

Supplementary Information

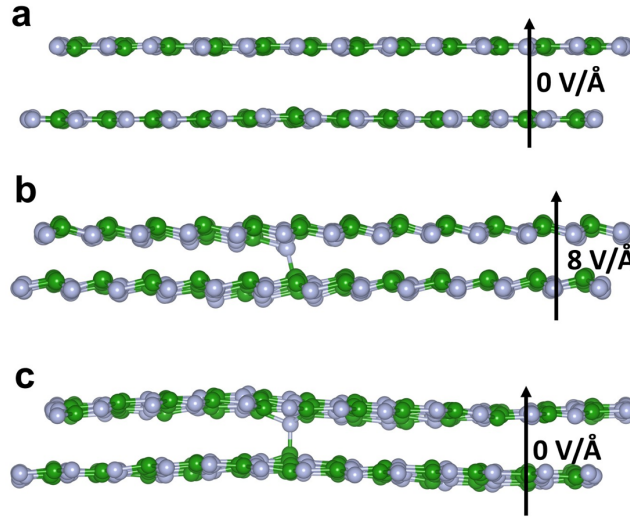
Atomistic description of conductive bridge formation in two-dimensional material based memristor

Sanchali Mitra¹ and Santanu Mahapatra²

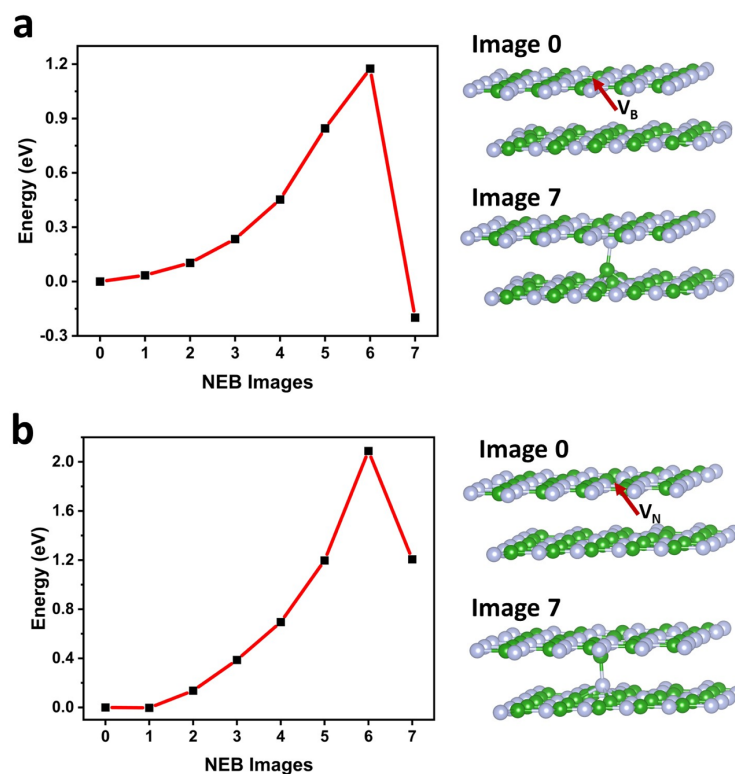
Nano-Scale Device Research Laboratory, Department of Electronic Systems Engineering,

Indian Institute of Science (IISc) Bangalore, Bangalore - 560012, India

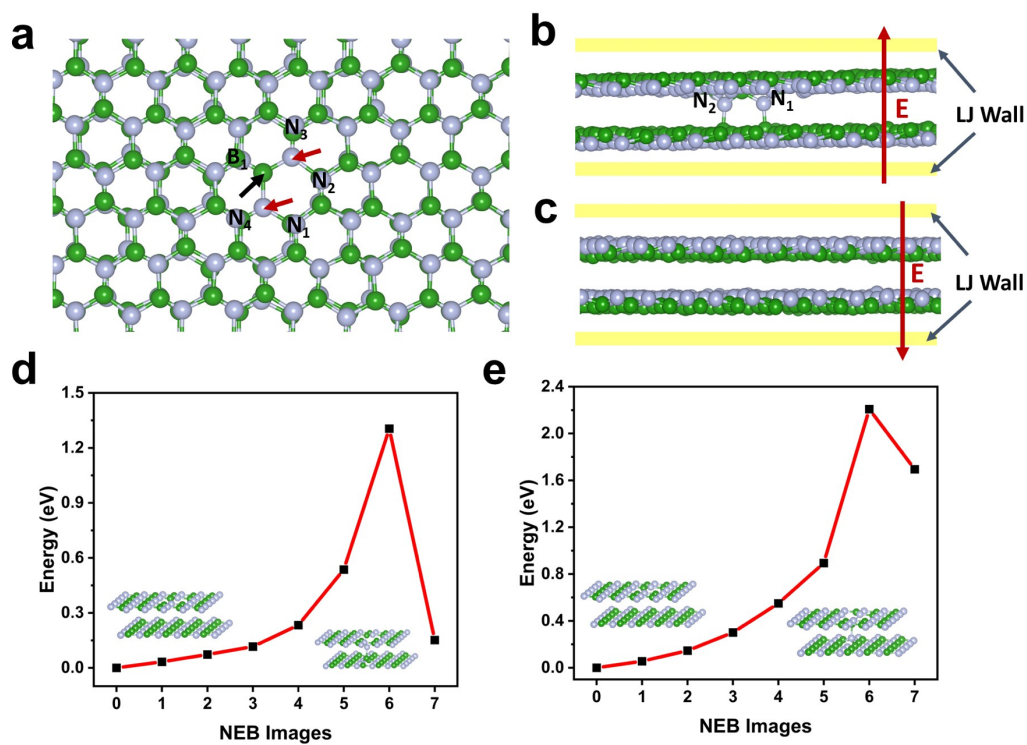
¹sanchalim@iisc.ac.in, ²santanu@iisc.ac.in



