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# Switching kinetics of SiC resistive memory for harsh environments

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Cu/a-SiC/Au resistive memory cells are measured using voltage pulses and exhibit the highest $R_{OFF}/R_{ON}$ ratio recorded for any resistive memory. The switching kinetics are investigated and fitted to a numerical model, using thermal conductivity and resistivity properties of the dielectric. The SET mechanism of the Cu/a-SiC/Au memory cells is found to be due to ionic motion without joule heating contributions, whereas the RESET mechanism is found to be due to thermally assisted ionic motion. The conductive filament diameter is extracted to be around 4nm. The high thermal conductivity and resistivity for the Cu/a-SiC/Au memory cells result in slow switching but with high thermal reliability and stability, showing potential for use in harsh environments. Radiation properties of SiC memory cells are investigated. No change was seen in DC sweep or pulsed switching nor in conductive mechanisms, up to 2Mrad(Si) using $^{60}$Co gamma irradiation. © *2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4926674]

Resistive memory is very promising for the next generation non-volatile memory with high density, low power and simple metal-insulator-metal structure.[1] The resistance of the memory cell can be switched between ON or low resistance state (LRS) and OFF or high resistance station (HRS) through an applied bias. Resistive memory can be categorized into two main classes depending on the conduction mechanism. Valence change memory (VCM) works via the movement of anions within the dielectric layer, whereas electrochemical memory (ECM) works through the movement of cations.[2]

ECM memory cells consist of an electrochemically active electrode, such as Cu[3] or Ag[4], with an inert counter electrode, such as Pt[5] or W[6], with a variety of electrolyte materials including GeSe[3] and $SiO_2$.[7] Silicon carbide, has also shown great potential with excellent state stability[8,9] and ultra-high ratio memory cells.[10,11] However these memory cells are reportedly slow in switching.

The slow switching has previously been attributed to the high diffusion barrier of SiC for Cu, as well as the high thermal conductivity.[8,12] It was reported that an addition of a thermal barrier layer into a SiC RM cell leads to reduced pulse width for RESET.[12] However the actual switching kinetics were not qualitatively investigated, nor were kinetics of the SET mechanism. Here the switching kinetics of Cu/a-SiC/Au memory cells are investigated. Pulsed measurements are performed, allowing conduction mechanism of SET and RESET to be studied and identified in relation to a previously reported analytical model for switching kinetics in ECM memory cells.[13] Due to silicon carbide's good thermal and state stability,[12,14] these memory cells show potential for use in space and nuclear applications. Radiation properties of ECM memory are evaluated by irradiating the Cu/a-SiC/Au memory cells, using $^{60}$Co ionizing radiation, up to a high total dose of 2Mrad(Si). This dose is on the same order of magnitude as high dose levels reported in space and nuclear environments.[15,16]

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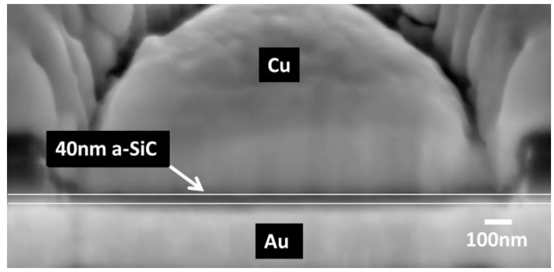


FIG. 1. Cross-sectional SEM image of 40nm dielectric in Cu/a-SiC/Au memory cell.

Cu/a-SiC/Au memory cells were fabricated as described in previous publications.[10] Figure 1 shows the 40nm thick SiC layer situated between the Cu and Au electrodes. DC measurements were conducted by applying a voltage to the Cu electrode whilst grounding the Au electrode, using an Agilent B1500A semiconductor device parameter analyser. The memory cells were formed followed by subsequent SET and RESET cycles, with a current compliance of 0.1mA, applied during the SET process. Typical I-V characteristics are shown in Figure 2(a). Reduced reproducible $V_{SET}$ and $V_{RESET}$ was achieved through the control of filament formation, as compared to our previous work.

