A Kinetic Monte Carlo study on the dynamic Switching properties of Electrochemical Metallization RRAMs during the SET Process

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Abstract—In this paper, a simulation process based on Kinetic Monte Carlo (KMC) for an electrochemical metallization (ECM) resistive RAM (RRAM) is demonstrated. This simulation tool can investigate all the major dynamics properties of such devices. In particular, the voltage sweep rate dependent I-V characteristics, the variations of SET voltage, writing speed, on-state resistance, filament overgrowth phenomena and the effect of material properties are studied.

I. INTRODUCTION

In recent years resistive random access memory (RRAM) has gained attention as one of the promising candidates for next generation memory applications. This is due to anticipated advantages versus Flash with respect to high density, low cost and fast read and write speed [1]. Among the various types of RRAMs described to date, the electrochemical metallization (ECM) RRAM has received a great deal of attention due to its very low on-state resistance and hence high read speed. A typical ECM RRAM consists of a layer of electrochemically active metal as an anode, an insulator layer and finally a layer of inert metal as a cathode. The insulator layer can either serve as an electrolyte, which has a large concentration of anode type metal ions and can thus contribute to filament formation processes (for example, systems such as Ag/Ag2S/Pt [2] and Ag/Ag33Ge20Se47/Ni [3]) or just serve a transportation layer for oxidized anode ions passing from the anode to the cathode (for example, systems such as Cu/SiO2/Pt [4] and Cu/Ta2O5/Pt [5]).

Although substantial experimental work has been performed to date, an atomic scale simulation tool is still lacking. Based on KMC, we propose a simulation process for ECM RRAMs. More specifically, we focus on the second class of ECM RRAM described above, where the insulator layer only serves as transportation medium for the oxidized anode ions. This methodology, however, can be generalized to other type of RRAMs as well, making it a generalized approach for RRAM simulation.

II. SIMULATION PROCEDURE

The various physical and chemical processes included in the KMC simulation are shown in Fig. 1. At the anode, the simulation includes oxidation/reduction \( (M = M^\prime + e) \) (processes 8, 9) and ion surface diffusion, adsorption and desorption (processes 10-12). To simplify the simulation, a flat anode surface is assumed such that if an ion gets reduced at the anode, it disappears. This does not introduce excessive error since the filament formation is dominated by cathode side processes. An isotropic insulator with no electronic conductivity is assumed, i.e., the ion diffusion energy barrier is the same in all the directions. Simulation proceeds by recognizing that filament formation on the cathode is a metal crystallization process. An adatom can be formed after the ion gets adsorbed on the cathode surface or the adsorbed ion can diffuse to a more favorable step or hole site through surface diffusion and can get reduced there. All the reaction and diffusion rates can be expressed as \( \Gamma_i = \frac{v \sigma_i}{\pi} \), where \( v \) is vibration frequency which we assume to be \( 10^{12} \text{ s}^{-1} \) for both atoms and ions, \( E_{a1} \) is the standard activation energy for that process (Table 1). All the \( E_a \) are modified (Fig. 2) in the presence of electrical field (due to space ion distribution and external voltage). The \( E_a \) for both forward and reverse transitions have to be modified by \( -aq\Delta \) and \( (1-\alpha)q\Delta \) respectively, where \( \alpha \) is typically 0.5 and \( \Delta \) is the change of potential across two states (for chemical reactions, \( \Delta \) is the voltage difference between the
standard and current reactions; for diffusion it is the effective voltage across one lattice distance of the ion hopping length). In the KMC simulation, after a transition is randomly chosen, the configuration of atoms and ions has to be updated and Poisson equation is solved at every step to update the potential.

III. RESULTS AND DISCUSSION

In the simulation performed here, each layer of the electrode consists of 150 atoms and the thickness of the insulator is 15nm. Fig. 3 shows the simulated I-V and related filament morphology (the voltage sweep rate is 3V/s). Current in region (1) is ionic current while (3) and (4) are ohmic current. The resistivity of metal filament is set to $5 \times 10^{-8} \Omega \cdot \text{cm}$. The external system resistance is taken as $R_{\text{ext}} = 100 \Omega$.

