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Simulation of electronic/ionic mixed conduction in solid ionic memory devices

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Abstract

The electronic/ionic mixed conduction is examined in solid ionic memory devices by numerically solving the Poisson–Nernst–Planck equations using the computational platform PROPHET. The boundary conditions for the Poisson–Nernst–Planck system are determined based on the theoretical treatments as a Dirichlet type. The chemical composition of the mixed conductor under the reference electrode and the magnitude of applied biases are considered as important parameters in the simulation. The results show that the deviation of carrier distribution increases from the analytical solutions with the increase of applied biases and the decrease of the partial pressure of the non-metallic component near the reference electrode in solid ionic memory devices.

Keywords: Electronic/ionic mixed conduction; Solid ionic memory devices; Poisson–Nernst–Planck equations; PROPHET; Carrier distribution

1. Introduction

Fabrication of nanoscale electronic devices [1–3] has attracted significant attention to overcome the physical and economic limitations of current silicon-based semiconductor devices. In recent years, solid ionic memory devices have been proposed as promising candidates for next-generation non-volatile memory devices due to their high scalabilities, ease of fabrication and low operation voltages [4–6]. Unlike conventional silicon non-volatile memory devices, solid ionic memory devices are based on the electrochemical control of nanoscale quantities of metal ions and electronic carriers in thin films of mixed conductors. A silver or copper reference electrode and an inert electrode formed in contact with a silver- or copper-containing mixed conductor film creates a device in which information is stored via electrical changes caused by the reduction of silver or copper ions in mixed conductors. At rest, the conductance between two electrodes is very low. When a negative bias is applied to the inert electrode, the conductance increases very rapidly, because silver or copper ions can move inside the silver- or copper-containing mixed conductor, congregating into filaments that provide a conduction path between two electrodes. These filaments persist in time, but can be dissolved into the mixed conductor film by applying a positive bias of magnitude similar to the writing-pulse bias. The state can be read by applying a small negative bias.

In this paper, we study the combined electronic/ionic mixed conduction phenomena in solid ionic memory devices. By solving the Poisson–Nernst–Planck equations numerically, we obtain the steady-state distributions of charged carriers and metal chemical potentials within solid ionic memory devices. The chemical composition of the mixed conductor under the reference electrode and the magnitude of applied biases are considered as important parameters in the simulation. We also discuss the mechanism of the formation of metal filaments based on the obtained simulation results.

2. Theory

The charge carrier distribution is one of the essential aspects for understanding the operation mechanism of solid ionic memory devices. The transport equations for ionic and electronic carriers in a mixed conductor were

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evaluated by Riess [7] and by Nafe [8] based on a constant ionic conductivity approximation. Under this approximation, the electronic transport was decoupled from the ionic transport by fixing the ionic-transport characteristics.

To obtain the charge carrier distribution in memory structures more rigorously using the numerical method, self-consistent Poisson–Nernst–Planck model is given for carrier transport in mixed conductors. The mixed conductor is, for simplicity of notation, presented as XY. It is assumed to conduct one kind of ions X^+ and quasi-free electrons e^-. The Y sublattice is assumed to be immobile. The ions interact with the electrons to form neutral atoms:

$$X^+ + e^- \rightleftharpoons X. \tag{1}$$

The concentration of hole is assumed negligibly small.

In the one-dimensional planar geometry case, the Nernst–Planck model that describes the particle flux j of species k with both diffusion and drift component is given by

$$j_k = -D_k\left(\frac{dn_k}{dx}\right) - \frac{n_k D_k z_k q}{k_B T}\left(\frac{d\phi}{dx}\right), \tag{2}$$

where D is the diffusivity, n the carrier concentration, z the valance, q the magnitude of the electronic charge, k_B the Boltzmann's constant, T the temperature, and ϕ the electrical potential. The subscript k denotes specie k. At steady state the flux is constant. Therefore we obtain

$$\left(\frac{d^2 n_i}{dx^2}\right) + \frac{q}{k_B T}\left(\frac{dn_i}{dx}\right)\left(\frac{d\phi}{dx}\right) + \frac{q}{k_B T} n_i \left(\frac{d^2\phi}{dx^2}\right) = 0, \tag{3}$$

