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A physical-based simulation for the dynamic behavior of photodoping mechanism in chalcogenide materials used in the lateral programmable metallization cells

Mehdi Saremi

School of Electrical, Computer, and Energy Engineering, Arizona State University, Tempe, AZ, USA

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ABSTRACT

Photodoping of chalcogenide glass (ChG) is an important process that has been used in several technology applications such as submicron lithography, diffraction gratings, and holographic recording. Today, one of the primary uses of photodoping is in the production of nonvolatile cation-based resistive random access memory (RRAM). Cation RRAM operates through electronic control of metal concentration within a ChG film, which alters the material between high resistance (HRS) and low resistance states (LRS). The process of photodoping is performed after the fabrication of ChG-based RRAM in order to introduce active metal into the film and lower switching energy. In spite of recent advances in the control of photodoping in ChG materials during manufacturing, the physical principles governing the dynamics of the process are still not fully understood. In this paper, we present a physical-based simulation for photodoping in ChG materials used in the lateral programmable metallization cells. The analysis structure is a lateral device that uses GeSe binary film as the ChG material with electrically active Ag anode and neutral Ni cathode contacts.

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1. Introduction

Alloys of group IV elements (such as Ge) with those of group VI (chalcogens such as Se) are able to form chalcogenide glasses (ChGs) [1]. Among the unique properties of ChG materials is their ability to be photodoped. The process of photodoping is characterized by the incorporation of active metal species (e.g., Ag) into the glass upon exposure to light. Today, photodoping is used in the fabrication of novel memory technologies [2–3], specifically Programmable Metallization Cells (PMCs) [4] and their commercial variant Conductive Bridge Random Access Memory (CBRAM). The PMC represents one type of resistive switching random access memory (RRAM) and is one of the leading candidates for replacing Flash memory in the next generation of low power and high density non-volatile memory [5–10]. Advantages associated with the PMC technology are its ultra-low power operation, scalability, and ease of integration into back-end-line (BEOL) CMOS processes [11].

While there have been significant refinements in the photodoping process to optimize it for use in RRAM manufacturing, several questions regarding the physics of photodoping remain unsolved. For example, the electrochemistry of photodoping is still not fully understood and accurate physically-based models for the process remain illusive. In this paper, physical simulations for the photodoping process of chalcogenide materials used in the fabrication of lateral PMCs are presented. Although, conventional PMCs consist of thin layer of ChG materials (e.g., GeSe, GeS) vertically sandwiched between an active anode (such

as Ag and Cu) and an inert cathode (such as Ni), this paper utilizes a lateral PMC device in order to properly understand the mechanism of the photodoping process. One of the main lateral PMC applications is its usage as a switch in microwave systems. Advantages of lateral PMCs over conventional vertical ones include low insertion loss, high isolation, low voltage operation, low power consumption, and excellent linearity [12].

By applying a positive voltage to the anode, an electrochemical reaction happens at the anode side where silver ions are generated. The ions migrate across the chalcogenide layer and are deposited at the cathode. A metal conductive filament forms a bridge between cathode and anode contact, and shunts the high resistance electrolyte; therefore, the device switches from a high resistance state (HRS) to a low resistance state (LRS). After applying reverse bias, the conductive filament tends to dissolve and the device returns to HRS. The mechanisms for resistive switching in PMCs are related to the formation or dissolution of conductive filaments within the glass that bridge two contacts [4,9,13].

The kinetics of silver ions through ChGs is modeled by the Mott-Gurney hopping mechanism [14], while the Butler-Volmer equation demonstrates the electrode Redox [15]. Moreover, electron tunneling between adjacent impurity sites is an alternate theory to Mott-Gurney ion hopping [16]. In addition, there are several mechanisms mapping the electron flow in the chalcogenide layer as follow: band conduction in the extended states [17], Mott's $T^{\frac{1}{4}}$ variable range hopping [17], Schottky thermionic emission [18], Poole-Frenkel emission [19], and Fowler-Nordheim tunneling [20–21]. The process of band conduction

in the extended state in ChGs is similar to carrier motions between conduction band and valence band in crystalline semiconductors. Mott's $T^{\frac{1}{4}}$ variable range hopping is a process in which electrons hop between localized states in the forbidden energy band and it dominates at low temperatures. Schottky emission demonstrates the movement of electrons from an electrode to the conduction band of ChGs by gaining enough energy. Poole-Frankel emission takes place under high electric field where decreasing of the energy barrier of traps enables electrons to jump to the next traps. In Fowler-Nordheim tunneling mechanism, electrons tunnel across a triangular quantum barrier into the conduction band of thin ChGs at high electric fields. On the experimental side, there are also several interesting articles dedicated to analyze and investigate the charge transfer in ChG materials while taking into account the interaction between ionic species and ChG bonds with the emphasis of the CBRAM and electrochemical metallization memory applications [22–25].

The physical simulation in this paper captures the light-induced release and transport of active metal (Ag) into ChG ($Ge_{30}Se_{70}$) with a two-dimensional drift-diffusion (flux-based) solver. Self-consistent transient solutions to a parameterizable set of differential equations that model ion reactions, transport, and photogeneration in the ChG film are obtained from numerical finite element simulations on virtual structures. The structures are two dimensional representations of lateral PMCs that are either unphotodoped or photodoped (i.e., exposed to UV light). Simulation results are presented and analyzed in Section 2 and conclusion is exhibited in Section 3.

