/∂t)_{irrev} value reflects the rate at which the system approaches its equilibrium state, which for the memristor signifies the loss of its functionality as a resistive memory cell. The memristor enters a degenerate state. The inverse of the time taken for the memristor to transition into its degenerate state $\xi^{-1}$ behaves similarly to (∂s/∂t)_{irrev}; it increases with temperature. Given that the degenerate state of the SDC memristor remains consistent across all temperatures, we can deduce that (∂s/∂t)_{irrev} ∝ $\xi^{-1}$. By substituting (∂s/∂t)_{irrev} for $\xi^{-1}$, in equation (6), we derive:

$$T^2\xi^{-1} \propto \exp \left( -\frac{U}{kT} \right),$$

where $U$ represents the activation energy of degradation. Figure 7 illustrates the relationship between the product of $T^2\xi^{-1}$ and the reciprocal thermodynamic temperature, which conforms to the Arrhenius law describing the degradation of the SDC memristor. The value of $U$ is determined to be 1.16 eV. It is worth noting that we have previously applied this approach, considering electromigration as the primary process in SDC memristors, to the analysis of HfO$_2$ bipolar memristor’s operation [20, 21], which indirectly supports the validity of Eqs. (6) and (7) for determining the activation energy of degradation.

The fact that the activation energy $U$ is nearly an order of magnitude higher than the activation energy of CF formation in the SDC memristor suggests the existence of an alternative mechanism for Ag$^+$ ion transport.
within the Ge$_2$Se$_3$ solid electrolyte, apart from migration along the structural block boundaries of the amorphous matrix. One possibility of the implementation of such a mechanism is the involvement of a group of point defects, which is typical in crystalline substances. This type of electromigration may occur spontaneously from time to time due to local spontaneous crystallization of the amorphous matrix, induced by factors such as thermal fluctuations, elastic stresses, electric field gradients, etc. According to a simplified model of heterophase fluctuations presented by Klinger L. [22], in metals with FCC lattice, the volume susceptible to thermal fluctuations capable of inducing a phase change contains approximately 15–20 atoms. This volume is comparable in size to the structural block of the amorphous matrix. The spontaneous local crystallization, covering regions larger than the size of the structural block of the amorphous matrix, disrupts fast diffusion paths and promotes "conventional" diffusion (typically occurring in crystalline substances). This form of diffusion involves a group of point defects in Ag$^+$ ion transport, characterized by a higher activation energy. Consequently, this disruption of the agglomeration mechanism for CF formation ultimately leads to the degradation of the SDC memristor.

5. Conclusion

In our study, we conducted a comprehensive analysis and estimation of the activation energy associated with both the CF formation and degradation processes in Ag/SnSe/Ge$_2$Se$_3$/W SDC memristors. This investigation involved the registration of I-V curves and measurements of the conductivity of the SDC memristor in both its basic electronic states: the LRS and the HRS. To estimate the activation energy for these processes, we employed the Arrhenius law and applied principles of thermodynamics of irreversible processes. The results reveal that the activation energy for CF formation is 0.24 eV, indicating that the SDC memristor can effectively maintain its resistive memory function even at high switching frequencies, extending up to $10^5$ Hz. This finding aligns with the agglomeration mechanism of CF formation, which is associated with the migration of Ag$^+$ ions along the boundaries of structured within the first coordination sphere blocks of the amorphous matrix of the Ge$_2$Se$_3$ solid electrolyte. In contrast, the elevated activation energy associated with memristor degradation aligns with the notion of Ag$^+$ ion migration occurring directly within the bulk of the amorphous matrix, potentially through mechanisms like local crystallization. This occurrence signifies a breakdown in the agglomeration process crucial for CF formation. Such a failure is the underlying cause of SDC memristor degradation, serving as an indicator that the behavior of the Ag/SnSe/Ge$_2$Se$_3$/W system deviates from its ideal state when subjected to a prolonged passage of direct electric current.

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Ethics declarations

The authors declare that they do not have any conflicts of interest.

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