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 $Ag/Ag_2S/Pt$ [2] and $Ag/Ag_{33}Ge_{20}Se_{47}/Ni$ [3]) or just serve a transportation layer for oxidized anode ions passing from the anode to the cathode (for example, systems such as $Cu/SiO_2/Pt$ [4] and $Cu/Ta_2O_5/Pt$ [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 ($M \leftrightarrows M^+ + e$) (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 $\Gamma_i = \nu e^{\frac{-E_{a,i}}{k_B T}}$, where ν is vibration frequency which we assume to be 10^{12} s^{-1} for both atoms and ions, $E_{a,i}$ 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 $-\alpha q\Delta$ and $(1-\alpha)q\Delta$ respectively, where α is typically 0.5 and Δ is the change of potential across two states (for chemical reactions, Δ is the voltage difference between the

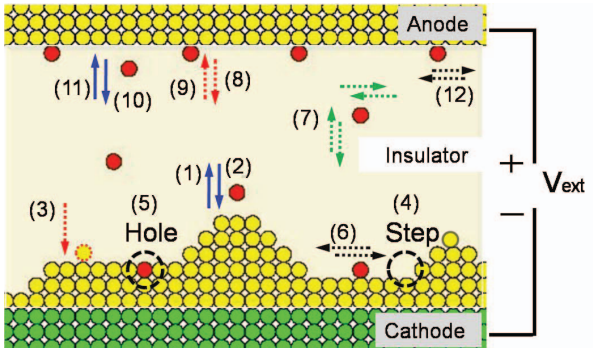

Fig. 1: All the physical and chemical processes in KMC simulation (refer to Table 1 for details). Yellow dots represent anode type metal atoms, green dots are cathode atoms and red dots are the anode metal ions.

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.

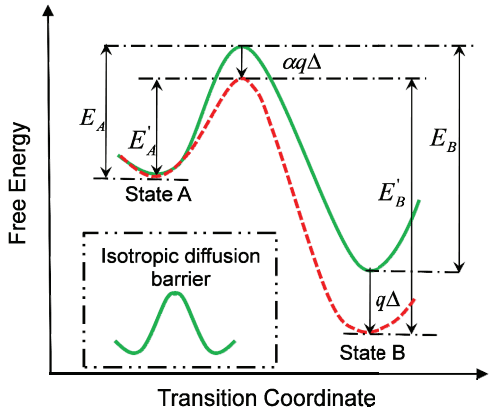

Fig. 2: The modification of E_a for both forward and reverse transitions (E_A to E'_A and E_B to E'_B) in the presence of electrical field. The transition can be either chemical reactions or physical diffusion (inset).

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 and is proportional to electrode area. The high field causes turn on at Voltage V_{SET} (Fig. 3) when the filament gets very close to the anode. Once the filament shorts the electrodes, electron current flows and the filament overgrowth process starts. Since the conductivity of the metal filament is not ideal, there is still a large voltage drop on it. Thus, the chemical process continues -- the width of the filament grows wider and its resistance keeps decreasing, until a steady state is achieved. During the overgrowth process, the resistance and voltage distributions on each layer of the filament have to be updated at every time step and serve as new boundary conditions in the KMC simulation.

Next, the relationship between V_{SET} and the voltage sweep rate is explored (Fig. 5). At a high voltage sweep rate, an exponential relationship is shown. However, at low sweep rate the V_{SET} approaches a threshold value of ~0.2V. To further confirm the result, the time (t_{SET}) needed to turn on the device at different voltage step levels is simulated (Fig. 6). Clearly, t_{SET} inverse exponentially depends on voltage when the applied voltage is high. However, t_{SET} increases dramatically when the voltage is low. It demonstrates that below the threshold, it takes a very long time to turn on the device. It is worthwhile to note that these results are consistent with previously reported experimental results [4].

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_{ON}) of the RRAM is far less than t_{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.

