# Modeling of diffusion and incorporation of interstitial oxygen ions at the TiN/SiO<sub>2</sub> interface

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#### Abstract

Silica based Resistive Random Access Memory (ReRAM) devices have become an active research area due to complementary metal-oxide-semiconductor (CMOS) compatibility and recent dramatic increases in their performance and endurance. In spite of both experimental and theoretical insights gained into the electroforming process,

many atomistic aspects of the set and reset operation of these devices are still poorly understood. Recently a mechanism of electroforming process based on formation of neutral oxygen vacancies  $(V_O^0)$  and interstitial O ions  $(O_i^{2-})$  facilitated by electron injection into the oxide has been proposed. In this work, we extend the description of the bulk  $(O_i^{2-})$  migration to the interface of amorphous (a)-SiO<sub>2</sub> with the polycrystaline TiN electrode, using density functional theory (DFT) simulations. The results demonstrate a strong kinetic and thermodynamic drive for the movement of  $O_i^{2-}$  to the interface, with dramatically reduced incorporation energies and migration barriers close to the interface. The arrival of  $O_i^{2-}$  at the interface is accompanied by a preferential oxidation of under-coordinated Ti sites at the interface, forming a Ti-O layer. We investigate how O ions incorporate into a perfect and defective  $\Sigma 5(012)[100]$  grain boundary (GB) in TiN oriented perpendicular to the interface. Our simulations demonstrate the preferential incorporation of O<sub>i</sub> at defects within the TiN GB and their fast diffusion along a passivated grain boundary. They explain how, as a result of electroforming, the system undergoes very significant structural changes with the oxide being significantly reduced, interface being oxidized and part of the oxygen leaving the system.

### Keywords

DFT, Oxygen Diffusion, ReRAM, Electroforming, Silicon dioxide, Titanium nitride

### 1 Introduction

Over the last 20 years, ReRAM devices have moved from the lab bench to a commercial reality, offering a range of advantages over the incumbent memory technologies.<sup>1,2</sup> Typically these devices are based upon oxides, with interest being focused on a variety of transition metal, rare earth and main group oxides, with varying degrees of success.<sup>1–4</sup> Regardless of the choice of dielectric, ReRAM devices operate by the field induced switching between a high resistance state (HRS) and a low resistance state (LRS). During the forming process a

conductive filament (CF) is created, the character of which is dependent upon device type. The most important measures of device efficiency center around the forming and switching voltages, with lower values being desirable. These efficiency measures are combined with a switching endurance to describe the overall performance of a device.<sup>1-3,5-8</sup>

A variety of oxides have been tested with great promise shown in devices based upon  $HfO_2$ , <sup>9-11</sup>  $TaO_x$ , <sup>12</sup> along with others. <sup>1,2,13-16</sup> Recently interest turned to SiO<sub>2</sub>, and the related suboxide  $(SiO_x)$ , <sup>5,6,17,18</sup> as they offer a variety of benefits from a processing, cost, and fabrication perspective. The processing and handling benefits are derived from the abundance of  $SiO_2$  expertise in the CMOS technology, particularly in the growth and electrical characterization of  $SiO_2$  films. The  $SiO_2$  based devices are divided into two main types: those based upon the inter-diffusion of metal ions, such as via electrochemical metalisation, <sup>19–26</sup> and valence change memory (VCM) where a CF is formed as a result of reduction under bias application.<sup>1,2,5–8,17</sup> In VCM the CF is made up of oxygen vacancies, dependent upon material and mode of operation either  $V_O$  or  $O_i$  are suggested to be the mobile species during forming.<sup>2</sup> Forming has been kinetically modeled in a range of other materials giving some valuable insights into the energy barriers and time-scales.  $^{27-29}SiO_2$  has only been of limited interest to the ReRAM community as dielectric breakdown of stoichiometric SiO<sub>2</sub> requires high bias application, as evidenced by its role as a gate oxide. Only substoichiometric  $SiO_x$ films, where x is in a range of approximately 1.35 - 1.95, demonstrate good switching behavior.  $^{5,17,30}$  These devices have been shown to have low forming voltages ( $\approx$  -2.6 V) and switching voltages  $(\pm 1 \text{ V})$ .<sup>30</sup> In addition to the stoichiometry, the film micro-structure resulting from the templated columnar growth has been shown to play an important role in device performance.<sup>31</sup>

