Simulation of multilevel switching in electrochemical metallization memory cells

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We report on a simulation model for bipolar resistive switching in cation-migration based memristive devices. The model is based on the electrochemical driven growth and dissolution of a metallic filament. The origin of multilevel switching is proposed to be direct tunneling between the growing filament and the counter electrode. An important result of our parameter simulation studies is that different materials show the same experimental multilevel behavior. Our model fully reproduces the experimental data and allows for an explanation of the transition from bipolar to nonpolar switching.

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I. INTRODUCTION

Memristive devices based on redox processes on the nanoscale have attracted a great deal of attention for their potential use in future nonvolatile memories. One potential candidate is electrochemical memory (ECM), which is based on the migration of Cu or Ag cations. Here, the switching is attributed to the electrochemical growth and dissolution of a Cu or Ag nano-sized filament. Typically, ECM cells consist of a Cu or Ag active electrode, an ion conducting switching layer (SL), and an inert electrode. The ECM effect has been observed in several materials. During the SET process, a positive potential is applied to the active electrode, which is oxidized. Ag or Cu cations are driven out of the active electrode and migrate through the SL. At the inert cathode the cations are reduced and a metallic filament grows toward the anode, resulting in a low resistive state (LRS). This filamentary growth can be attributed to preferred ionic drift path within the SL. In a former study it was also shown that only one filament is responsible for SET operation due to the current compliance. To reset the device to a high resistive state (HRS), the voltage polarity is reversed, leading to the dissolution of the filament. ECM cells show multilevel programming capabilities and strongly nonlinear switching dynamics. In former studies, the origin of this nonlinear switching dynamic was attributed to ion hopping at high electric fields or to electron transfer reactions at the electrodes. Multilevel programming is often explained as a variation in the width of the conductive filament, resulting in a different LRS. The LRS can be modulated by an external current compliance (CC) or a load resistor $R_l$ over several orders of magnitude with values above GΩ and below $\Omega$. The resistance of a single-atom contact is about 12.9 kΩ. It is therefore hard to explain the whole range of multilevel states with variation of the filament diameter. A second big issue is connected to the proposed reset mechanism based on a combination of Joule heating and an electrochemical dissolution of the filament. In order to achieve significant Joule heating in thin filaments for typical reset voltages in ECM cells below 0.5 V, reset currents higher than one μA are expected to be necessary. For high LRS, however, RESET currents can be less than one μA excluding Joule heating. In addition, nonpolar (unipolar) switching modes also have been demonstrated when the LRS is below 20 kΩ, which should be covered by a suitable model.

II. SIMULATION MODEL

In this work, we report on a continuous 1D physical simulation model to explain bipolar resistive switching in ECM cells based on the modulation of a tunneling gap between the electrochemically growing filament and the counter electrode. Different LRSs in this model are represented by a corresponding tunneling gap, which can be adjusted by an external current compliance. This current control method has been used to fabricate electrode pairs with distinct angstrom-sized gaps. To achieve a 1D model, we approximate the shape of the growing filament as a cylinder with a constant radius. In a microscopic picture, the filament will have some curvature, and deposition might take place at the very top as well as at the sides. Thus the filament radius and the tunneling gap should be regarded as effective parameters, which allows for continuous values.

Figure 1 shows a schematic of the simulation model. The metallic cylindrical filament grows from the inert bottom electrode through the SL and modulates the effective tunneling gap $x$. Within the SL, ionic and electronic tunneling currents are present. The ionic current path is modeled by two voltage controlled current sources, which represent the electron-transfer reactions at the boundaries (see explanation below) and the resistance due to ionic drift $R_{ion}(x)$. The electronic current path is attributed to electronic tunneling, represented by one voltage controlled current source. The LRS is reached as the tunneling gap becomes small enough to enable significant tunneling current. The filament

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charge neutrality, the ionic currents at the active and the inert electrodes are equal. Therefore, the overpotential at the active electrode–SL interface $\eta_{\text{ac}}$ can be expressed by the filament/SL overpotential $\eta_{\text{fil}}$, where $A_{\text{ac}}$ is the area of the active electrode involved in the redox reaction and $A_{\text{fil}}$ is the filament area.