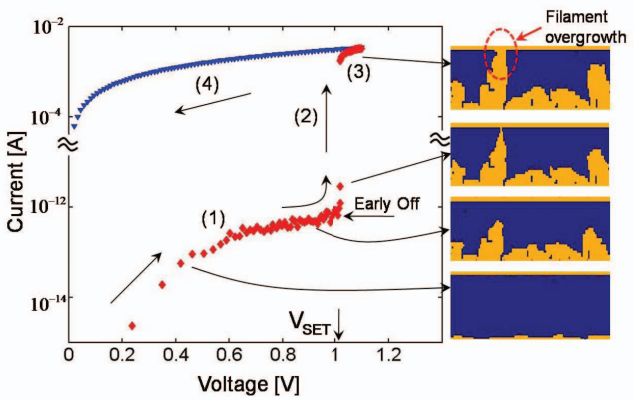

Fig. 3: The KMC simulated I-V and related filament shape. The voltage sweep rate is 3V/s. Region (1) is ionic current while (3) and (4) are ohmic current. The resistivity of metal filament is set to $5\times10^{-8}\Omega$m. The external system resistance is taken as $R_{ext}=100\Omega$.

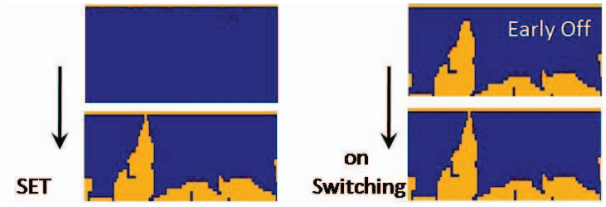

Fig. 4 : The comparison between SET and ON Switching processes

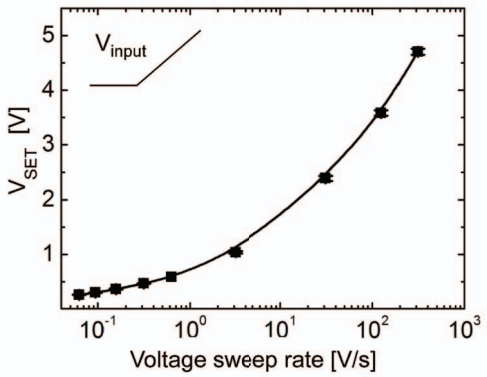

Fig. 5 : Simulated SET voltage V_{SET} versus input voltage sweep rate.

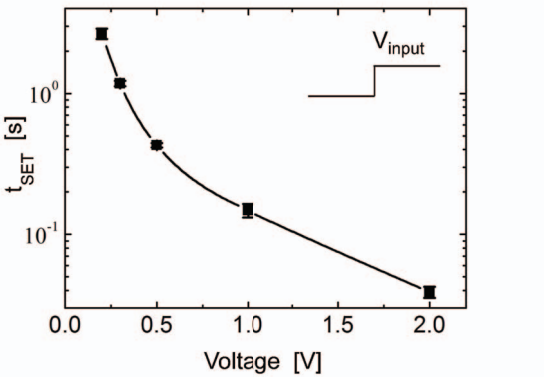

Fig. 6 : Simulated SET time t_{SET} versus applied voltage step.

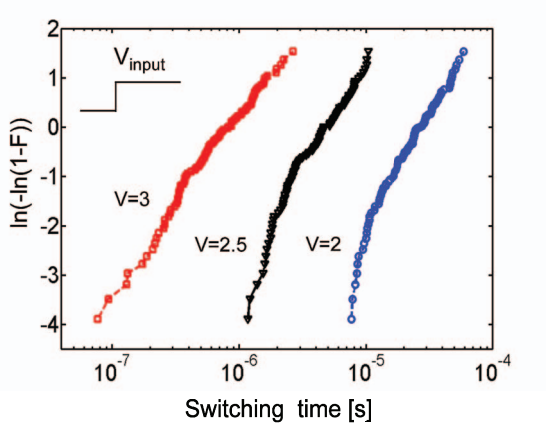

Fig. 7 : Simulated switching time t_{ON} distribution under different input conditions

