

OPEN ACCESS

Analytical Relationship between Anion Formation and Carrier-Trap Statistics in Chalcogenide Glass Films

To cite this article: M. Saremi et al 2015 ECS Electrochem. Lett. 4 H29

View the article online for updates and enhancements.

You may also like

 Non-isothermal crystallization kinetics and memory switching properties of TI-Se-Ge-Sb chalcogenide semiconductor alloy for thermally stable phase change memory applications

E G El-Metwally and A M Ismail

- Enhanced mid-infrared gas absorption spectroscopic detection using chalcogenide or porous germanium waveguides

waveguides Rami Zegadi, Nathalie Lorrain, Loc Bodiou et al.

- <u>Research progress of third-order optical</u> <u>nonlinearity of chalcogenide glasses</u> Xiao-Yu Zhang, , Fei-Fei Chen et al.



This content was downloaded from IP address 3.144.104.29 on 08/05/2024 at 19:43



Analytical Relationship between Anion Formation and Carrier-Trap Statistics in Chalcogenide Glass Films

M. Saremi,^{a,*,z} H. J. Barnaby,^a A. Edwards,^b and M. N. Kozicki^a

^a School of Electrical, Computer and Energy Engineering, Arizona State University, Tempe, Arizona 85287, USA ^bAir Force Research Laboratory, Space Vehicles Directorate, Kirkland Air Force Base, New Mexico 87117, USA

An analytical mapping for electron trapping in chalcogenide glass (ChG) films is derived which equates anion formation (dissolution) reactions and carrier-trap statistics. Glass binaries composed of chalcogen atoms contain high densities of negative charge that result from chemical reactions involving free electrons. This process of anion formation and dissolution between an electron and a neutral species is shown to be equivalent to standard models for carrier statistics. The derived equivalence reduces chemical reaction equations into statistics calculations performed through conventional semiconductor device simulation. The proposed mapping is shown to be valid for both equilibrium and steady state photogeneration conditions.

© The Author(s) 2015. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0061507eel] All rights reserved.

Manuscript submitted January 13, 2015; revised manuscript received April 13, 2015. Published May 15, 2015.

One important, although often overlooked, aspect of modern solid state materials and devices is the relationship between electrical and chemical effects.¹ In solid state electrolytes, for example, when electrons are released from an atom, the resulting positively charged ions can transport under an electric field. The process of oxidation can be reversed when an ion captures an electron through reduction.^{1–10} Through these reduction-oxidation (RedOx) processes, atoms converted to ions at one location can be deposited at another. The ion-conducting materials are often compounds of oxygen (O),^{11–19} sulfur (S),^{20–23} and selenium (Se)^{5,24–30} characterized by their relatively high ion mobility.¹

One of the main applications for solid electrolytes/ion conductors is in nano-ionic memristive nonvolatile memory devices, e.g., Conductive Bridge Random Access Memory (CBRAM) based on the Programmable Metallization Cell (PMC) technology platform.³¹ In CBRAM, the ion conductors are often chalcogenide glasses (ChG), typically alloys of group IV elements with those of group VI. Among the unique properties of ChG materials is their ability to be photodoped. Photodoping (photodiffusion) is characterized by the incorporation of metals (Ag, Cu) into the glass upon exposure to light. During photodoping the negatively charged chalcogen atoms and positively charged metallic ions form intrinsic electric fields that can be sufficient for the metallic ions to overcome the barrier energy at the interface. The difference in electrochemical potentials facilitates the penetration of ions into ChG materials during exposure.³²⁻³⁴ The relatively rigid covalent bonds mixed with soft van der Waals interconnections enable the ChG materials to form traps where electrons, generated by light or ionizing radiation, are absorbed.⁴ As shown in Eq. 1, an initially twofold covalently bonded chalcogenide atom can turn into an anion possessing a single covalent bond and an excess electron,4,35

$$C_2^0 + e^- \to C_1^-.$$
 [1]

While there have been significant refinements to the photodoping process to optimize it for use in current technology applications, several questions regarding the physics of photodoping remain unsolved. For example, the precise role anions play in the photo-induced diffusion of metal into GhG films is not well understood. Modeling chemical reactions with carrier statistics enables standard semiconductor Poisson solvers to be used in the analysis of photodoping as well as ion transport and RedOx processes. In order to investigate the relationship between anion formation/ dissolution and well known principles of device physics, we propose an equivalence mapping between the chemical reaction presented in Eq. 1 and conventional semiconductor device theory equations, by treating the chalcogenide atom as an acceptor-like trap. The physical model, which utilizes Shockley-Read statistics³⁶ is shown to be equivalent to anion formation and dissolution reaction models in both equilibrium and non-equilibrium steady state conditions (i.e., constant photogeneration). This model can be generalized to all chemical reactions in which there is an electron and/or hole reaction with immobile neutral and/or charged species. The model is verified by 2D Technology Computer-Aided-Design (TCAD) simulations.³⁷