$$\left(\frac{d^2 n_e}{dx^2}\right) - \frac{q}{k_B T}\left(\frac{dn_e}{dx}\right)\left(\frac{d\phi}{dx}\right) - \frac{q}{k_B T} n_e \left(\frac{d^2\phi}{dx^2}\right) = 0, \tag{4}$$

for metal ion X^+ and quasi-free electron e^-, respectively. Formally Eqs. (3) and (4) are related by the Poisson equation

$$\left(\frac{d^2\phi}{dx^2}\right) = -\frac{q}{\varepsilon}(n_i - n_Y - n_e), \tag{5}$$

where ε is the permittivity of the mixed conductor, and n_Y the concentration of the immobile sublattice Y.

In solid ionic memory devices, the ionic current vanishes in a steady state, and it follows that

$$\frac{d\eta_i}{dx} = \frac{d\mu_i}{dx} + q\frac{d\phi}{dx} = 0, \tag{6}$$

where η denotes the electrochemical potential and μ the chemical potential. Then the difference in the electrochemical potential of the metal ion between two boundaries can be expressed as

$$\Delta\eta_i = \Delta\mu_i + q\,\Delta\phi = 0. \tag{7}$$

Eqs. (1) and (7) relate η_i, η_e, and μ_X:

$$\Delta\eta_i + \Delta\eta_e = \Delta\eta_e = \Delta\mu_e - q\,\Delta\phi = \Delta\mu_X. \tag{8}$$

The voltage V applied to the inert electrode is related to $\Delta\eta_e$ by

$$-qV = \eta_e[E(L)] - \eta_e[E(0)] = \Delta\eta_e, \tag{9}$$

where L is the device length, $E(L)$ is the inert electrode, and $E(0)$ the reference electrode.

Eqs. (7)–(9) yield

$$-qV = \Delta\mu_X = \Delta\mu_e - q\,\Delta\phi = \Delta\mu_e + \Delta\mu_i. \tag{10}$$

Based on Boltzmann statistics, Eq. (10) can be expressed as

$$-qV = k_B T\, n\left(\frac{n_e(L)}{n_e(0)}\right) + k_B T\,\ln\left(\frac{n_i(L)}{n_i(0)}\right), \tag{11}$$

where $n_e(L)$, $n_i(L)$ are the electron and metal ion concentration at the boundary with the inert electrode, and $n_e(0)$, $n_i(0)$ are the electron and metal ion concentration at the boundary with the reference electrode.

Based on the charge neutrality approximation, the concentration of excess ions (δn) formed by the applied voltage can be assumed to have the same value with that of excess electrons:

$$n_i(L) = n_i(0) + \delta n, \tag{12}$$

$$n_e(L) = n_e(0) + \delta n. \tag{13}$$

Inserting Eqs. (12) and (13) into Eqs. (7) and (11), we obtain

$$\Delta\phi = -\frac{\Delta\mu_i}{q} = -\left(\frac{k_B T}{q}\right)\ln\left(\frac{n_i(0) + \delta n}{n_i(0)}\right), \tag{14}$$

and

$$\delta n = \Big(-[n_i(0) + n_e(0)] + \Big([n_i(0) + n_e(0)]^2 - 4\left(1 - e^{-qV/k_B T}\right) n_i(0) n_e(0)\Big)^{1/2}\Big) \Big/ 2. \tag{15}$$

The chemical composition of the mixed conductor under the inert electrode is not fixed by interaction with the surrounding since this interaction is partially blocked by the electrode. Instead, the composition is determined by the temperatures, applied biases, and the chemical composition of mixed conductors under the reference electrode. Using Eqs. (14) and (15), the boundary conditions for the Poisson–Nernst–Planck equations can be determined by a Dirichlet type.

3. Results and discussion

The model described above was implemented using the computational platform PROPHET [9]. The PROPHET simulator provides a convenient scripting framework for defining, discretizing, and solving an arbitrary system of partial differential equations. Physical properties for simulation can be assigned to the different regions of the computational domain at run time. The non-linear