$$I_{\text{ion}} = I_{\text{BV}}(\eta_{\text{fil}}) = I_{\text{BV}}(\eta_{\text{ac}})$$

$$\Leftrightarrow -2 j_0 A_{\text{fil}} \sinh \left( \frac{z e}{2 kT} \eta_{\text{fil}} \right) = 2 j_0 A_{\text{ac}} \sinh \left( \frac{z e}{2 kT} \eta_{\text{ac}} \right)$$

$$\Rightarrow \eta_{\text{ac}} = \frac{2 kT}{z e} \arcsinh \left( \frac{A_{\text{fil}}}{A_{\text{ac}}} \sinh \left( \frac{z e}{2 kT} \eta_{\text{fil}} \right) \right).$$

Note that the algebraic signs of the Butler-Volmer currents in Eq. (4) are different due to the inverse redox reactions occurring at the interfaces. Using Kirchhoff’s first law, the cell current is calculated as the sum of the ionic and tunnel currents $I_{\text{cell}}$ in the switching layer as

$$I_{\text{cell}} = I_{\text{Tu}}(V_{\text{Tu}}) + I_{\text{ion}}(V_{\text{Tu}}) + I_{\text{BV}}(\eta_{\text{fil}}).$$

The tunnel voltage $V_{\text{Tu}}$ is equal to the voltage drop across the ionic current path according to Kirchhoff’s second law. It can be calculated as the sum of $\eta_{\text{fil}}$, $\eta_{\text{ac}}$, and the voltage drop due to the ionic transport in the insulating layer by

$$V_{\text{Tu}} = \eta_{\text{ac}} - \eta_{\text{fil}} + I_{\text{BV}}(\eta_{\text{fil}}) R_{\text{ion}}(x) = f(\eta_{\text{fil}}, x).$$

The ionic resistance is calculated as $R_{\text{ion}} = \rho_{\text{ion}} x / A_{\text{ion}}$, with the ionic resistivity $\rho_{\text{ion}}$ and the effective area of ionic transport within the insulator $A_{\text{ion}}$. For an intermediate voltage range and a trapezoidal barrier, $I_{\text{Tu}}$ is calculated according to Simmons as

$$I_{\text{Tu}} = \frac{e A_{\text{fil}}}{2 \pi h^2} \left( \varphi_0 - \frac{e V_{\text{Tu}}}{2} \right) \exp \left( - \frac{4 \pi x}{h} \sqrt{m_{\text{eff}}/2} \sqrt{\varphi_0 - \frac{e V_{\text{Tu}}}{2}} \right)$$

$$- \frac{e A_{\text{fil}}}{2 \pi h^2} \left( \varphi_0 + \frac{e V_{\text{Tu}}}{2} \right) \exp \left( - \frac{4 \pi x}{h} \sqrt{m_{\text{eff}}/2} \sqrt{\varphi_0 + \frac{e V_{\text{Tu}}}{2}} \right),$$

where $\varphi_0$ is the tunneling barrier height and $m_{\text{eff}} = m_i m_o$ is the electron effective mass of the insulating material. In the equivalent circuit diagram, Eq. (7) is represented by a voltage-controlled current source with controlling voltage $V_{\text{Tu}}$. Due to the exponential dependence of $I_{\text{Tu}}$ on $x$, the LRS is very sensitive to small variations in $x$. For small voltages $V_{\text{Tu}}$, the tunnel junction shows an Ohmic behavior, which is consistent with the experimentally observed characteristic of LRS in ECM cells. Note that a real tunnel barrier has a more parabolic shape and a shorter effective gap. Both effects lead to higher currents than predicted using Eq. (7). The real gaps should thus be larger than in our simulations. Using Eq. (6) with Eq. (7), the tunneling current can be expressed as a function of $\eta_{\text{fil}}$ and $x$. With Eq. (5), Eq. (6), and Eq. (7), the cell voltage $V_{\text{cell}}$ can be calculated using

$$V_{\text{cell}} = V_{\text{Tu}} + I_{\text{cell}}(R_{\text{fil}}(x) + R_{\text{el}} + R_L) = f(\eta_{\text{fil}}, x).$$