Mathematical Model

TCAD simulations are performed with Silvaco's ATLAS device simulator.³⁷ Unlike, most device simulation tools, ATLAS *is* capable of simulating the transport of and chemical reactions between a limited number of atomic species. Transport properties for each species are primarily controlled by the diffusion coefficient (D) which is defined as

$$D = a^2 v \exp\left(\frac{-E_a}{kT}\right),$$
[2]

where *a* is the average hopping distance, v is the attempt (to escape) frequency, and E_a is the activation energy for hopping. Parameters *k* and *T* have their common meanings as Boltzmann's constant and material temperature respectively. Because we are equating trapping statistics to chemical reactions and that traps generally do not move in a material, we assume that the chalcogenide atoms (both neutral and charged) are immobile. Thus the diffusion coefficient for each species (C_2^0 , and C_1^-) should be very small ($D \ll 10^{-10}$ cm²/s). In equilibrium, the forward reaction rate is equal to the reverse reaction rate in each chemical reaction as follows:

$$fN_{C_2^0}n\exp\left(\frac{-E_{af}}{kT}\right) = rN_{C_1^-}\exp\left(\frac{-E_{ar}}{kT}\right).$$
 [3]

In Eq. 3, the left side of the equation is the forward reaction, where f is the forward reaction rate, E_{af} is the forward activation energy, $N_{C_2^0}$ and n are C_2^0 and electron concentrations, respectively. The right side of Eq. 3 is the reverse reaction, where r is the reverse reaction rate, E_{ar} is the activation energy and $N_{C_1^-}$ is the concentration of C_1^- in Eq. 1. Using standard carrier statistics equations, the ratio of C_1^- to the total concentration of $C_1^- + C_2^0$ is calculated as

$$\frac{N_{C_1^-}}{N_{C_2^0} + N_{C_1^-}} = \frac{f}{r} n_i \exp\left(\frac{E_{Fn} - E_i}{kT}\right) \exp\left(\frac{E_{ar} - E_{af}}{kT}\right), \quad [4]$$

where E_{Fn} is the quasi Fermi energy level for electrons and n_i is the intrinsic carrier concentration in the material. An acceptor-like trap is neutral when empty and negatively charged when filled with an electron. Based on this definition, we may define the species C_2^0 in Eq. 1 as

^{*}Electrochemical Society Student Member.

^zE-mail: msaremi1@asu.edu

an acceptor-like trap. Donor-like traps can be used for the complementary equation of Eq. 1 ($C_2^0 \rightarrow C_1^+ + e^-$). The probability of ionization of acceptor-like traps assumes that the capture cross sections are constant for all energies and the ionization probability is calculated as³⁸

$$F_{tA} = \frac{v_n SIGNn + e_{pA}}{v_n SIGNn + v_p SIGPp + e_{nA} + e_{pA}},$$
[5]

where *SIGN* and *SIGP* are the carrier capture cross sections for electrons and holes respectively, and v_n and v_p are the thermal velocities for electrons and holes. For acceptor-like traps, the electron and hole emission rates, e_{nA} and e_{pA} , are defined as

$$e_{nA} = DEGENv_n SIGNn_i \exp\left(\frac{E_t - E_i}{kT}\right),$$
 [6]

and

$$e_{pA} = \frac{1}{DEGEN} v_p SIGPn_i \exp\left(\frac{E_i - E_i}{kT}\right),$$
[7]

where E_i is the intrinsic Fermi level, E_t is the trap energy level, and *DEGEN* is the degeneracy factor of the trap center. *DEGEN* takes into account that spin degeneracy exists and that empty and filled traps have different spin and orbital degeneracy. To simplify equations, we set *DEGEN* equal to 1. Since holes play no role in the reaction described in Eq. 1, we assume *SIGP* \ll *SIGN* to eliminate hole reactions from the statistical calculation. Without holes, the ionization probability of acceptor-like traps is reduced to Eq. 8, the standard Fermi-Dirac statistical form,³⁹

$$F_{tA} = \frac{1}{1 + \exp\left(\frac{E_t - E_{Fn}}{kT}\right)}.$$
[8]