During the actual write and erase switching operation, it only takes a few layers of atoms on top of the filament (Fig. 4) to turn on/off the device. Thus the on-state switching time ($t_{\text{ON}}$) of the RRAM is far less than $t_{\text{SET}}$, which is the time required to form an entire filament, rather than that required to form the last few layers required to complete the residual filament from a previous write/erase cycle. This is one major advantage of RRAMs, since they show significantly improved speed after burn-in.

![Fig. 2: The modification of $E_a$ for both forward and reverse transitions ( $E_a \to E'_a$ and $E_b \to E'_b$ ) in the presence of electrical field. The transition can be either chemical reactions or physical diffusion (inset).](image)

![Fig. 3: The KMC simulated I-V and related filament shape. The voltage sweep rate is 3V/s. Region (1) is ionic current while (3) and (4) are ohmic current. The resistivity of metal filament is set to $5 \times 10^{-8} \Omega \cdot \text{cm}$. The external system resistance is taken as $R_{\text{ext}} = 100 \Omega$.](image)

![Fig. 4: The comparison between SET and ON Switching processes](image)

![Fig. 5: Simulated SET voltage $V_{\text{SET}}$ versus input voltage sweep rate.](image)

![Fig. 6: Simulated SET time $t_{\text{SET}}$ versus applied voltage step.](image)
Fig. 7 shows the \( t_{\text{ON}} \) distribution at different input voltages. At 2V, at least 60\( \mu \)s is needed in order to turn on 99% of the devices, whereas only 3 \( \mu \)s is needed at 3V. The variation of the on state resistance (R\(_{\text{ON}}\)) in the switching process is also studied, as shown in Fig. 8. At low voltages, a wider time pulse (thus a longer time filament overgrown process) has to be applied to reduce the R\(_{\text{ON}}\), yet it still has a large variation problem. In contrast, at high voltages, a much shorter pulse is sufficient to obtain low R\(_{\text{ON}}\) with less variation. Fig. 9 shows the effect of \( E_{\text{bulk}} \) on the device switching properties. The switching time \( t_{\text{ON}} \) decreases as the migration barrier of the insulator decreases (smaller \( E_{\text{bulk}} \)) until the oxidation and metal crystallization become limiting factors.

Finally, Fig. 10 shows the impact of variations in surface diffusion and reduction \( E_a \) on filament shape. When the surface diffusion of the adsorbed ion becomes difficult (larger \( E_{\text{surf}} \)), a pattern similar to electrical breakdown [6] is obtained(Fig.10 (a)). While Fig.10 (b) shows the condition when the adsorbed ion has enough time to diffuse to a more preferred step or hole sites, thus the deposited metal surface is much smoother and looks like electrochemical plating. Therefore, we see that a wide range of switching modes can be modeled using this methodology by appropriate choice of the system parameters.

![Fig. 7](image1.png)

**Fig. 7**: Simulated switching time \( t_{\text{ON}} \) distribution under different input conditions

![Fig. 8](image2.png)

**Fig. 8**: Simulated on-state resistance distribution under different input conditions

![Fig. 9](image3.png)

**Fig. 9**: Simulated switching time versus diffusion barrier of the solid electrolyte.

![Fig. 10](image4.png)

**Fig. 10**: Simulated Filament shape formed under different conditions. (a) when the activation energy \( E_{\text{surf}} \) is large while \( E_{\text{aden}} \) is small (b) when \( E_{\text{surf}} \) is small and \( E_{\text{aden}} \) is large.

<table>
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### IV. SUMMARY

A KMC simulation process to study the switching properties of ECM RRAMs is demonstrated. Various dynamic characteristics of such devices are simulated and found to match well with experimental observations. Overall, it is shown that KMC can be a powerful tool for RRAM design and optimization.
REFERENCES