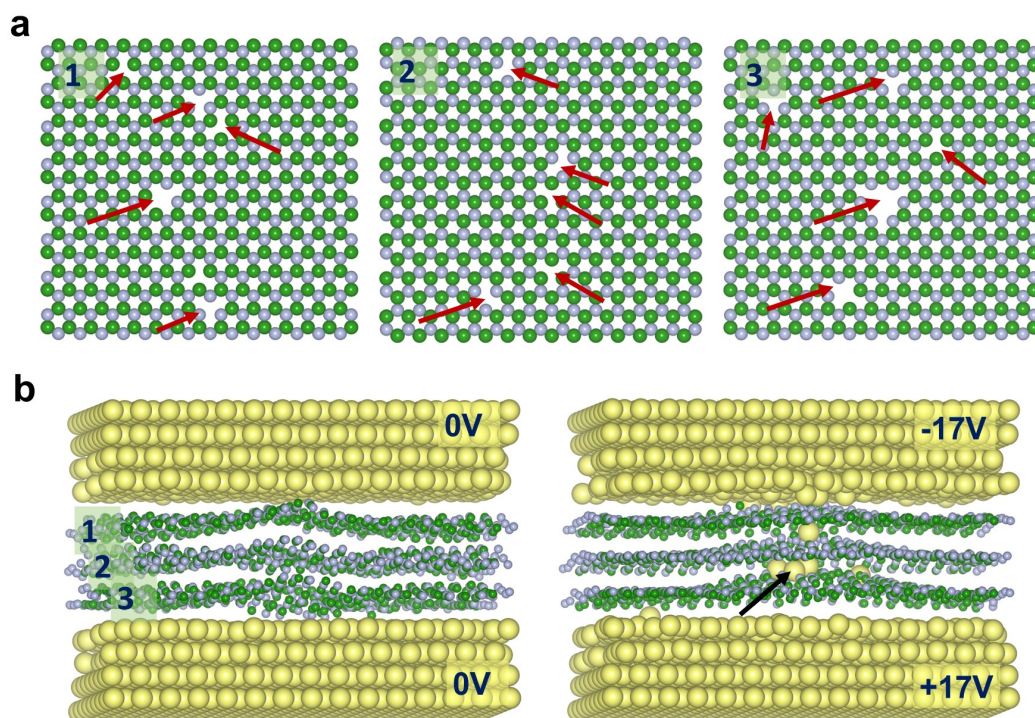
Supplementary Figure 1. SET in bilayer h-BN without LJ wall. Atomistic snapshots of side view of bilayer h-BN **a** without electric field, **b** when an electric field of 8V/Å is applied for 0.25ns, **c** when the electric field is withdrawn. In this simulation, no virtual wall is used outside the h-BN layers. The absence of virtual walls leads to a lower threshold value of the electric field to create an “N-B bridge”. B and N atoms are represented by green and silver balls, respectively.