Pulsed measurements were performed using a -5V, 0.5s pulse for RESET and +10V, 0.01s pulse for SET. Figure 2(b) shows that an ultra-high ratio is achieved for multiple cycles with an average $R_{ON} \sim 30\Omega$, $R_{OFF} \sim 10^{10}\Omega$, resulting in $R_{OFF}/R_{ON} \geq 10^8$. This is the highest ratio recorded for pulse switching of resistive memory. The large ratio is a result of large $R_{OFF}$ values, which it is thought to originate from the presence of a Schottky Barrier between the Cu and

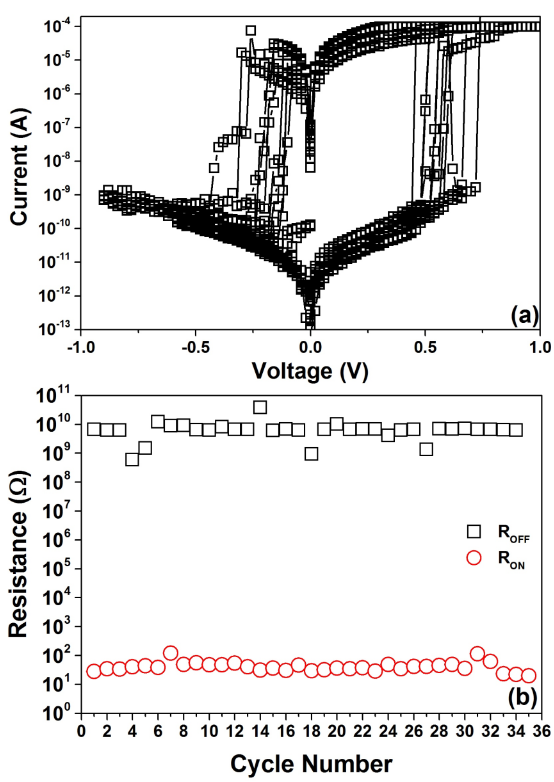


FIG. 2. Cu/a-SiC/Au memory cell measured using (a) DC voltage sweeps exhibiting $R_{OFF}/R_{ON} \sim 10^7$, $V_{SET} \sim 0.6V$ and $V_{RESET} \sim -0.2V$ (b) pulses using a -5V and +10V amplitude and a 0.5s and 0.01s width for RESET and SET respectively, exhibiting $R_{ON} \sim 30\Omega$, $R_{OFF} \sim 10^{10}\Omega$, resulting in $R_{OFF}/R_{ON} \geq 10^8$.

the SiC.[10] The DC sweep ratio is slightly lower due to the current compliance limiting the $R_{ON}$ resistance.

A numerical model has been reported, to study both the SET and RESET switching mechanisms for ECM memory cells in Ref. 13. The switching mechanisms are modelled as filament growth and reduction based on ion migration through thermally assisted hopping. The filament growth rate is given by (1) for the SET process,

$$\frac{d\Phi}{dt} = Ae^{-\frac{E_{A0}-\alpha qV}{kT_0(1+\frac{V^2}{8T_0\rho k_{th}})}}, \tag{1}$$

where $\Phi$ is the filament diameter, $A$ is a constant, $E_{A0}$ is the energy barrier for ion hopping, $\alpha$ is the barrier lowering coefficient, $q$ is elementary charge, $V$ is the applied voltage, $k$ is the Boltzmann constant, $T_0$ is room temperature, $\rho$ is the electrical resistivity and $k_{th}$ is the thermal conductivity. The RESET process follows the same equation, with a negative sign inserted on the right.

