A Unified Model of Metallic Filament Growth Dynamics for Conductive-Bridge Random Access Memory (CBRAM)

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Abstract—**A unified model is developed for the first time to explain the metallic filament growth from either anode or cathode for conductive-bridge random access memory (CBRAM). Both electrochemical reactions and ion/electron transport are considered. Simulation results reveal that diffusion coefficient and mobility of cations in the electrolyte are responsible for determining the growth direction of the conductive metallic-filament. The simulation results for the forming process of CBRAM are compared to experimental data and good agreement is achieved.**

Keywords—Conductive-bridge random access memory ; CBRAM; metallic filament; growth direction

I. INTRODUCTION

As one of the most promising candidates for NAND flash memory, conductive-bridge resistive memory (CBRAM) has high performance in many aspects such as fast speed, and low power consumption. [1] Previous experimental and theoretical studies on CBRAM have provided reasonable understanding on filaments growth from the cathode towards anode. Recently, new experiments have been reported that filament could also be grown from the anode as well. [2][3] Disputes regarding the exact growth mechanism still exist and theoretical work is highly desired to clarify the underlying principles. In this paper, we have developed a unified physical model to describe two metallic filament growth modes, which are growths from either the cathode or anode. In addition to the chemical reaction on the surfaces of electrodes, also considered in the electrolyte are chemical reaction as well as ion/electron transport in the presence of the electric field, both of which are not fully reflected in the previous CBRAM models. The relationship between the two filament growth modes is also discussed.

II. MODELING AND SIMULATION

Based on recent experiment results of CBRAM [2][3], two contrary directions of filament growth have been observed with different electrolytes (called the work medium). The switching processes are depicted in Figs. 1 (b-c), respectively. In order to find out the most vital factors that take effects in filament growth dynamics, a one-dimensional (1D) model has been proposed in the scenario shown in Fig. 1(a).
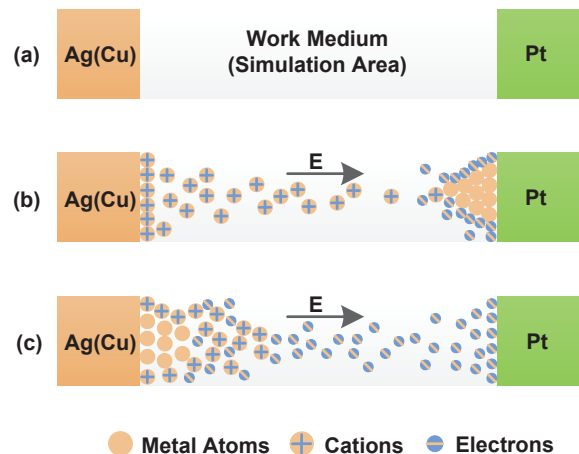

Fig.1 (a) 1D simulation schematic. (b) Illustration of filament growth from cathode to anode. (c) Illustration of filament growth from anode to cathode.

A 250nm thick layer of electrolyte is sandwiched between anode (e.g., made of Ag or Cu) and cathode (Pt), where cations (e.g. Ag^+ for Ag-anode or Cu^{2+} for Cu-anode) and electrons move under the influence of electric field caused by the applied bias. Further considered are the cation reduction (through combination with electrons) and oxidation of metallic atoms within the electrolyte. In this paper, we mainly consider the forming process, which is generally required to set the initial switching condition for RRAMs. The forming process consists of four steps: the oxidation of atoms on the surface (adjacent to the electrolyte) of the anode; the movement of cations and electrons, which are in opposite direction in the electrolyte; redox reaction for metallic species (reduction for cations and oxidation for atoms) in the electrolyte; and finally the reduction of cations on the surface of the cathode. The three unknown variables to be solved in our simulation within electrolyte are mobile particles cations (in our case, we take Ag^+) and electrons, and immobile metal atoms (here it is Ag). There are three corresponding equations governing these variables. In the following, we explain the rational for these equations, which are listed in Table I and solved using numerical analysis.

A. Continuity equations for cations and electrons (Eqs.(1)-(2))

In this model ion transport plays an important role to explain filament growth dynamics. Ion transport including both diffusion and drift varies apparently with different electrolytes in the work medium. The oxidation of metallic atoms and reduction of cations serve as generation and recombination of cations, respectively. The oxidation and reduction rates depend on the concentration of cations and electrons, which is determined by ion and electron transport and chemical reaction induced by the electrical field. Electrical field distribution in the work medium is calculated by solving the Poisson's equation.