![FIG. 1. Schematic of the switching model with equivalent circuit diagram. A switching layer of thickness $L$ is sandwiched between the active top electrode and the inert bottom electrode. A cylindrical filament grows within the SL and modulates the tunneling gap $x$ between active electrode and filament. The elements of the equivalent circuit are an optional load resistor $R_L$, the electrode resistors $R_{\text{el,ac}}$ and $R_{\text{el,fil}}$, and the filament resistor $R_{\text{fil}}(x)$. In the switching layer, the ionic current path (left path) is represented by two voltage controlled current sources with controlling voltages $\eta_{\text{ac}}$ and $\eta_{\text{fil}}$ and the ionic resistance $R_{\text{ion}}(x)$. The electronic current path (right path) within the SL is given by one voltage controlled current source with controlling voltage $V_{\text{Tu}}$.](image-url)
Here the filament resistance is calculated using  
\[ R_{\text{fil}} = \rho_{\text{fil}} \frac{(L - x)}{A_{\text{fil}}} \]
where \( L \) is the SL thickness. \( V_{\text{cell}} \) is thus a function of \( \eta_{\text{fil}} \) and \( x \). The resistances \( R_{\text{el}} \) and \( R_{\text{L}} \) correspond to the added resistance of both electrodes and an optional load resister, respectively. Due to the low resistance of the conductive filament and the electrodes, almost the complete cell voltage will drop across the two interfaces and the solid electrolyte.

With this set of equations, the switching behavior of ECM can be simulated. For a given \( V_{\text{cell}} \), Eq. (1) is solved along with Eq. (8), and in CC Eq. (1) is solved along with Eq. (5). Note that Eq. (5) and Eq. (8) are implicit equations and have to be solved for \( \eta_{\text{fil}} \) in each time step in order to solve the ordinary differential equation Eq. (1). This set of equations describes an implicit memristive system. When simulating the SET operation, Eq. (1) is solved along with Eq. (8), as long as the cell current is lower than the current compliance. As soon as CC is reached, Eq. (1) is solved along with Eq. (5) until the end of the SET operation. This differs from real current compliance, which turns back to voltage control as the cell current drops below the SET value.

As a model system for our simulations, we use a cylindrical Cu/SL/Pt structure. Both electrodes have a thickness of 20 nm and a 100 nm radius, which leads to an electrode resistance \( R_{\text{el}} = 76 \, \text{m}\Omega \). \( R_{\text{L}} \) is in zero in all simulations. The SL thickness is \( L = 20 \, \text{nm} \). For numerical simplicity, we set \( A_{\text{ion}} = A_{\text{ac}} = A_{\text{fil}} = \pi r_{\text{fil}}^2 \). Other parameters are \( z = 2 \), \( \rho_{x} = 8.95 \, \text{g/cm}^3 \), \( M_{\text{Cu}} = 1.06 \times 10^{-22} \, \text{g} \), and \( T = 300 \, \text{K} \). The remaining parameters \( \rho_{x}, \sigma_{x}, r_{\text{fil}}, \sigma_{\text{ion}}, \) and \( j_{0} \) depend on the electronic properties of the SL material, its microstructure, and the solubility of Cu ions in the SL. These parameters are varied in our simulations in order to investigate their influence on resistive switching. As reference material in our simulations, we choose SiO\(_2\), and thus \( \phi_{\text{Cu/SiO}_2} = 4.2 \, \text{eV} \) and \( m_{\text{Cu/SiO}_2} = 0.86 \). The remaining reference values are \( \rho_{\text{ion}} = 10^{-2} \, \text{\Omega} \cdot \text{m} \), \( j_{0} = 10^{-2} \, \text{A/m}^2 \), and \( r_{\text{fil}} = 2 \, \text{nm} \).