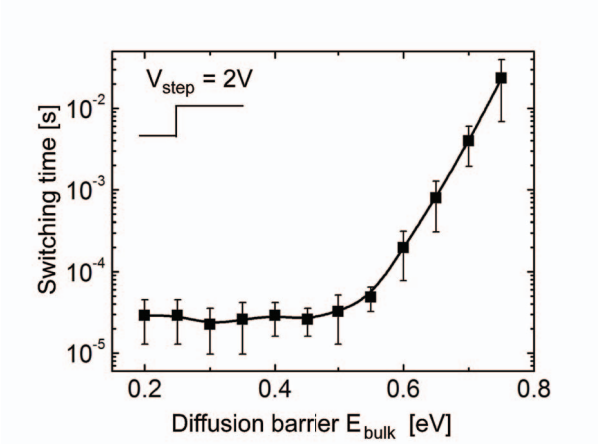

Fig. 9 : Simulated switching time versus diffusion barrier of the solid electrolyte.

Fig. 7 shows the t_{ON} distribution at different input voltages. At 2V, at least 60µs is needed in order to turn on 99% of the devices, whereas only 3 µs is needed at 3V. The variation of the on state resistance (R_{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_{ON}, yet it still has a large variation problem. In contrast, at high voltages, a much shorter pulse is sufficient to obtain low R_{ON} with less variation. Fig. 9 shows the effect of E_{bulk} on the device switching properties. The switching time t_{ON} decreases as the migration barrier of the insulator decreases (smaller E_{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_{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.

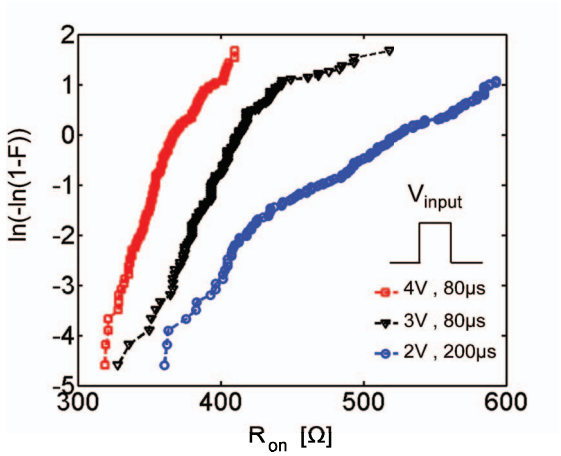

Fig. 8 : Simulated on-state resistance distribution under different input conditions

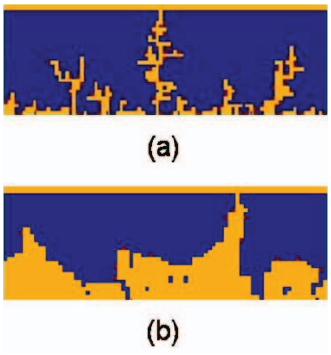

Fig. 10 : Simulated Filament shape formed under different conditions. (a) when the activation energy E_{surf} is large while E_{adatom} is small (b) when E_{surf} is small and E_{adatom} is large.

TABLE I. SUMMARY OF BASIC PROCESSES IN KMC SIMULATION

No.	Process name:	E_a symbol	Value: (ev)
(1)	Desorption, cathode	E_{dsp}	0.45
(2)	Adsorption, cathode	E_{adp}	0.4
(3)	Adatom formation	E_{adatom}	0.65
(4)	Ion reduction at step site	E_{step}	0.55
(5)	Ion reduction at hole site	E_{hole}	0.45
(6)	Ion surface diffusion	E_{surf}	0.55
(7)	Ion bulk diffusion	E_{bulk}	0.4
(8)	Oxidation, anode	E_{ox}	0.625
(9)	Reduction, anode	E_{red}	0.65
(10)	Desorption, anode	E_{dsp}	0.45
(11)	Adsorption, anode	E_{adp}	0.4
(12)	Ion surface diffusion	E_{surf}	0.55

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.

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