Using the above equations, it is possible to define an acceptor-like trap that produces an effect equivalent to the reaction presented in Eq. 1. By setting Eqs. 4 and 8 equal, the equivalent acceptor-like trap energy is found to be a function of the forward and reverse reaction rates and activation energies of the chemical reaction, i.e.,

$$E_t = kT \ln\left(\frac{r}{fn_i}\right) + E_{af} - E_{ar}.$$
[9]

It should be noted that in Eq. 9 E_{Fn} is assumed without loss of generality to be pinned to zero energy when no bias voltage is applied. The significant advantage of Eq. 9 is that it is applicable to both equilibrium and steady-state conditions. To verify Eq. 9, we use the numerical device simulator ATLAS to calculate equilibrium and steady-state (non-equilibrium) solutions on a ChG material often used in cation-based memristors. Fig. 1 shows the 2D structure used



Figure 1. Cross-section of the ChG simulation structure, i.e., $Ge_{30}Se_{70}$ material sandwiched between ohmic anode and cathode contacts.

Table I. Parameters of Ge₃₀Se₇₀ material [42].

Material Parameter for Ge ₃₀ Se ₇₀	Value
Bandgap (eV)	1.86
Affinity (eV)	3.05
Density of States in Conduction Band (per cc)	1×10^{19}
Density of States in Valence Band (per cc)	1×10^{20}
Electron Mobility (cm ² /Vs)	10^{-5}
Hole Mobility (cm ² /Vs)	10
Dielectric Constant	40.9

Table II. Typical parameters of the chemical reaction based on Eq. 1.

Parameter	Value
F	1
R	8×10^{19}
E_{af}	0.7 eV
Ear	1 eV

for the simulations while there is not any bias applied to the device. The bulk material is a pure chalcogenide glass ($Ge_{30}Se_{70}$) without any metallic dopants and the device anode and cathode terminals are defined for simplicity as neutral contacts. The parameters of the $Ge_{30}Se_{70}$ material and parameters for the chemical reaction of Eq. 1 are listed in Table I⁴⁰ and Table II, respectively. The length of the device, which corresponds to the distance between two contacts, is 10 μ m and its height/thickness is also 60 nm.

By substitution of parameters from Table II in Eq. 9, the trap energy is found to be 0.65 eV above E_{Fn} . As previously mentioned, the ATLAS code can solve not only standard carrier statistics for solid state material, but chemical reactions similar to those shown in Eq. 1 between a limited number of species. This allows us to use ATLAS to compare both methods and thereby validate the equivalence function, Eq. 9. We model the chemical reaction in one simulation with the initial C_2^0 concentration of 10^{20} cm⁻³ and a second simulation uses acceptor-like traps of equal concentration with trap energies set by Eq. 9 (specifically 0.65 eV above E_{Fn}). Simulations are performed under equilibrium and non-equilibrium steady-state conditions. For the non-equilibrium case, carrier generation is modeled with a virtual light source. As mentioned above, exposure to light, specifically UV, is a common post-processing manufacturing technique, used for some variants of ChG-based non-volatile memory. For the steady state light exposure condition, a fixed generation rate (G) is set to $2.72 \times$ 10²¹ /cm³s which is consistent with what might be expected during exposure to UV light at the power density of 10 mW/cm².

Fig. 2 plots C_1^- , from the chemical reaction solver method and compares the results to the concentration of filled acceptor-like traps calculated from carrier-trap statistics for both equilibrium and non-equilibrium steady-state (photogeneration). As seen in Fig. 2, there is an excellent agreement between chemical reaction results and those of



Figure 2. The C_1^- concentration vs filled trap concentration in the equilibrium and steady-state (photogeneration).



Figure 3. Filled trap concentration vs trap energy in the equilibrium. The middle point (trap energy of 0.65 eV) is obtained from chemical reaction simulation.

model with traps. The sensitivity of the filled trap concentration to trap energy is shown in Fig. 3. As shown in this figure, the concentration in the log scale is linearly dependent to the trap energy with constant slope of 1/[log(e)kT], which can be derived from Eq. 8 (e is the Euler's constant).

Conclusions

An accurate mathematical function that relates the parameters of anion formation/ dissolution reactions to the energies of equivalent acceptor-like traps is derived. This is done by equating anion reaction in equilibrium (Eq. 4) to the conventional carrier statistics captured in the Fermi-Dirac equation (Eq. 8). Through device simulation, it is verified that this equivalence relation can be accurately extended to non-equilibrium steady state relationship while it is independent of the parameters of a typical photogeneration source. Therefore, it enables us to model the impact of reaction species in ChG materials in both equilibrium and in the steady state conditions that exist during photogeneration. This equivalence can be used to simply model anion reactions in standard TCAD tools. The model may be easily extended to other chemical reactions including positively charged species and/or holes.