To allow systematic refinement and optimization of the  $SiO_x$  based ReRAM devices requires a detailed understanding of the mechanisms of forming, set, and reset. The recent works<sup>32–35</sup> explored the mechanism of electron injection mediated Frenkel pair formation in a-SiO<sub>2</sub>. It has been demonstrated that electrons injected into a-SiO<sub>2</sub> can trap at precursor sites with wide O–Si–O angles, present in the regular amorphous structure.<sup>32–34</sup> Trapping two electrons at these sites induces a strong distortion of the surrounding network, which weakens the Si–O bonds. This significantly reduces the barrier for O-ion displacement into an interstitial position, giving an average field free barrier of  $\approx 0.7 \text{ eV}^{35}$  and results in the formation of a neutral V<sub>O</sub>, and a negatively charged O interstitial ion,  $O_i^{2-}$ . The migration barrier for  $O_i^{2-}$  diffusion was calculated to be 0.2 eV and is reduced further in the electric field applied during forming.<sup>35,36</sup> This process creates mobile  $O_i^{2-}$  ions, which under the applied field move towards the top electrode. These results accord well with the observations reported in <sup>5,6,31</sup> and describe the mechanism of oxide reduction and creation of mobile oxygen interstitials. The fate of these interstitial O ions has not been considered further in detail at the atomistic level and is the main focus of this paper.

TEM studies<sup>5,31</sup> on the TiN/a-SiO<sub>x</sub> systems raise a number of important questions that consideration of the bulk system alone cannot answer. These are focused on the effect of the interface and the observed outflow of oxygen through the TiN. There appears to be an incorporation of oxygen at the interface and transport through the TiN upon forming, suggesting that the TiN/a-SiO<sub>x</sub> interface is not acting as a hard barrier and is evolving during the forming process. Moreover, oxygen diffuses through the polycrystaline TiN film and desorbs into the gas phase, as observed in ref.<sup>5</sup> The aim of this work is to provide a quantitative view of  $O_i^{2-}$  migration to the interface, interaction with the interface, and subsequent out diffusion of oxygen through TiN.

### 2 Methodology

Experimental data shows that TiN films grown using sputter deposition on  $SiO_2$  have a polycrystalline morphology, with many resulting grain boundaries.<sup>5,31</sup> Our previous calculations<sup>37</sup> demonstrate that oxygen does not diffuse through perfect bulk TiN and hence grain boundaries should play an important role in oxygen penetration through TiN film and des-

orption into the gas phase observed in ref.<sup>5</sup> In the first approximation we assume that these boundaries can be modeled as relatively simple  $\Sigma 5(012)[100]$  symmetric grain boundaries. Sputter deposited TiN films are known to be quite defective, with Ti and N vacancies present both in the bulk and at GBs.<sup>38,39</sup> To achieve our aims we consider O diffusion in the a-SiO<sub>2</sub> and TiN systems separately and then at the interface between TiN with GB and SiO<sub>2</sub>.

Modeling such a complex multi-component system requires each region to be well described geometrically and electronically (at the very least in the energy range of interest). In addition to this, the combined system must reproduce the experimental observations in terms of band-offset and microstructure from HR-TEM. A combination of molecular dynamics (MD), and spin polarized density functional theory (DFT) calculations are performed to generate and characterize the systems of interest.

Common to all the calculations, defect formation energies are calculated using the standard formalism of Northrup and Zhang,<sup>40</sup> with the chemical potentials taken from the respective monoatomic crystals, and as half of the total energy of a molecule in the gas phase in the case of nitrogen and oxygen. For charged defects, finite size charge corrections are employed using the Lany-Zunger method to correct the formation energies for image charge interaction.<sup>41</sup> To explore the migration barriers climbing image nudged elastic band (CI-NEB) calculations are used, in each case the convergence criteria is 0.01 eV / Å with 5 - 13 images along the band.<sup>42</sup> The number of images are selected based upon the path length to ensure the separation between images is maintained.

When considering oxygen diffusion through defective TiN we need to compare energies of oxygen configurations on Ti and N sublattices, as well as between the substitutional and interstitial oxygen configurations. The relative formation energy ( $\Delta E$ ) is calculated according to equation 1

$$\Delta E = E_{sub} - E_{int} + \mu \tag{1}$$

where,  $E_{sub}$  is the total energy of the system with a substitutional oxygen defect,  $E_{int}$ 

is the total energy of the system with an interstitial oxygen defect, and  $\mu$  is the chemical potential of the substituted atom, nitrogen or titanium, respectively. Following equation 1, the interstitial oxygen configuration is used as the reference state, and the sign of  $\Delta E$  determines whether the investigated substitutional configuration is energetically more favorable (negative sign) or less favorable (positive sign) compared to the interstitial configuration. Computing  $\Delta E$  requires knowledge of the chemical potentials of Ti and N. As sputter deposited TiN films are generally N-deficient,<sup>38,39</sup> two limiting cases for the chemical potential are considered i) N-deficient and, ii) stoichiometric TiN. These are calculated using the Hagen and Finnis<sup>43</sup> and Mishin *et al.*<sup>44</sup> schemes under the dilute solution approximation, as detailed by Popov *et al.*<sup>45,46</sup>