2. Physical-based simulation

In order to develop physical-based numerical simulations of the photodoping process, material parameters for the device must be set. The work functions of Ag and Ni contacts obtained from literature are 4.29 and 5.15 eV, respectively. Defining the work function value for each contact means that the contacts are Schottky. Table 1 lists additional parameters associated with the $Ge_{30}Se_{70}$ film, which include bandgap (E_g), affinity (Φ), density of states in conduction band and valence band (N_C and N_V), electron and hole mobilities (μ_n and μ_p), and dielectric constant [26]. In order to have better visualization, Fig. 1 exhibits bandgap and affinity of the ChG as well as contacts' workfunctions. The intrinsic carrier concentration (n_i) of ChG material is calculated based on Eq. (1).

$$n_i = \sqrt{N_C N_V} \exp\left(-\frac{E_g}{2kT}\right) \tag{1}$$

Because the intrinsic Fermi level of the ChG is higher than workfunctions of both contacts based on the red arrows in Fig. 1, there are several holes without any electron in the system like a p^+-type semiconductor [27]. Because of higher difference between the intrinsic Fermi level and Ni workfunction, the hole concentration at the interface of ChG and cathode is much higher than that of at the interface of ChG and anode.

Fig. 2 represents the device schematic in which the length and height of the device are 10 μm and 60 nm, respectively. The anode (Ag) and cathode (Ni) have 1 μm length and 20 nm height at left and right sides of the structure, respectively. In order to show simulation results, a cutline across the device from left side to right side as shown in

Table 1
The parameters of the $Ge_{30}Se_{70}$ as ChG material.

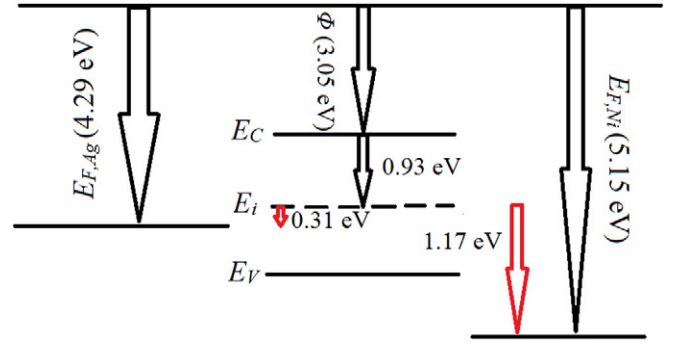|	
Bandgap at 300 K (E_g) [eV]	1.86
Affinity (Φ) [eV]	3.05
Density of states in conduction band (N_C) [per cc]	10^{19}
Density of states in valence band (N_V) [per cc]	10^{20}
Electron mobility (μ_n) [cm^2/Vs]	10^{-5}
Hole mobility (μ_p) [cm^2/Vs]	10
Dielectric constant	40.9

Fig. 1. The band diagram of the system (Ag/ChG/Ni) before connection.

Fig. 2 is used. In favor of making simulations realistic, Ag concentration of 10^{23} cm^{-3} in anode (see Fig. 2) is assumed equal to the electron concentration of silver contact which is calculated based on Eq. (2).

$$n = \frac{8\sqrt{2}\pi m^{3/2}}{h^3}\left(\frac{2}{3}E_F^{3/2}\right) \tag{2}$$

In Eq. (2), h is the Planck constant, m is the electron mass, and E_F is the Fermi level which is equal to the metal workfunction (4.29 eV). By substituting values of parameters in Eq. (2), the Ag concentration is around 10^{23} cm^{-3}. The photodoping simulation, exercised with Silvaco's ATLAS device simulator [28], is based on the reaction, expressed in Eq. (3) which is the standard reduction–oxidation (RedOx) reaction for active metals in ChG films. Neutral Ag atoms have tendency to lose one electron, because the highest energy of the atomic valence state is above the conduction band edge of the ChG material. Therefore; Ag atoms are readily ionized at the anode/ChG interface and the forward activation energy (0.5 eV) is assumed smaller than the reverse activation energy (0.7 eV). In Eq. (3), the forward and reverse rate constants are assumed unit. Due to the higher diffusivity of Ag$^+$ as well as their capacity to drift in the presence of a local electric field, silver ions will transport into the films within several monolayers of the Ag-ChG interface. The diffusivity (D) of each species is calculated with Eq. (4), where a is the average hopping distance, ν is the attempt to escape frequency, E_A is the activation energy for hopping, k is Boltzmann's constant, and T is material temperature. E_A can be directly obtained from atomistic calculations using the nudged elastic band method [29]. This method is not the exact technique but is robust yielding a complete reaction path along with the activation energy. The diffusivity parameters for Ag and Ag$^+$ are listed in Table 2. The relation of the mobility (μ) and D is based on the Einstein relation presented in Eq. (5). Based on the values of the diffusivity and mobility the Ag species is essentially immobile in the glass film.
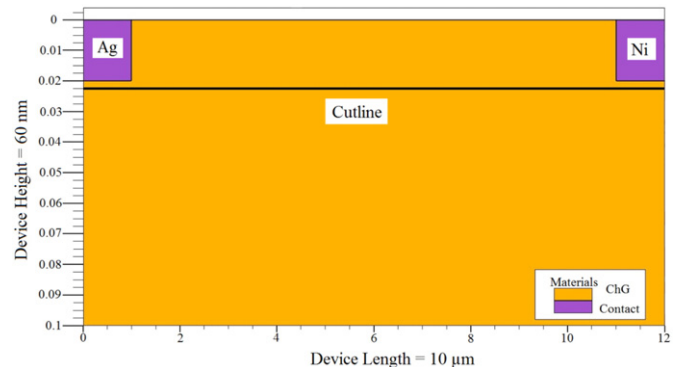
$$Ag \leftrightarrow Ag^+ + e^- \tag{3}$$

Fig. 2. Cross-section schematic of the simulation structure.