As can be seen by (1), the SET and RESET process depend strongly on the resistivity of the electrolyte layer, along with the thermal conductivity and activation energy. In this work, a condition of the numerical model is proposed enabling the switching mechanism to be determined. If $\rho k_{th} >> V^2/8T_0$, (1) reduces to,

$$\frac{d\Phi}{dt} = Ae^{-\frac{E_{A0}-\alpha qV}{kT_0}}, \qquad \tau_{pulse} \propto e^{\frac{E_{A0}-\alpha qV}{kT_0}}, \tag{2}$$

indicating the mechanism is due to ionic motion only, without joule heating. If however $\rho k_{th} << V^2/8T_0$, (1) reduces to,

$$\frac{d\Phi}{dt} = Ae^{-\frac{E_{A0}8\rho k_{th}}{kV^2}}, \qquad \tau_{pulse} \propto e^{\frac{E_{A0}8\rho k_{th}}{kV^2}}, \tag{3}$$

resulting in thermally assisted ionic motion.

Figure 3 is a plot of $\rho k_{th}$ for various reported ECM memory cells of a variety of materials for both SET and RESET. An implied filament size of 5x5nm$^2$ was used for all memory cells making them comparable. $\rho k_{th}$ for the SET mechanism was calculated using $k_{th}$ of the dielectrics from literature and $R_{OFF}$ from the pulsed switching results. $\rho k_{th}$ for the RESET mechanism was calculated using $k_{th}$ of the metallic conducting filament and $R_{ON}$ from the pulsed switching results. For the SET process in the Cu/a-SiC/Au memory cells, high thermal conductivity ($k_{th}$=490W/mK[19]) along with extremely high $R_{OFF}$ resistance leads to an ultra high $\rho k_{th}$ value compared to other memory cells, resulting in purely ionic motion with no joule heating contribution. A relation has been shown to exist between the RESET state conditions and the SET switching kinetics.[20] In order

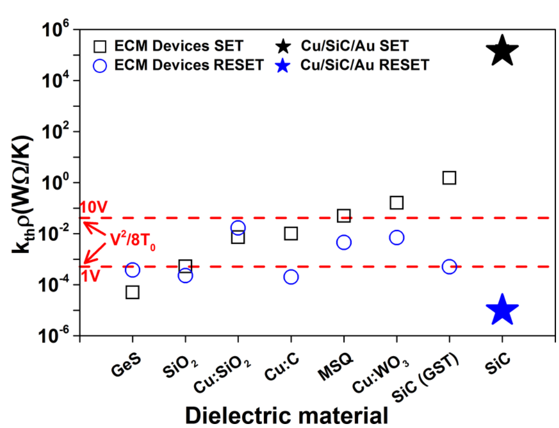


FIG. 3. Thermal conductivity and resistivity of reported ECM cells and Cu/a-SiC/Au cells for SET and RESET. Dashed red line determines the switching mechanism; above it indicates ionic without joule heating whilst below indicates ionic motion with joule heating contributions, at 1V and 10V. The SET mechanism for the reported memory cells is well into the ionic only regime, even at 10V. The references are GeS,[4] $SiO_2$,[7] Cu:$SiO_2$,[6] Cu:C,[17] MSQ,[5] CU:$WO_3$[18] and SiC(GST).[12]

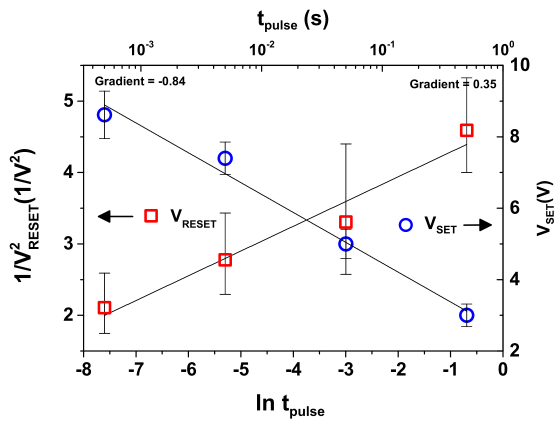


FIG. 4. Time dependencies of pulsed switching for Cu/a-SiC/Au memory cells, using pulse widths of 500$\mu$s-0.5s. The SET process shows exponential decrease in SET pulse width for increase in pulse amplitude and the RESET process shows exponential decrease in RESET pulse width with $1/V^2$ relation.

to investigate the SET and RESET mechanism of SiC memory cells, the switching kinetics were experimentally identified using pulses with varied durations.