Acknowledgment

This work was funded in part by the Defense Threat Reduction Agency under grant no. HDTRA1-11-10055 and the Air Force Research Laboratory Det 8/RVKVE under grant no. FA9452-13-1-0288.

References

- M. N. Kozicki and M. Mitkova, "Mass transport in chalcogenide electrolyte films – materials and applications," *Journal of Non-Crystalline Solids*, 352, 567 (2006).
- D. B. Strukov and R. S. Williams, "Exponential ionic drift: fast switching and low volatility of thin-film memristors," *Appl Phys A*, 94, 515, (2009).
- S. Stehlik, K. Shimakawa, T. Wagner, and M. Frumar, "Diffusion of Ag ions under random potential barriers in silver-containing chalcogenide glasses," *J. Phys. D: Appl. Phys.*, 45, 205304, (2012).
- M. Mitkova and M. N. Kozicki, "Ag-photodoping in Ge-chalcogenide amorphous thin films – reaction products and their characterization," *Journal of Physics and Chemistry of Solids*, 68, 866 (2007).
- M. Frumar and T. Wagner, "Ag doped chalcogenide glasses and their applications," Solid State and Materials Science, 7, 117 (2003).
- S. Kim, S. Choi, and W. Lu, "Comprehensive physical model of dynamic resistive switching in an oxide memristor," ACS Nano, 8, 2369 (2014).
- J. D. Greenlee, W. L. Calley, M. W. Moseley, and W. A. Doolittle, "Comparison of interfacial and bulk ionic motion in analog memristors," *IEEE Transactions on Electron Devices*, 60, 427 (2013).
- Electron Devices, 60, 427 (2013).
 8. S. Yu and H.-S. P. Wong, "Compact modeling of conductive-bridge random-access memory (CBRAM)," *IEEE Transactions on Electron Devices*, 58, 1352 (2011).