Electron transport has almost been neglected in previous modeling works, because previous works only focus on filament growth from cathode and, in that case, ion transport outweighs electron transport. In the case of filament growth from anode to cathode, electron transport makes important contribution to the process and has been considered in this model.

Initially no metal atoms or cations exist in the electrolyte. When applying voltage on the device, certain amount of cations generated by oxidation reaction on the anode serves as the initial condition. Boundary conditions are listed below the equations (Eqs. (1-2)). We assume that the flow of cations from the anode and the flow of electrons from the cathode are remained to be a constant value in the process, since the anode can always provide enough metal atoms needed for filament growth. These two flows (cation flow from the anode and electron flow from the cathode) are equal to each other in value because the overall charge neutrality for the entire device is required. The incoming flux of cations on the cathode must be zero since no cations can accumulate on the cathode. This is also true of the situation of electrons on the anode. Once an electron reaches the anode, it will be drifted to the external electrical wire immediately.
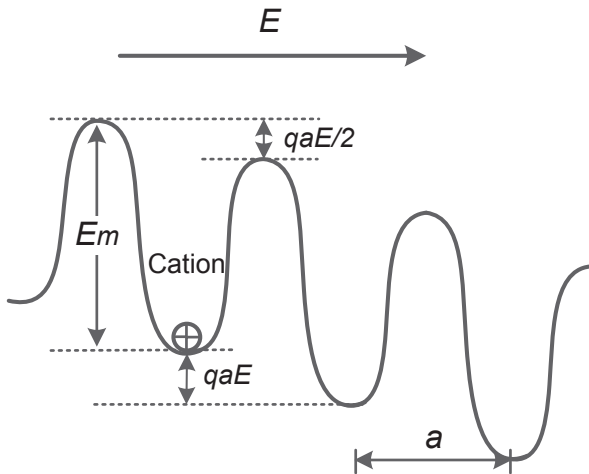

Fig. 2 Schematic of cation migration under electrical field. The migration energy for a cation declines in the direction of electrical field, thus the velocity of the cation has been accelerated.

TABLE I Physical models in the simulation

Eq.(1) Ion Continuity Equation

$$\frac{\partial C_{Ag^+}}{\partial t} = D_{Ag^+}\frac{\partial^2 C_{Ag^+}}{\partial x^2} - v_{Ag^+}\frac{\partial C_{Ag^+}}{\partial x} + K_o \cdot C_{Ag} - K_r \cdot n_{e^-} \cdot C_{Ag^+}$$

Boundary conditions:

$$F_{Ag^+}\big|_{x=0} = -D_{Ag^+}\frac{\partial C_{Ag^+}}{\partial x} + v_{Ag^+} \cdot C_{Ag^+} = C$$

$$F_{Ag^+}\big|_{x=L} = -D_{Ag^+}\frac{\partial C_{Ag^+}}{\partial x} + v_{Ag^+} \cdot C_{Ag^+} = 0$$

Eq.(2) Electron Continuity Equation

$$\frac{\partial n_{e^-}}{\partial t} = D_{e^-}\frac{\partial^2 n_{e^-}}{\partial x^2} + v_{e^-}\frac{\partial n_{e^-}}{\partial x} + K_o \cdot C_{Ag} - K_r \cdot n_{e^-} \cdot C_{Ag^+}$$

Boundary conditions:

$$F_{e^-}|_{x=0} = -D_{e^-}\frac{\partial n_{e^-}}{\partial x} - v_{e^-} \cdot n_{e^-} = 0$$

$$F_{e^-}|_{x=L} = -D_{e^-}\frac{\partial n_{e^-}}{\partial x} - v_{e^-} \cdot n_{e^-} = C$$

Eq.(3) Generation Rate of Metal Atoms

$$\frac{\partial C_{Ag}}{\partial t} = -K_o \cdot C_{Ag} + K_r \cdot n_{e^-} \cdot C_{Ag^+}$$

Eq.(4) Diffusion Coefficient Model[4]

$$D_{Ag^+} = D_{Ag_0^+} \cdot exp\left(-\frac{E_m}{kT}\right) , D_{Ag_0^+} = \frac{1}{2} \cdot a^2 \cdot f$$

Eq.(5) Drift velocity Model[4]

$$v_{Ag^+} = a \cdot f \cdot \exp(-\frac{E_m}{kT}) \cdot sinh(\frac{qEa}{2kT})$$

C_{Ag^+} and C_{Ag} are for Ag+ and Ag concentration respectively. D_{Ag^+} and v_{Ag^+} are for diffusion coefficient and mobility of Ag+. D_{e^-} and v_{e^-} are for diffusion coefficient and mobility of Ag+. K_o and K_r are for oxidation and reduction rate of Ag and Ag+. n_{e^-} is for electron concentration. f is for the attempt-to-escape frequency. a is for the effective hopping distance. E_m is for migration barrier. k is for the Boltzmann constant and T is for temperature. q is for electron charge.