Figure 4 shows that the SiC memory cells, for the SET mechanism, have an exponential relation between $V_{SET}$ and $t_{SET}$. This can be seen in (2), showing agreement with the model whereby the SET process in these memory cells are determined by ionic motion without joule heating contribution. Using the SET gradient of Figure 4, the barrier lowering coefficient, $\alpha$, is extracted to be 0.02. $\alpha$ can be approximated by $\delta z/2L_{CF}$, where $\delta z$ is the ion hopping distance between states and $L_{CF}$ is the filament length.[21] Assuming the filament length is equal to the dielectric thickness, an ion hopping distance of 1.52nm is found. The large $V_{SET}$ required for these memory cells can be attributed to the lack of joule heating contribution, originating from the low resistivity and high thermal conductivity of SiC, in agreement with Ref. 20.

Figure 4 shows the RESET mechanism has an exponential relation between pulse width and $1/V^2_{RESET}$ , in agreement with the model, indicating a dominant thermally assisted process. It is thought the dominant RESET mechanism is diffusion of metal ions away from areas of the filament with highest resistance, and therefore temperature, due to joule heating effects, rather than oxidation near the filament tip, in agreement with Refs. 22 and 23. Using the RESET gradient of Figure 4 and the relation given by (3), the conductive filament diameter is extracted to be $\Phi$ ~4nm, using $k_{th}$=401W/mK and $E_{A0}$ = 0.69 eV.[24] This is in good agreement with previously reported diameter sizes for Cu nano-filaments.[25]

Although these memory cells are limited by the speed of switching, the high ratio and stability show their potential for use in harsh environments. The Cu/a-SiC/Au memory cells were irradiated with $^{60}$Co ionizing radiation up to 2Mrad(Si), using the set-up described in Ref. 26. Figure 5 shows two sets of pulsed measurements, before and after radiation, using a 50ms pulse width, with increasing steps from -0.4V to -2.5V for RESET and +8V for SET. The ultra-high average $R_{OFF}/R_{ON}$ of $\geq 10^8$ remained present after radiation.

Along with pulsed measurements, DC sweep measurements were conducted allowing the conduction mechanism, post irradiation, to be compared with pre irradiation. As previously reported, the conduction mechanism for the LRS state of these memory cells is most likely Cu filament ohmic conduction, shown by a linear relation in ln(I)-ln(V).[11] Figure 6(a) plots ln(I)-ln(V) for the LRS state after DC sweep measurements and after pulsed measurements, before and after irradiation. The difference in $R_{LRS}$ for the DC sweep and pulsed modes originates from the higher current compliance used for the DC sweep measurements. A linear relation is exhibited for both pre and post radiation, for pulsed and DC sweep modes, indicating no change in LRS conduction mechanism. The conduction mechanism for the HRS state has previously been reported to most likely be Schottky emission,[11] displayed by a linear fit in ln(I)-$V^{1/2}$. Figure 6(b) shows ln(I)-$V^{1/2}$ for HRS and pristine sweeps before and after irradiation. The slightly reduced resistance for HRS

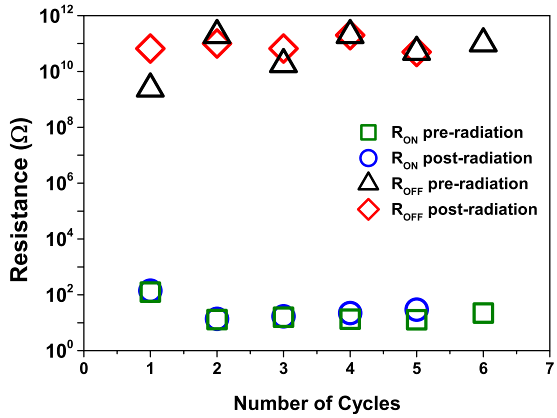


FIG. 5. Pulsed measurements for Cu/a-SiC/Au memory cell before and after ionizing irradiation using a 50ms pulse width, with increasing steps from -0.4V to -2.5V for RESET and at +8V for SET.

compared to pristine is most likely due to small residual filaments remaining after the form step. No notable difference is seen post irradiation, with Schottky emission remaining as the HRS conduction mechanism.

