A Mechanism of Electroforming in SiO_2 Based ReRAM Devices Facilitated by Electron Injection

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The TiN/SiO_2/TiN stack (Fig.1) described in [1] is used as a model system to study the mechanisms of electroforming is SiOx based resistive random access memory devices (ReRAM) using density functional theory (DFT) and atomistic modelling. The bulk system (far from the interface) is approximated as stoichiometric amorphous (a)-SiO_2 whereas the SiO_2/TiN interface is considered explicitly and constructed using DFT simulations (Fig. 3,4). It has previously been demonstrated that electron injection can facilitate the creation of Frenkel defects in a-SiO_2 at structural precursor sites composed of wide O-Si-O bond angles [2]. These sites act as deep electron traps (Fig. 2) and can accommodate up to two extra electrons. Trapping of two electrons at intrinsic sites results in weakening of Si-O bonds and emergence of efficient bond breaking pathways for producing neutral O vacancies and interstitial O_i^{2-} ions with low activation barriers [2]. Inside the a-SiO_2 film, a low barrier for migration (Fig. 5) of the O^{2-} ion ($\approx$ 0.2 eV) is further reduced by bias application. These barriers are further reduced at the TiN/SiO_2 interface facilitating diffusion of O_i^{2-} from the bulk towards the interface coupled to a lowering of the incorporation energies for the O_i^{2-} as a function of the distance from the interface. The charge transition level for the O_i (0/--) moves towards that of the TiN Fermi level as the O_i approaches the interface. This results in a transfer of the electrons to the TiN electrode at the interface. Once the interstitials arrive at the interface, there is an initial 'oxidation' of the interface *via* the formation of a TiO layer (Fig. 6), preferably at Ti-interface sites, in accordance with the transition electron microscopy and electron energy loss spectroscopy observations [3]. The Ti-O bonds (Fig. 6) are strong and show high barriers (> 1.2 eV) for dissociation and migration along the surface. Once the interface Ti-sites are occupied, O_i are incorporated at or in the layers directly below the interface or diffuse inside TiN via grain boundaries and desorb into gas [1].

[1] A. Mehonic, et al., Adv. Materials, **28**(34), 7486-7493 (2016)

[2] D. Z. Gao, et al., Nanotechnology, **27**(50), 505207 (2017)

[3] M. S. Munde, et al., Scientific Reports, **7**, 9274 (2017)

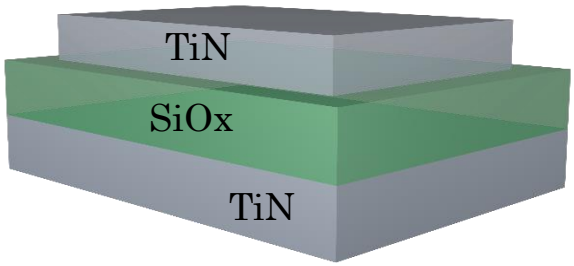

Fig.1: Symmetric MIM design TiN/SiOx/TiN structure used for unipolar resistive switching [1].

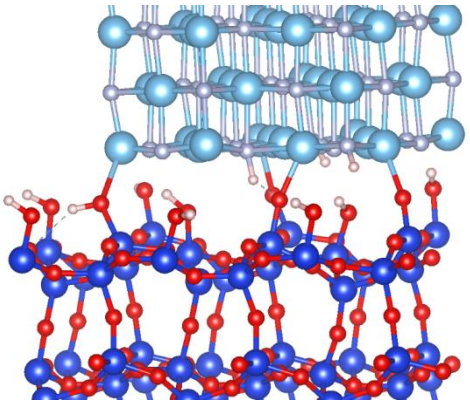

Fig.4: The model of SiO2/TiN stack where the SiO2 surface is partially hydroxylated, forming silanols (H is shown in white, Si-blue and O-red).

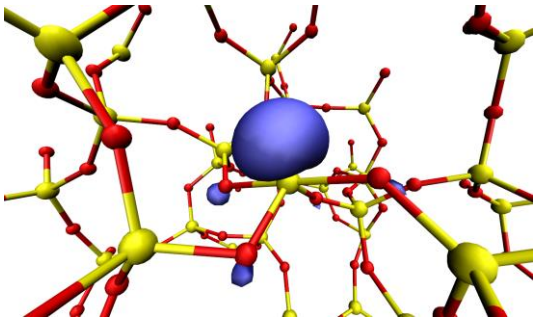

Fig.2: The electron density distribution (blue) of two electrons trapped at a Si atom (yellow) in amorphous SiO2 structure. The O-Si-O angle after trapping is 176°.

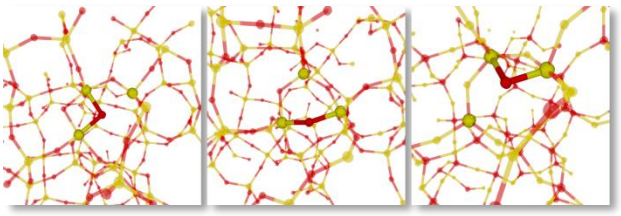

Fig.5 Sequence of atomic configurations corresponding to the interstitial O^{2-} diffusion in a-SiO_2. The middle configuration corresponds to the barrier point. The average barrier for diffusion is about 0.2 eV.

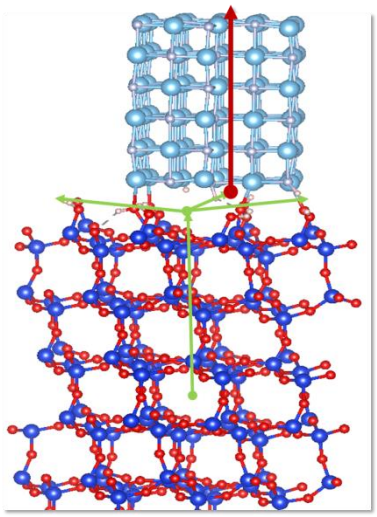

Fig.3: The model of SiO_2/TiN stack. SiO2 is represented by the α-cristobalite crystalline structure. Red arrows indicate the directions of O interstitial ion diffusion considered in simulations.

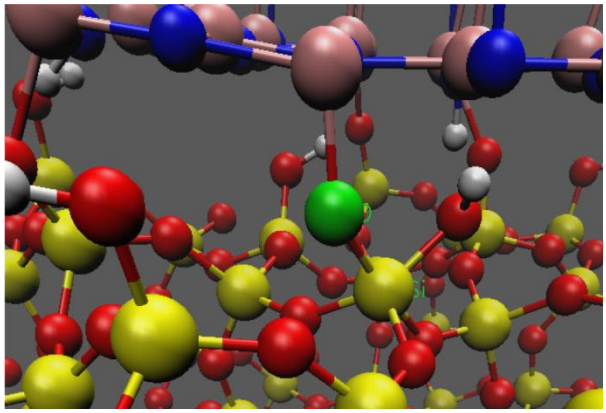

Fig.6: Close-up of the interface between a-SiO_2 and TiN showing the formation of Ti-O-Si bond .