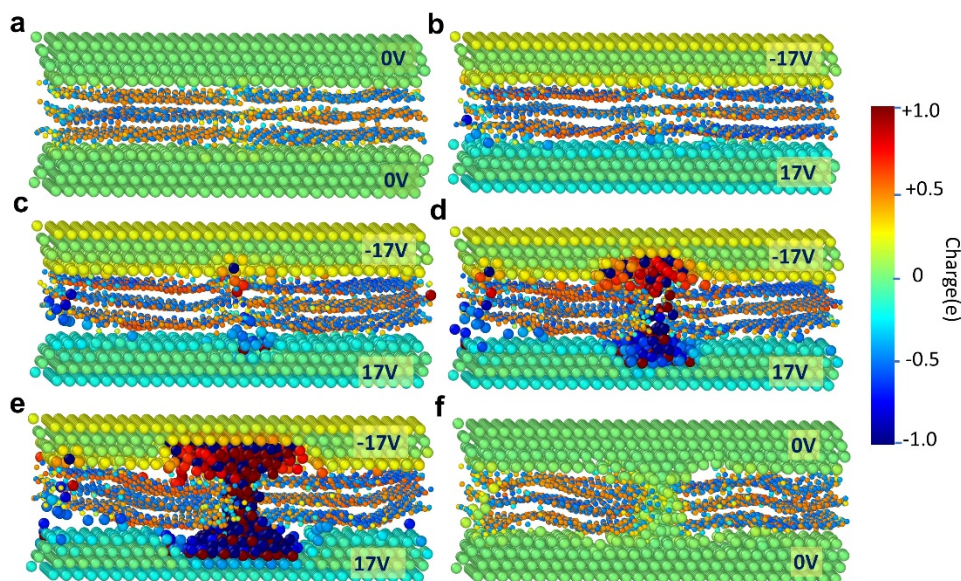
Supplementary Figure 2. Nudged elastic band calculations using ReaxFF. Plot of energies along the path of a one “N-B bridge” formation b “B-N bridge” formation. B and N atoms are denoted by green and silver balls, respectively.



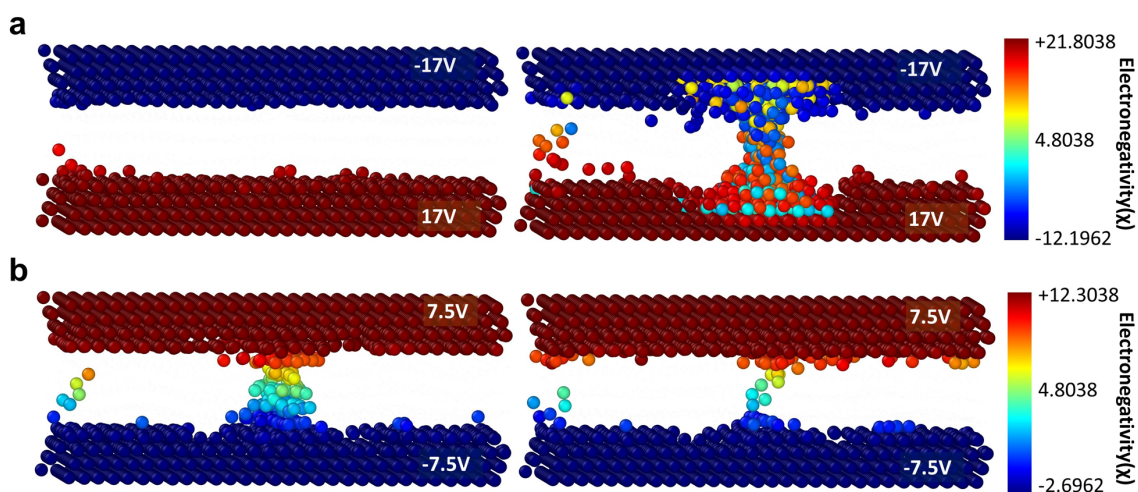
Supplementary Figure 3. Intrinsic RS in h-BN due to presence of B_2N vacancy. **a** top-view of a bilayer h-BN consisting of one B_2N vacancy in the upper layer. The Red arrows show the two B vacancies and black arrow points to the N vacancy. The four undercoordinated N atoms are denoted as N_1 , N_2 , N_3 and N_4 whereas the undercoordinated B atom is denoted as B_1 . Snapshots of side views of h-BN layers at **b** $+15V/\text{\AA}$ and **c** $-15V/\text{\AA}$. Plot of energies along the path of **d** one “N-B bridge” formation N_1 **e** “B-N bridge” formation with B_1 atom. The initial and final images of the NEB simulations are depicted inside the graphs. B and N atoms are denoted by green and silver balls, respectively. The yellow rectangles in **b** and **c** represent the virtual walls placed across the h-BN layers during the MD simulations.



Supplementary Figure 4. RS in multilayer h-BN consisting of scattered vacancies. **a** top view of the three layers of h-BN. The left, middle, and right panels show the upper, middle, and lower h-BN layers. The red arrows point to the vacancies present in the layers. **b** Side view of the three-layer h-BN-based device at 0V and 34V. Only a few Ni atoms from the bottom electrode move up to the middle h-BN layer through the B_3N vacancy present in the lower h-BN layer. These atoms remain confined in the h-BN layer. As a result, no continuous filament connecting the two electrodes is formed. No other atomic movements are detected. Ni, B, and N atoms are represented by yellow, green, and silver balls, respectively.

