Kinetic Monte Carlo simulation of resistive switching and filament growth in electrochemical RRAMs

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In recent years, Resistive Random Access Memory (RRAM) has received attention as a promising candidate for scaled memories [1]. An atomic-scale simulation tool that can describe the dynamics of RRAM operation is still lacking. Using a two dimensional (2D) Kinetic Monte Carlo (KMC) method, we have simulated the switching I-V characteristic and related filament morphology of electrochemical metallic (ECM) type RRAMs. These are considered promising for both memory and configurable logic applications due to their low-power switching and very low resistance on-state. As a result, an understanding of the underlying physics and dependencies is particularly important. In our simulation, because most important physical and chemical processes, such as oxidation, reduction, metal crystallization, ion adsorption, desorption and transportation have been taken into account, the simulated I-V curve accurately shows all the typical RRAM SET stage behaviors, including the filament overgrowth effect.

The KMC technique is an ideal tool to study the atomic-scale evolution of a system. By precisely assigning different activation energies (E_a) to particles according to their local structure, the detailed properties of a system can be obtained. In order to investigate the electrical properties of the ECM cells, all the physical and chemical processes must be identified (Fig.1). At the anode side, an electrical double layer is formed and it includes oxidation/reduction reactions ($M \leftrightarrows M^+ + e$), ion surface diffusion, desorption and adsorption processes. To simplify the simulation, we assume the anode surface is flat such that if an ion gets reduced at the anode, it disappears. This is a non-limiting assumption since the filament formation is dominated by cathode side processes. Filament formation at the cathode is essentially a crystallization process. As shown in Fig. 1, after the ion is adsorbed on the cathode surface, it can reduce to form an adatom as shown in process (9), and it can also reach a step or hole sites (processes (11) and (12)) through surface diffusion. The E_a for ions reduced to adatoms is higher than its value when reduced at step or hole sites. Therefore, ions are more likely to be reduced at step or hole sites. Finally, an isotropic electrolyte with zero electron conductivity is assumed, which means the bulk ion diffusion E_a is the same in every direction and there is no electron current through the electrolyte. The E_a values associated with all the processes are listed in Table 1. These can either be obtained from Ab initio or experimental results. Next, all the transition rates associated with any process that can occur in the next time step is expressed as $\Gamma_i = v e^{\frac{-E_{a,i}}{k_B T}}$, where v is frequency factor which we assume to be 10^{12} s^{-1} and $E_{a,i}$ is the activation energy for that process. All E_a values have to be modified (Fig. 3) in the presence of an electrical field, which comes from both the ion space charge distribution and the external voltage supply. The E_a for the forward and reverse transitions have to be modified by $-\alpha q\Delta$ and $(1 - \alpha)q\Delta$ respectively, where α typically is 0.5 and $q\Delta$ is the potential change across two states. Follow the flow- chart provided in Fig. 2, the KMC simulation can be performed. The simulation is performed on an atomic matrix with a size of 150×30, which resembles a device with an electrode size of 6nm×6nm and a 15nm thick electrolyte. For easy visualization, the result is normalized to a device with a cross-sectional area of 50μm×50μm. The simulation results show that the current in region 1 (Fig. 4) is proportional to the electrode area while that in regions 2, 3 and 4 is area-independent. This is expected, since the number of immature filaments formed in region 1 is proportional to electrode area, thus the ionic current is also, while regions 2-4 are dominated by local filament conduction and it is area-independent. The current has a sharp turn on in region 2, when the filament shorts two electrodes. Once a short is formed, the ohmic electron current flows. And since the conductivity of the filament is not ideal, there is still a large voltage drop across it and thus the chemical process continues (filament grows wider and its conductivity keeps increasing) until a steady state is achieved with the external test system. In the KMC simulation, the voltage distribution across each layer of the filament has to be updated in every step.

Besides the I-V characteristics, the simulation is also able to investigate the impact of physical parameters on device behavior. Fig. 5 shows the impact of variations in surface diffusion and reduction activation energies on filament shape. Fig5 (a) is similar to electrical breakdown [2] while (b) is more like electro-chemical plating. This attests to the usefulness of this simulation methodology both for understanding and modeling device behavior, as well as for studying impact of various physical effects on device performance.

[1] Rainer Waser, et al.. *Advanced Material* 21, p. 2632, 2009   [2] Niemeyer, L et al.. *Physical Review Letter* 52, p.1033, 1984
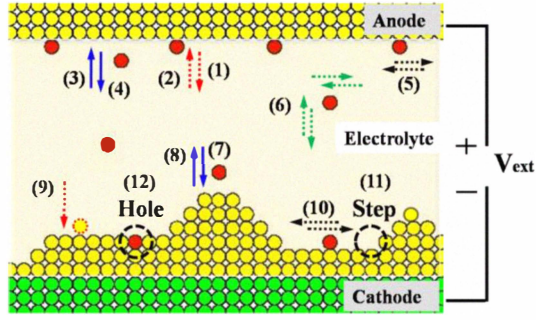
Fig.1 All the physical and chemical processes included in the KMC simulation for an ECM device. Yellow dots represent anode type metal atoms, green dots are cathode atoms and red dots are the anode metal ions. At the anode side: (1) oxidation (2) reduction (3) ion adsorption (4) ion desorption (5) ion surface diffusion. In the electrolyte : (6) bulk diffusion. At the cathode side (7) adsorption (8) desorption (9) adatom formation though reduction (10) surface diffusion (11) step site (12) reduction at hole site.
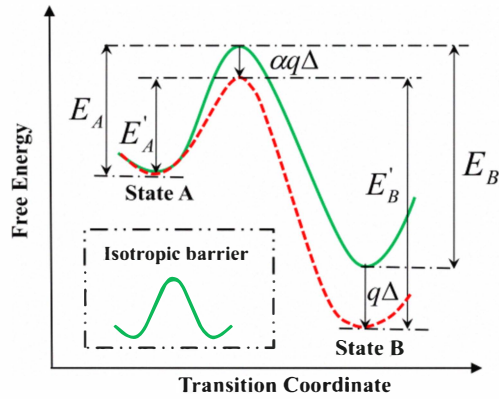