B. Generation rate of metal atoms (Eq. (3))

On the surface of anode/cathode, only oxidation/reduction is considered because the reverse reaction on the electrodes are too weak to take any effect in the process. However, in the electrolyte, both oxidation and reduction reactions are included. The process of cations in the electrolyte being reduced to generate metal atoms and the

oxidation of metal atoms to reduce the number of atoms is related to the recombination and generation of cations and electrons respectively in Eqs. (1)- (2). The relative value of these two terms determines the generation rate of metal atoms. We describe this process in a rate equation, not as a continuity equation, because metal atoms are unmovable in the electrolyte. The coefficients K_o and K_r are used to illustrate the reaction rates for oxidation and reduction reaction, respectively. The reaction rates in the electrolyte are much smaller than those on the electrode surface. Oxidation and reduction reaction rates in the electrolyte are directly related to the distribution of metal atom and electron concentrations as described in Eq. (3). Both reactions are described in the differential equation to determine the distribution of metal atom concentration in the electrolyte.

C. Calculation of diffusion coefficient and mobility (Eqs. (4)-(5))[4]

According to the 1D ion model in Mott theory [4], the diffusion coefficient of metallic ions obeys Arrhennius plot in Eq. (4). Both the diffusion coefficient and mobility are closely related to migration barrier E_m (~1eV), attempt-to-escape frequency f (~10^{13}Hz) and the hopping distance a (~1 nm).[4] The drift velocity is also affected by the electric field in a nonlinear relationship in Eq. (5) as the schematic shown in Fig. 2. Diffusion coefficient and mobility of electrons obey the Einstein relationship and are considered as constants in this model.
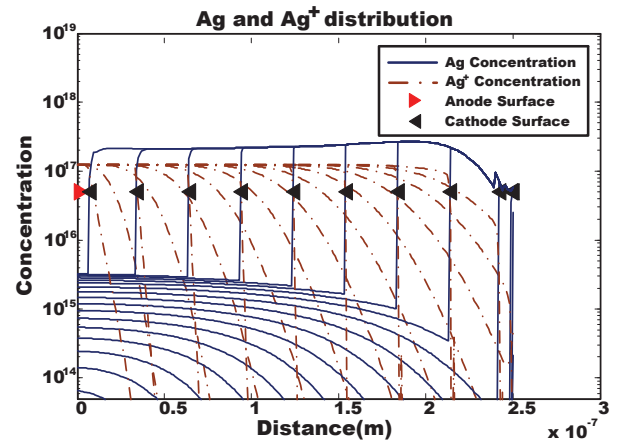
D. Filament growth

In the initial condition, we treat both electrodes as filament surfaces. A threshold value of metal atom concentration is set as a requirement for the successful formation of metallic filament. During the simulation, once the local concentration of cations reaches a preset threshold, the filament will grow accordingly. The direction of filament growth is determined naturally by the judgment of metal atom concentration. The surface of the filament is updated in every time step.
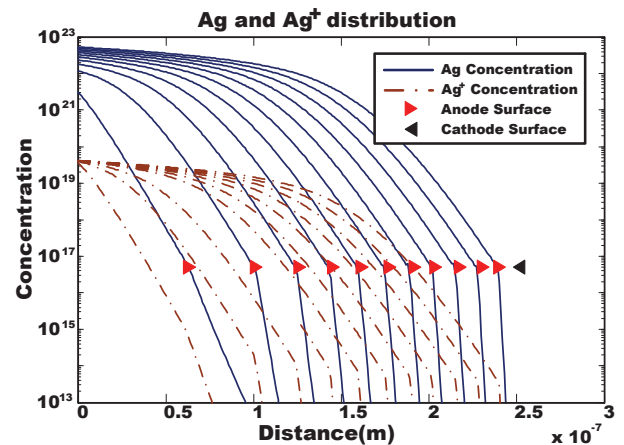
III. RESULTS AND DISCUSSION