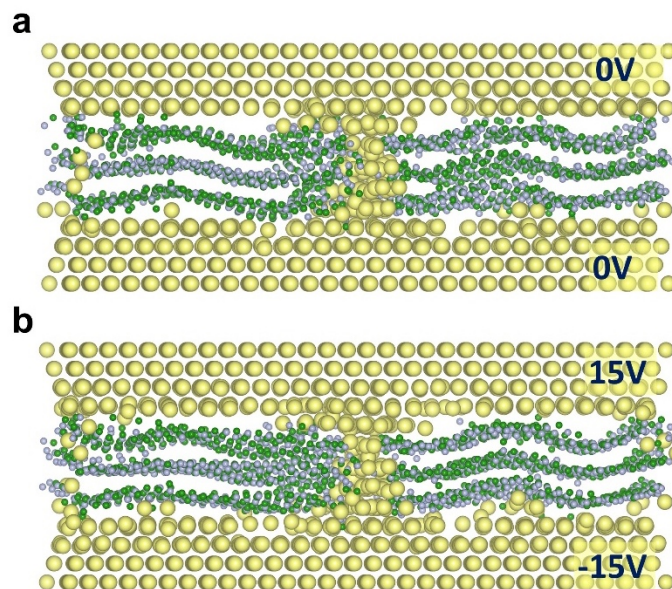


Supplementary Figure 5. Atomic charge distribution during SET. Snapshots showing partial atomic charges **a** before applying voltage; at 34V after **b** 0.0005ns, **c** 0.005ns, **d** 0.001ns, **e** 0.02 ns MD run; **f** after withdrawing SET voltage. The atoms are colored according to their partial charge calculated using charge equilibration method coupled with ReaxFF. The colour bar shows the values of charge corresponding to different colors. The radii of B and N atoms are reduced compared to Ni atoms for better clarity.

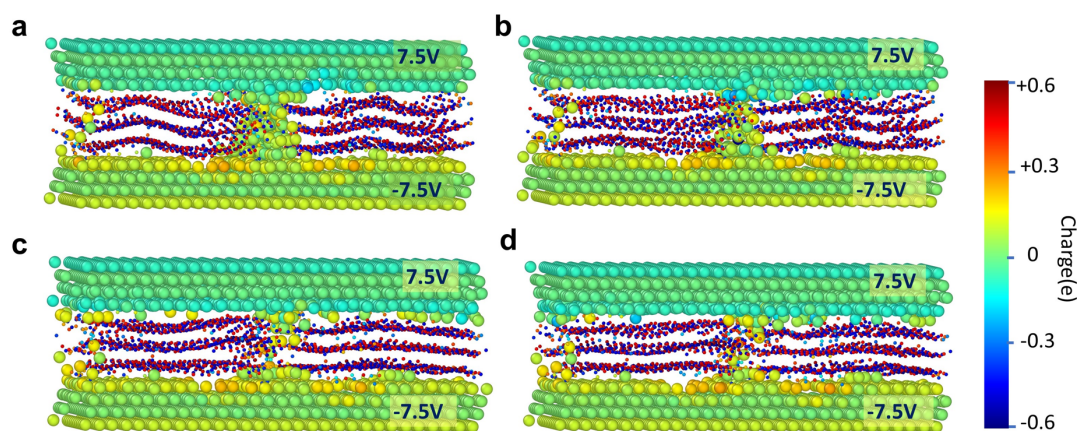


Supplementary Figure 6. Electronegativities of electrode atoms. Snapshots showing the electronegativities in Ni atoms during **a** SET (Left and right plots show the snapshots after 0.0005ns and 0.02ns MD run at 34V, respectively), and **b** RESET (Left and right plots show the snapshots after 0.0005ns and 0.66ns MD run at -15V). The Ni atoms are colored according to their electronegativities. For clarity, the B and N atoms are hidden. The color bar shows the values of electronegativity corresponding to different colors. As the SET and RESET voltages are different, two separate color bars are used for better visualization. According to EchemDID, when a voltage v is applied during SET, the electronegativities of

Ni atoms at the top and bottom electrodes are changed to $\chi_0 - v/2$ and $\chi_0 + v/2$, respectively; where, χ_0 is the standard electronegativity of Ni atom. The ReaxFF parameters show the value of χ_0 is 4.8038. During filament formation, the electronegativity values of Ni atoms vary according to their distance from their source electrode. At the beginning of RESET, the Ni atoms located inside the filament are assigned to their standard electronegativity value.