These results show no noticeable radiation induced change in conduction mechanisms, with little impact on $R_{OFF}/R_{ON}$ up to 2Mrad(Si), indicating their potential for use in space and nuclear

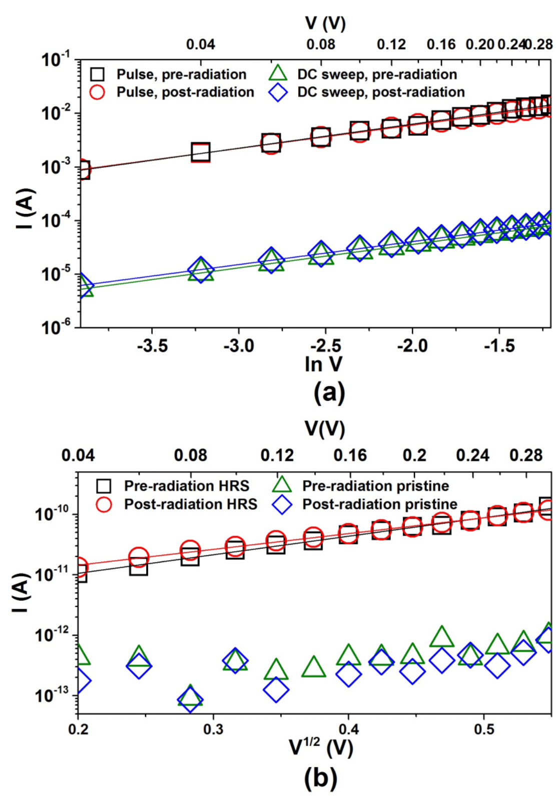


FIG. 6. I-V plots before and after irradiation of Cu/a-Si/Au memory cells showing (a) LRS after pulsed and DC sweep measurements, with error bars the same size as the data points. A gradient of $1.00 \pm 0.02$ indicates ohmic conduction. A higher resistance is seen for DC sweep measurements compared to pulsing measurements, due to lower current compliance; (b) HRS and pristine sweeps, after DC sweep measurements. Linear fit for HRS indicates Schottky Emission. No noticeable change in conduction mechanism is observed after radiation for LRS, HRS or pristine modes.

industries. Previously reported hafnium oxide RRAM cells have also shown high ionizing radiation tolerance with negligible change seen in memory cell parameters up to 10Mrad(Si).[26–28] This indicates that the radiation sensitive region within a memory circuit is not the RRAM cell but rather the select device or peripheral circuit, where isolation oxides in transistors have previously been identified as highly susceptible to radiation effects.[29]

Cu/a-SiC/Au memory cells have shown pulsed switching with ultra-high $R_{OFF}/R_{ON} \geq 10^8$, the highest published ratio to date, originating from high OFF resistance. The high OFF resistance and thermal conductivity of these memory cells indicates that, using the condition $\rho k_{th} >> V^2/8T_0$, the switching mechanism for the SET process is due to ionic motion without any joule heating contributions resulting in slow switching memory cells. The agreement between deduced measurements of the simple resistive memory cells, with extreme parameters, and the numerical model indicates this model works for a full range of memory cell parameters. These Cu/a-SiC/Au memory cells are radiation hard up to 2Mrad(Si) with negligible change seen for ratio and conduction mechanisms, indicating the potential for these memory cells to be used in harsh environments.

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