Fig.2 The flowchart of the KMC simulation process. RN and RN' are random numbers uniformly distributed between [0 1].

Fig.3. The modification of E_a in the presence of an electrical field. The effective potential Δ across two states causes the E_a change for both forward (E_A to E'_A) and reverse(E_B to E'_B) transitions. α is typically 0.5. For chemical reactions Δ is the effective voltage difference before and after reaction. For bulk diffusion, it is the effective voltage drop across one lattice constant. (The insertion shows symmetric diffusion barrier for bulk isotropic electrolyte without electrical field applied).
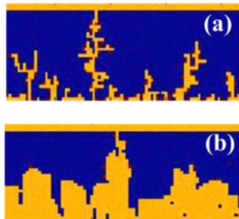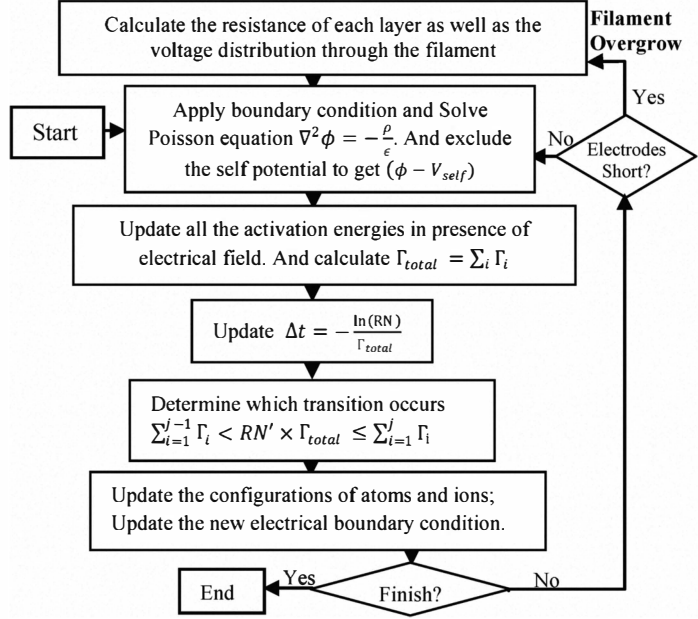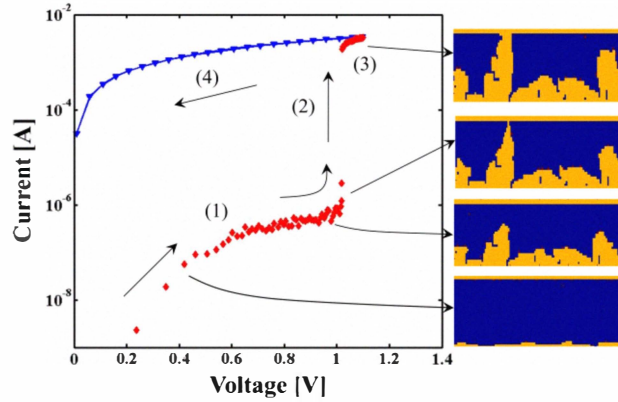

Fig.4. The KMC simulation results of the switching I-V and the related filament morphologies for the ECM device. The voltage sweep rate is 3V/s. Only current in region (1) depends on the electrode area. In addition, (1) is ionic current while (3) and (4) are ohmic electron current and (2) is a transition region from ionic to ohmic. After the filament shorts the two electrodes, filament overgrown process starts. The width of the filament gradually become larger until the equilibrium is reached. The resistivity of metal filament is set to $5 \times 10^{-8} \Omega m$. And the external system resistance is taken as $R_{ext} = 100\Omega$

Fig.5. Comparison of filament shape formed under different physical condition. (a) when the activation energy E_{a_surf} is large while E_{a_adatom} is small (b) when E_{a_surf} is small and E_{a_adatom} is large.

Table 1: Summary of basic processes and their E_a in KMC simulation for the ECM cell

Process name:	Symbol	E_a (ev)	Process name:	Symbol	E_a(ev)
At cathode:			**At anode**:		
Adtom formation	E_{a_adatom}	0.65	Oxidation	E_{a_ox}	0.625
Ion reduction at step site	E_{a_step}	0.55	Ion reduction	E_{a_red}	0.65
Ion reduction at hole site	E_{a_hole}	0.45	Ion Surface diffusion	E_{a_surf}	0.55
Ion surface diffusion	E_{a_surf}	0.55	Ion adsorption	E_{a_ads}	0.4
Ion adsorption	E_{a_adp}	0.4	Ion desorption	E_{a_dsp}	0.45
Ion desorption	E_{a_dsp}	0.45			
			At Electrolyte : Bulk diffusion	E_{a_bulk}	0.4