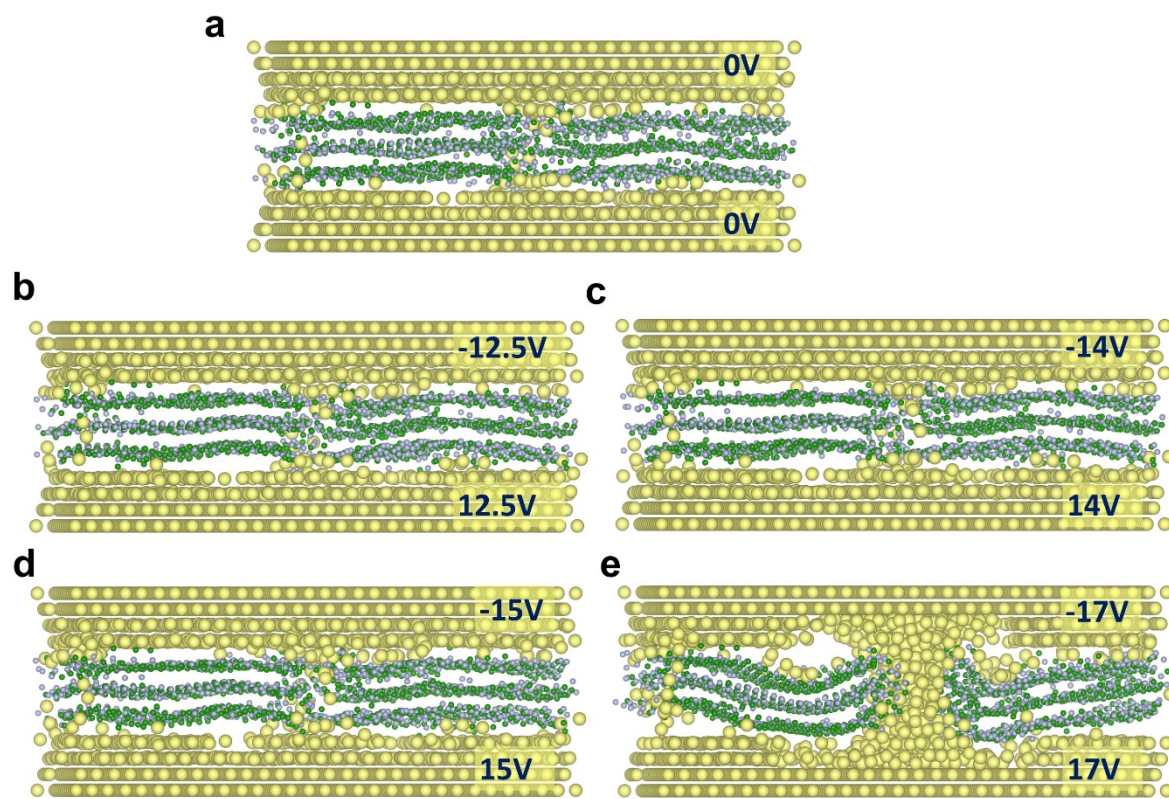


Supplementary Figure 7. Atomic snapshots showing effect of reverse voltage without Joule heating in Ni/h-BN/Ni device. Side views of the device **a** at 0V after SET **b** when -30V is applied for 0.07ns to reset the device. In this case, no Joule heating is applied. It is found that filament width remains same even if a reverse voltage is applied implying Joule heating is essential in RESET. Ni, B, and N atoms are represented by yellow, green, and silver balls, respectively.

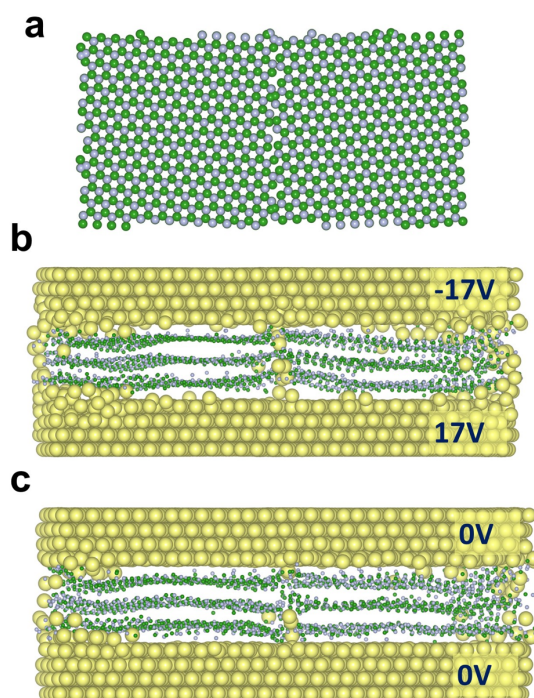


Supplementary Figure 8. Charge distribution at Ni/h-BN/Ni during RESET. Snapshots showing the partial atomic charges at -15V after **a** 0.0005ns **b** 0.05ns **c** 0.25ns, and **d** 0.66ns MD run. The atoms are coloured according to their partial charge calculated using QEq