### III. SIMULATION RESULTS AND DISCUSSION

Figure 2(a) shows the simulated \( I\!V \) characteristic (red solid line) using a current compliance of 10 \( \mu\text{A} \). The ECM cell is initially in a HRS. For excitation, a triangular voltage with a 1 V amplitude and 1 s rise time is used (see inset in Fig. 2(a)). The initial 2 s correspond to the SET operation, and the following 2 s to the RESET operation. Obviously, the LRS exhibits an Ohmic behavior, as expected from Eq. (7) for low voltages. During the SET operation, the actual cell voltage is not equal to the applied voltage \( V_{\text{ap}} \) (blue curve in Fig. 2(a)). As soon as the set CC is reached, \( V_{\text{cell}} \) drops abruptly. Afterward it decreases gradually during the current control. This behavior can be explained by interpreting the transient data of \( I_{\text{ion}}, I_{\text{Tu}}, \) and \( x \) during SET and RESET, shown in Fig. 2(c) and Fig. 2(d), respectively. When \( V_{\text{ap}} \) is raised, \( I_{\text{ion}} \) increases according to Eq. (4) and \( x \) starts decreasing. This leads to an increase of \( I_{\text{Tu}} \) (see Eq. (7)), and finally the set CC is reached. A further decrease of \( x \) is compensated for by the abrupt drop of \( V_{\text{cell}} \). In conclusion, \( I_{\text{ion}} \) is reduced by three orders of magnitude (see Figure 2(c)), and the filament growth is suppressed. At the end of the SET pulse, a gap of 0.32 nm remains. Note that \( x \) still decreases in CC, which allows for a metallic contact at a longer time scale. During RESET, \( I_{\text{Tu}} \) is orders of magnitude larger than \( I_{\text{ion}} \) (see Figure 2(d)), but it is very sensitive to \( x \). Thus, even a low ionic current is sufficient to reset the cell. Then, \( I_{\text{Tu}} \) drops to zero and the filament dissolves completely. The simulation results are in good agreement with the experimental data shown in Fig. 2(b).

Note that the field across the remaining gap is very high and can be in the range of dielectric breakdown fields, which should be discussed in terms of reliability and stability of the LRS.

In order to study multilevel programming, we performed simulations with varying CC in which \( I_{\text{CC}} \approx I_{\text{SET}} \).

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**FIG. 2.** (Color) (a) Simulated \( I\!V \) curve (red) and corresponding relation between \( V_{\text{cell}} \) and \( V_{\text{applied}} \) (blue). The applied voltage vs time is shown as an inset. Also shown are the corresponding simulated transient tunneling (dashed blue line), ionic currents (solid blue line), and transient gap (solid red line) during (c) SET and (d) RESET. The absolute values are shown in (d). A gap of 0.32 nm remains after the SET operation. (b) Experimental \( I\!V \) characteristic for a Cu/SiO\(_2\)/Pt cell (preparation in Ref. 14).
Again, a voltage triangle of a 1 V peak voltage with a rise time of 1 s is used, and $r_{fil}$ is set to 8 nm. The simulated LRS values as a function of $I_{SET}$ are shown in Fig. 3(a), along with experimental data. Evidently, the proposed tunneling model is capable of explaining multilevel switching over the full range of SET currents. The remaining gap $x_{\text{min}}$ is proportional to $\log(I_{SET})^{-1}$ and changes from 1.10 nm at 1 pA to 0.13 nm at 398 $\mu$A. At higher SET currents the gap is closed completely, resulting in a metallic contact. Also, for the relation between RESET and SET, the current experimental data and simulation data are consistent (see Figure 3(b)). Let us now consider how one deposited Cu atom will affect the LRS resistance. As the gap is changed 0.26 nm, the resistance changes by a factor of about 250 according to our simulations. The cylindrical filament area in this simulation consists of approximately 3600 atoms for a filament radius of 8 nm. So, if a single Cu atom is placed on top of this filament, the resistance will change by a factor of approximately 250/3600, which is about 7%. For thinner filaments this factor is higher and discrete resistance steps might occur.