In the simulation, we obtain both filament growth dynamics by only adjusting the value of the migration barrier E_m (~1eV [4]), which determines diffusion coefficient and mobility of cations in different electrolytes and dominates the competition between ion transport speed and reduction reaction rate. All the parameters used for simulation are listed in Table II [4][5]. The simulation results have been illustrated in Figs. 3 (a-b), corresponding to Figs. 1 (b-c). In Fig. 1(b), cations generated from oxidation reaction on the anode depart from the anode and finally get reduced on the cathode. For some electrolytes, such as GeS$_2$, which have high mobility and diffusion coefficient for cations (Ag$^+$ or Cu^{2+}), cations can obtain a relatively high transport speed towards the cathode. In this case, the velocity of ion transport outweighs that of redox reactions in the electrolyte. The mass reduction then happens on the surface of cathode, resulting in the filament growth from cathode towards anode. The simulation results

TABLE II Parameters used in 1D modelling[4][5]

Parameters	Filament growth from cathode to anode	Filament growth from anode to cathode
a	1nm	
f	2×10^{13}Hz	
E_m	0.7eV	1.0eV
T	598K	
K_r	10^{-14}(TE), 10^{-14}(WM),10^{-9}(BE)	
K_o	100(TE), 0.01(WM), 0.01(BE)	

(a)

(b)

Fig.3 Simulation results of filament growth dynamics. (a) Black triangles mark the change of cathode surface positions which proves the process of filament growth from cathode to anode. (b) Filament growth from anode to cathode is illustrated by the moving anode surface positions towards cathode.

in Fig. 3(a) show the relevant process of filament growth marked by black triangles. The coordinates of these marks in Fig.3 are equivalent to the preset threshold of the concentration of metal atoms. The direction of the black triangles which are heading towards the anode (on the left side) reflects the filament growth direction in this case. Initially there are only two marks in the simulated electrolyte region, which represent the surface of the anode (red) and the surface of the cathode (black), respectively. As cations migrate towards the cathode, some of the cations are reduced within the electrolyte. Most of the cations, however, succeed in reaching the cathode and get reduced there. Therefore, although there is an accumulation of metal atoms within the electrolyte, the concentration of metal atoms is far less than that on the surface of cathode, there the threshold of concentration is reached and the filament growth from cathode occurs. Once the filament starts to grow, the enhanced electric field on the tip of the filament makes the filament growth process a self-accelerating process, which also helps the growth of filament. For the other case in Fig. 1(c), since cations (Ag^+ or Cu^{2+}) have low mobility and diffusion coefficient in some electrolytes (such as amorphous Si), cations gain a very slow migration velocity compared to the redox reaction speed. Meanwhile certain quantities of electrons transit at a relatively high speed driven by the electric field. Ion transport is thus at a disadvantage, leading to most cations to stay close to the anode. The abundant cations there are reduced near the anode by the emerging electrons which migrate towards the anode. The red marks heading towards the cathode (on the right side) in Fig. 3(b) show that the filament grows from anode towards cathode. Unlike the situation of filament growth from the cathode, the gradually increasing concentration of metal atoms near the anode side finally reach the preset threshold to make it possible for filament growth from the anode.

IV. CONCLUSION

A unified model for CBRAM forming process is proposed to describe filament growth. By merely adjusting migration barrier of cation, filament growth from both anode-to-cathode and cathode-to-anode can be realized in consistency with experimental observations. Simulation results show the importance of cation diffusion and drift in the electrolyte. The model provides a reasonable way to understand different filament growth dynamics and may be helpful to settle filament growth dispute in CBRAM forming process.

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REFERENCES

[1] W. Rainer, and M. Aono, "Nanoionics-based resistive switching memories." Nature materials, vol. 6, pp. 833-840, 2007.

[2] Y. Yang, P. Gao,S. Gaba, ,T. Chang, ,X. Pan, W. Lu,"Observation of conducting filament growth in nanoscale resistive memories." Nature Communications, vol. 3, pp. 732, 2012.

[3] Q.Liu, J. Sun,H. Lv, S. Long, K. Yin, N. Wan, Y. Li, L. Sun, and M. Liu. "Real‐Time Observation on Dynamic Growth/Dissolution of Conductive Filaments in Oxide-Electrolyte-Based ReRAM." Advanced Materials, vol. 24, pp. 1844-1849, 2012.

[4] N. F. Mott and R. W. Gurney, Electronic Processes in Ionic Crystals.London, U.K.: Oxford Univ. Press, 1948.

[5] J. D.McBrayer, ,R. M. Swanson, , and T. W.Sigmon, "Diffusion of metals in silicon dioxide." Journal of The Electrochemical Society, vol. 133, pp. 1242-1246,1986.