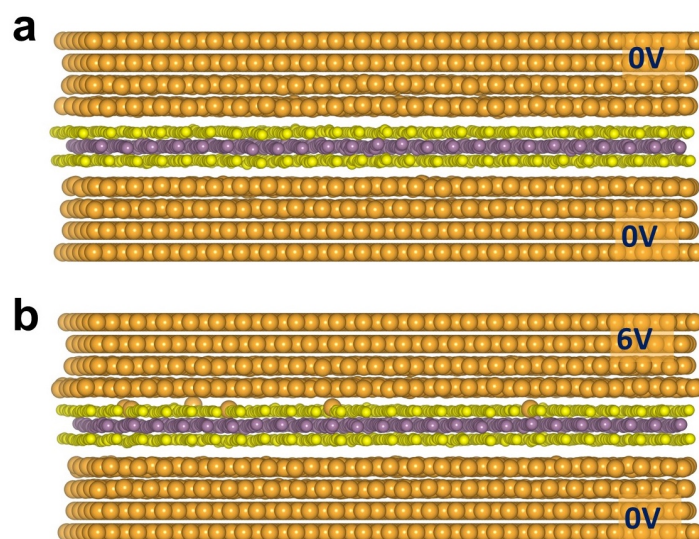
method. The colour bar shows the values of charge corresponding to various colours. The radius of B and N atoms are reduced compared to Ni atoms for better clarity.



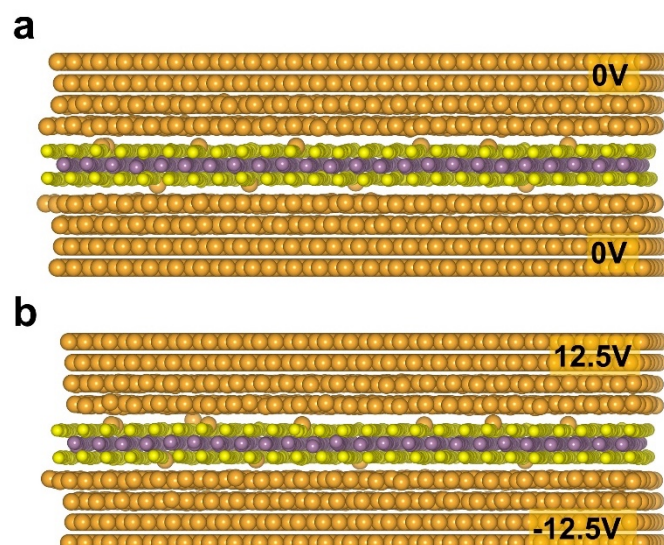
Supplementary Figure 9. Atomic snapshots of SET Process in second cycle in Ni/h-BN/Ni. **a** side views of the device after the first RESET cycle (as shown in Fig. 5f); **b-e** side views of the device when different voltage pulses of width 0.05ns are applied separately after first RESET cycle. The values of applied voltages are **b** 25V, **c** 28V, **d** 30 V and **e** 34V. It is found that, like first cycle, the filament formation through grain boundary occurs at 34V. Presence of metal atoms after the RESET, does not affect the operation of next cycle. SET voltage remains same in two consecutive cycles.



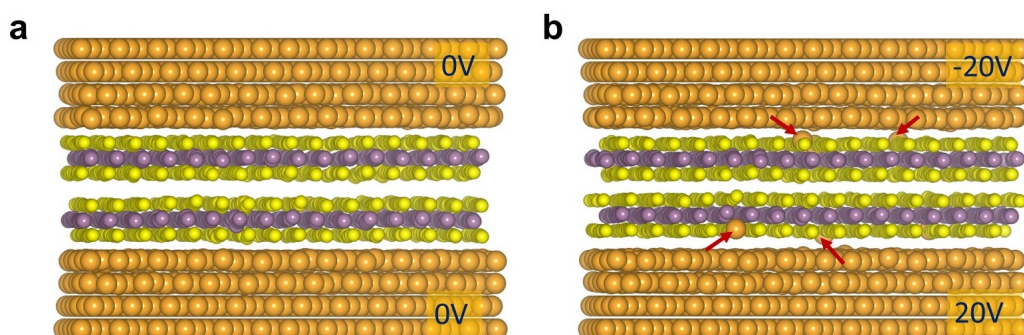
Supplementary Figure 10. Volatile switching in h-BN multilayer. **a** top-view image of h-BN consisting grain boundary at the center of the film. The grain boundary is created by rotating the two grains at angles $\pm 26^\circ$ around the out-of plane axis. Side views of the device at **b** 34 V during SET, **c** 0V after SET. At 34 V, a thin filament forms along the grain boundary joining the two electrodes; however, the filament ruptures as the voltage is withdrawn.