- R. Waser, R. Dittmann, G. Staikov, and K. Szot, "Redox-based resistive switching memories-nanoionic mechanisms, prospects, and challenges," *Adv. Mater.*, 21, 2632 (2009).
- F. Pan, S. Yin, and V. Subramanian, "A detailed study of the forming stage of an electrochemical resistive switching memory by KMC simulation," *IEEE Electron Device Letters*, 32, 949 (2011).
- E. Antolini, "LiCoO₂: Formation, structure, lithium and oxygen nonstoichiometry, electrochemical behavior and transport properties," *Solid State Ion.*, **170**, 159 (2004).
- F. Argall, "Switching phenomena in titanium oxide thin films," *Solid State Electron*, 11, 535 (1968).
- A. Baikalov, Y. Q. Wang, B. Shen, B. Lorenz, S. Tsui, Y. Y. Sun, Y. Y. Xue, and C. W. Chu, "Field-driven hysteretic and reversible resistive switch at the Ag-Pr_{0.7}Ca_{0.3} MnO₃ interface," *Appl. Phys. Lett.*, 83, 957 (2003).
- W. R. Hiatt and T. W. Hickmott, "Bistable switching in niobium oxide diodes," *Appl. Phys. Lett.*, 6, 106 (1965).
- C.-Y. Lin, C.-Y. Wu, T.-C. Lee, F.-L. Yang, C. Hu, and T.-Y. Tseng, "Effect of top electrode material on resistive switching properties of ZrO₂ film memory devices," *IEEE Electron Device Lett.*, 28, 366 (2007).
- A. Odagawa, T. Kanno, and H. Adachi, "Transient response during resistance switching in Ag/Pr0.7Ca0.3 MnO3/Pt thin films," *J. Appl. Phys.*, 99, 016101–016101 (2006).
- H. Sim, D. Choi, D. Lee, S. Seo, M.-J. Lee, I.-K. Yoo, and H. Hwang, "Resistanceswitching characteristics of polycrystalline Nb₂O₅ for nonvolatile memory application," *IEEE Electron Device Lett.*, 26, 292 (2005).
- C. Schindler, S. C. P. Thermadam, R. Waser, and M. N. Kozicki, "Bipolar and unipolar resistive switching in Cu-doped SiO₂," *IEEE Trans. Electron Devices*, 54, 2762 (2007).
- M. N. Kozicki, C. Gopalan, M. Balakrishnan, and M. Mitkova, "A low-power nonvolatile switching element based on copper-tungsten oxide solid electrolyte," *IEEE Trans. Nanotechnol.*, 5, 535 (2006).
- Z. Wang, P. B. Griffin, J. McVittie, S. Wong, P. C. McIntyre, and Y. Nishi, "Resistive switching mechanism in Zn_xCd_{1-x}S nonvolatile memory devices," *IEEE Electron Device Lett.*, 28, 14 (2007).
- T. Sakamoto, H. Sunamura, H. Kawaura, T. Hasegawa, T. Nakayama, and M. Aono, "Nanometer-scale switches using copper sulfide," *Appl. Phys. Lett.*, 82, 3032 (2003).
- K. Terabe, T. Hasegawa, T. Nakayama, and M. Aono, "Quantized conductance atomic switch," *Nature*, 433, 47 (2005).
- C. Pi, Y. Ren, and W. K. Chim, "Investigation of bipolar resistive switching and the time-dependent SET process in silver sulfide/silver thin films and nanowire array structures," *Nanotechnology*, 21, 085709 (2010).
- J. Orava, T. Kohoutek, T. Wagner, Z. Cerna, M. Vlcek, L. Benes, B. Frumarova, and M. Frumar, "Optical and structural properties of Ge-Se bulk glasses and Ag-Ge-Se thin films," *Journal of Non-Crystalline Solids*, 355, 1951 (2009).
- M. Jin, P. Boolchand, and M. Mitkova, "Heterogeneity of molecular structure of Ag photo-diffused," *J. Non-Cryst. Solids*, 354, 2719 (2008).
- M. N. Kozicki, M. Park, and M. Mitkova, "Nanoscale memory elements based on solid-state electrolytes," *IEEE Trans. Nanotechnol.*, 4, 331 (2005).
- S. Kaeriyama, T. Sakamoto, H. Sunamura, M. Mizuno, H. Kawaura, T. Hasegawa, K. Terabe, T. Nakayama, and M. Aono, "A nonvolatile programmable solidelectrolyte nanometer switch," *IEEE J. Solid-State Circuits*, 40, 168 (2005).
- M. A. Urena, A. A. Piarristeguy, M. Fontana, and B. Arcodo, "Ionic conductivity (Ag⁺) in AgGeSe glasses," *Solid State Ionics*, **176**, 505 (2005).
- R. Soni, M. Meier, A. Rüdiger, B. Holländer, C. Kügeler, and R. Waser, "Integration of "Ge_xSe_{1-x}" in crossbar arrays for non-volatile memory applications," *Microelectron. Eng.*, 86, 1054 (2009).
- M. Saremi, S. Rajabi, H. J. Barnaby, and M. N. Kozicki, "The Effects of Process Variation on the Parametric Model of the Static Impedance Behavior of Programmable Metallization Cell (PMC)," *MRS Proceedings*, 1692, cc09–39 (2014).
- M. Kozicki, M. Mitkova, M. Park, M. Balakrishnan, and C. Gopalan, "Information Storage using Nanoscale Electrodeposition of Metal in Solid Electrolytes," *Superlattices and Microstructures*, 34, 459 (2004).
- A. V. Kolobov, S. R. Elliott, and M. A. Taguirdzhanov, "On the mechanism of photodoping in vitreous chalcogenides," *Philos. Mag. B*, 61, 859 (1990).
- I. Z. Indutni, V. A. Danko, A. A. Kudryavtsev, E. V. Michailovskaya, and V. I. Minko, "Photodoping in As2S3 – Ag structure," *J. Non-Cryst. Sol.*, 185, 176 (1995).
- A. V. Kolobov and G. E. Bedel'baeva, "Effect of conductive substrate on dissolution and lateral diffusion of metals in vitreous chalcogenides," *Philos. Mag. B*, 64, 21 (1991).
- M. Kastner, D. Adler, and H. Fritzsche, "Valence-alternation model for localized gap states in lone-pair semiconductors," *Physical Review Letters*, 37, 1504 (1976).
- W. Shockley and W. T. Read, "Statistics of the recombinations of holes and electrons," *Phys. Rev.*, 87, 835 (1952).
- SilvacoATLAS Device Simulator SilvacoInc., Santa Clara, CA, USA http://www.silvaco.com/products/device_simulation/atlas.html.
- J. G. Simmons and G. W. Taylor, "Nonequilibrium steady-state statistics and associated effects for insulators and semiconductors containing an arbitrary distribution of traps," *Phys. Rev. B*, 4, 502- (1971).
- P. A. M. Dirac, "On the theory of quantum mechanics," in *Proc. R. Soc. Lond.*, **112**, 661 (1926).
- S. Rajabi, M. Saremi, H. J. Barnaby, A. Edwards, M. N. Kozicki, M. Mitkova, D. Mahalanabis, Y. Gonzalez-Velo, and A. Mahmud, "Static impedance behavior of programmable metallization cells," *Solid-State Electronics*, **106**, 27 (2015).