To determine which parameters control the LRS, we performed SET simulation studies with varying reference values for $I_{SET} = 100$ nA, 1 $\mu$A, and 10 $\mu$A. For each simulation study, only one reference value is varied, and the others are kept constant. For excitation we used 1 ms long 1 V SET pulses with a rise and fall time of 10 ns. This ensures that SET switching occurs during the hold time. Figure 4 shows that the LRS is virtually invariant with the barrier height $E_b$, the effective mass $m_r$, and the filament diameter $A_{fil}$, and it is regulated by $I_{SET}$. For $I_{SET}$, $m_r$, and $A_{fil}$ determine $x_{\text{min}}$ as these parameters relate to $I_{\text{Tu}}$ (Eq. (7)). With a variation of $j_0$ of over four orders of magnitude, a small variation of LRS is observed (Fig. 4(c)), whereas $x_{\text{min}}$ changes accordingly. This variation is directly related to Eq. (3) and Eq. (1). If $j_0$ is increased, the growth velocity increases analogously. Thus the CC is reached faster and the filament can grow for a longer time under current control. This leads to a slightly lower LRS resistance. Note that a variation of $\rho_{\text{ion}}$ does not change the LRS resistance or $x_{\text{min}}$ as the switching speed is limited by the electron transfer reaction.

FIG. 3. (Color) (a) LRS resistance vs SET current and (b) corresponding RESET current vs SET current. The simulation results for (a) and (b) are depicted as solid black lines. Experimental data are displayed as blue triangles for a Ag:GeSe system and as red squares for a Cu:SiO$_2$ system (Ref. 14). The filament radius $r_{fil} = 8$ nm.

FIG. 4. (Color) LRS resistance (blue lines) and corresponding remaining gap (red lines) vs (a) effective mass, (b) barrier height, (c) exchange current density, and (d) filament radius for SET current levels of 100 nA, 1 $\mu$A, and 10 $\mu$A.
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rent compliance. In this case the SET current is given by

this simulation study differs if a load resistor is used as cur-

event is higher for higher voltages. Note that the result of

Interestingly, the initial cell resistance after the switching

takes place. This allows for an explanation of the transition from bipolar to nonpolar switching. The former

oscillating as long as a tunneling gap remains, whereas nonpolar

transition from bipolar to nonpolar switching. The former

might involve Joule heating and thus allows for a nonpolar

 Reset. For very thin filaments, a resistance jump might

occur as the filament achieves a metallic contact. This jump

possibly smears out for thick filaments.

perimental multilevel behavior. Small differences in LRS

are then attributed to the switching speed of the cell and

hence longer growth times. A metallic contact is still possi-

ble for a high $I_{\text{SET}}$. This allows for an explanation of the

transition from bipolar to nonpolar switching. The former

occurring as long as a tunneling gap remains, whereas nonpolar

switching occurs for a metallic contact. The material param-

eters $E_{\text{th}}$, $m_*$, and $A_{\text{eff}}$ control the remaining gap, as well as the

required $I_{\text{SET}}$, to achieve a metallic contact. Its dissolution

might involve Joule heating and thus allows for a nonpolar

Reset. For very thin filaments, a resistance jump might

occur as the filament achieves a metallic contact. This jump

possibly smears out for thick filaments.

Fig. 5. (Color) (a) LRS resistance (blue) and corresponding remaining gap (red) vs pulse voltage at SET currents of 100 nA, 1 μA, and 10 μA. (b) Trans-

ient cell resistance (blue) and gap (red) during the SET pulse for the 10 μA data in (a).

In a further simulation study, the amplitude of the volt-

age pulse is varied. The simulation results in Fig. 5(a) clearly

show that this has no influence on the LRS resistance and,

thus, $x_{\text{min}}$. This behavior can be understood by evaluating the

transient gap and the cell resistance in Fig. 5(b). Increasing

the pulse voltage leads to faster switching, but finally the

transient behavior is determined by $I_{\text{SET}}$, which is constant.

Interestingly, the initial cell resistance after the switching

event is higher for higher voltages. Note that the result of

this simulation study differs if a load resistor is used as cur-
ent compliance. In this case the SET current is given by

$I_{\text{SET}} = V_{\text{pulse}}/R_L$, which then controls the LRS.

IV. CONCLUSIONS

In conclusion, we have presented a physical simulation

model for resistive switching in ECM cells that gives a

remarkably good description of the experimental data. We

proposed tunneling as the origin of multilevel switching

rather than filament diameter variation, with the LRS level

controlled by $I_{\text{SET}}$. In this case its value does not relate to

the filament diameter. An important implication of our

parameter studies is that different materials show the same

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Fig. S1.