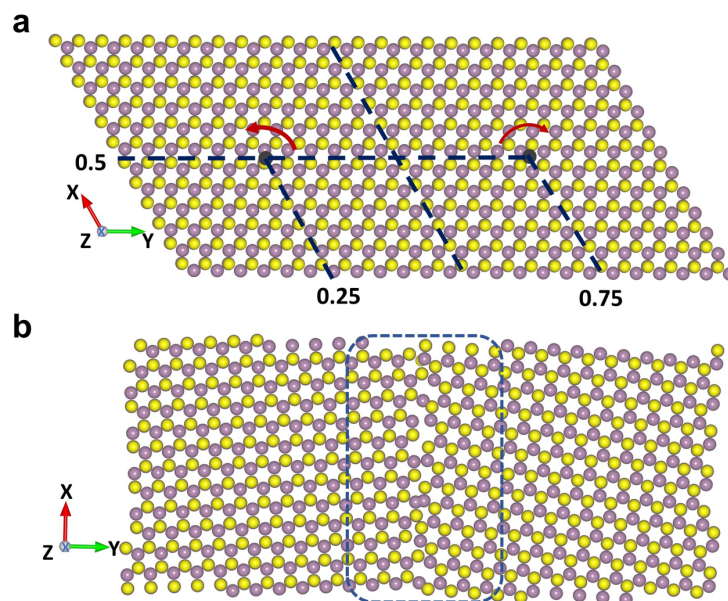
Supplementary Figure 11. Au adsorption in ML MoS₂ at low voltage. Atomic snapshots during MD simulations at **a** 0V and **b** 6V. Here, EchemDID is not used to apply voltage. The electronegativities of Au atoms only in upper electrodes are manually changed to model the applied voltage. The electronegativities of lower electrode atoms remain same.



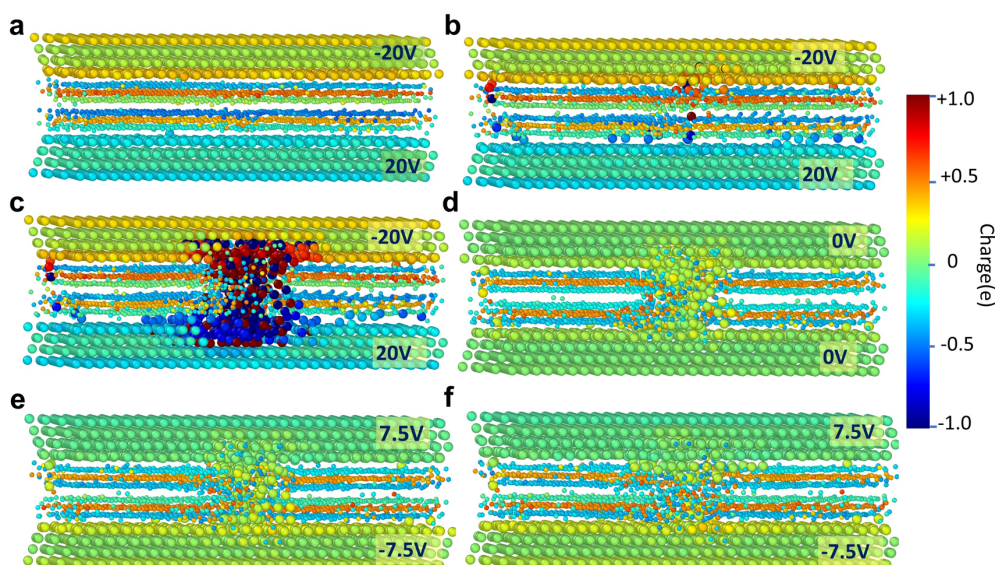
Supplementary Figure 12. Atomic snapshots showing effect of reverse voltage without Joule heating in Au/ML MoS₂/Au. Side views of the device **a** at 0V after SET **b** when -25V is applied for 0.5ns to reset the device. In this case, no Joule heating is applied. It is found that no adsorbed Au atom returns in the electrode even if a sufficiently large reverse voltage is applied.



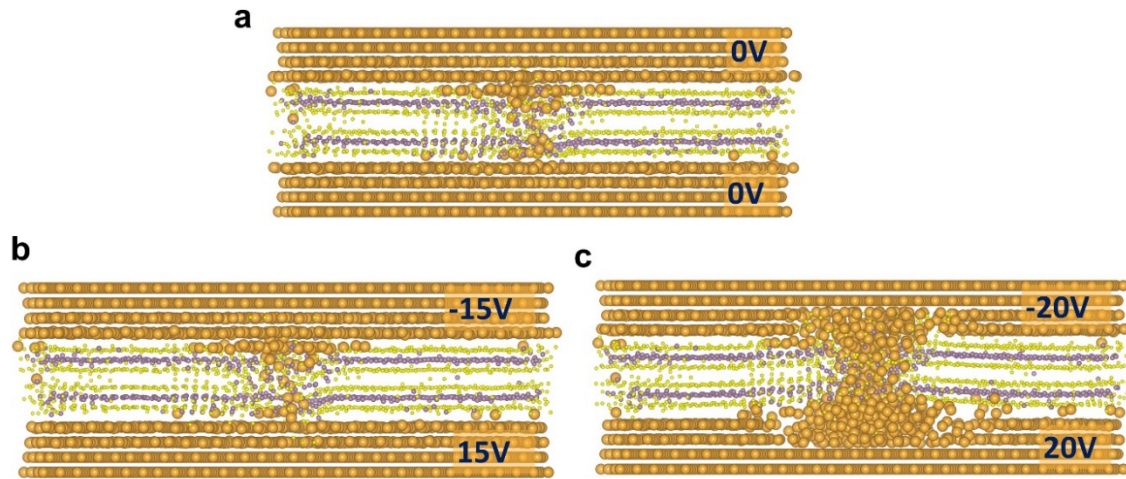
Supplementary Figure 13. RS in multilayer MoS₂ with scattered S vacancies. Side-view images of bilayer MoS₂ based device at **a** 0V **b** at 40V. Au atoms get adsorbed only on the S vacancies present in the surface S planes. No vacancy or Au atom migrations are found.



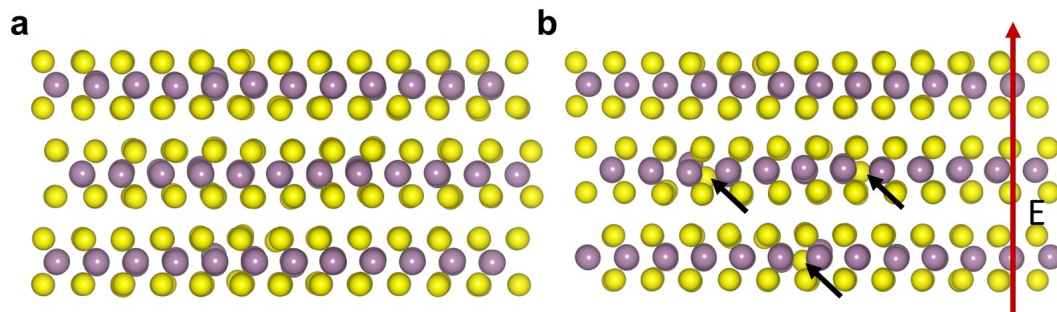
Supplementary Figure 14. Grain boundary in MoS₂. **a** top-view image of the supercell of MoS₂. The MoS₂ is first divided into two grains at the center of the y-plane. The grains are then rotated by $\pm 34^\circ$ around the z-axis. The red arrows show the centers of rotation angles of each grain. **b** top view image of grain boundary along the middle of the MoS₂ layer. The dotted box indicates the grain boundary region.



Supplementary Figure 15. Charge distribution at Au/MoS₂/Au during SET and RESET. Snapshots showing partial charges on each atom during the MD simulations at **a** 40V after 0.0005ns, **b** 40V after 0.06ns, **c** at 40V after 0.1ns, **d** 0 V after SET, **e** -15V after 0.0005ns, and **f** -15V after 1.95ns. The atoms are coloured according to their partial charge calculated using QEq method. The colour bar shows the values of charge corresponding to various colours. The radius of Mo and S atoms are reduced compared to Au atoms for better clarity.



Supplementary Figure 16. Atomic snapshots of SET Process in second cycle in Au/MoS₂/Au. **a** side view of the device after the first RESET cycle (as shown in Fig. 5f); side views of the device when different voltage pulses of **b** 30V and **c** 40V of width 0.05ns are applied separately after first RESET cycle. Like first cycle, the filament formation through the grain boundary occurs at 40V. Presence of metal atoms after the RESET, does not affect the operation of next cycle.



Supplementary Figure 17. Intrinsic RS properties in multilayer MoS₂. Side-views of three layered MoS₂ consisting of S mono vacancies in lower S planes of each layer **a** before applying electric field, **b** after applying electric field of 4V/Å. Due to the electric field S atoms opposite the S vacancies pop into the Mo plane. No interlayer bridge formation is found.