### 2.1 TiN

The properties of bulk TiN and periodic grain boundary calculations were performed using the Vienna *ab initio* Simulation Package (VASP).<sup>47–50</sup> To model the TiN/SiO<sub>2</sub> interface, TiN was represented by a finite cluster. These calculations were performed using the CP2K code,<sup>51–54</sup> which provides greater efficiency. The PBEsol functional has been shown to perform well for the TiN system in a series of previous studies.<sup>45,46,55,56</sup> The change in codes allows each region to be treated as accurately as possible, while allowing simulation cells of sufficient size to be constructed. The specifics of each calculation are described under the relevant header along with the performance of the optimized parameter set.

#### 2.1.1 TiN bulk and grain boundary

The bulk TiN calculations were performed using VASP and a 40 atom periodic cell. The plane wave cutoff was converged at 400 eV, with a  $\Gamma$ -centered 8 × 8 × 8-Monkhorst-Pack k-point scheme. The lattice vectors and ion positions were fully optimized to converge the forces with a tolerance of 5 × 10<sup>-3</sup> eV/Å, reproducing the experimental lattice parameters to  $\approx 1 \%$  (4.218 Å). The calculated density of states (DoS) shown in Figure 1 is in excellent

agreement with the previous TiN studies confirming that the region around the Fermi level is composed primarily of Ti d-states.<sup>45,46,57</sup> This will act as an important reference for the GB system, the cluster representation of TiN, and the interface with SiO<sub>2</sub> as the DoS around the Fermi level needs to be well described, with an experimental valence band-Fermi level offset with a-SiO<sub>2</sub> of 4.2 eV.<sup>58</sup>



Figure 1: The calculated a) DoS, and b) band structure for the bulk TiN system.

The periodic calculations of TiN GB are performed for the Duffy-Tasker  $\Sigma 5(012)[100]$  GB<sup>59</sup> and extend the previous work on Cu diffusion in this GB.<sup>45,46</sup> In common with the bulk TiN, VASP was utilized with the PBEsol functional.<sup>55,56</sup> In this case the  $12 \times 6 \times 1$  Monkhorst-Pack k-point mesh was used, with a plane wave energy cutoff of 400 eV. The GB has been modeled by a TiN slab with a supercell containing one GB and 160 atoms. The lattice parameter used is 4.218 Å, with a converged vacuum gap of 11.2 Å (Figure 2a). The DoS was calculated and is shown in Figure 2b.

Migration energy barrier calculations used the CI-NEB, with 13 images along the band, with a convergence criteria of 0.01 eV / Å.<sup>42</sup> The migration energy barrier is calculated as the maximum energy difference between the initial and final states on the migration paths.

#### 2.1.2 TiN cluster

Constructing a model of TiN  $GB/a-SiO_2$  interface presents a significant challenge due to the disparity between the two surfaces and absence of a connection scheme between O ions



Figure 2: a) The TiN Duffy-Tasker  $\Sigma 5(012)[100]$  GB model considered in this work. GB plane is indicated by the red dashed line, and solid lines depict the layer index convention. Light blue and grey spheres depict Ti and N atoms, respectively. b) The density of states for the TiN GB system.

of the SiO<sub>2</sub> surface and Ti ions of TiN. Therefore, instead of using an epitaxial model of the type used in,<sup>60–62</sup> we explored different interface configurations using a finite cluster representation of TiN GB. If a freestanding cluster of sufficient size can capture the properties of the periodic system, this cluster can then be tessellated over the a-SiO<sub>2</sub> surface to allow a variety of connection schemes to be tested in an efficient manner.

In these calculations CP2K<sup>51-54</sup> is used in the place of VASP as this code offers greater computational efficiency. The calculations are performed at the  $\Gamma$ -point, with the PBEsol functional<sup>55,56</sup> and a plane wave cut-off of 600 Ry. These parameters are converged to the tolerances described above and the cell size is increased until the periodic GB geometry and DoS (Figure 3) are reproduced by the cluster without having to resort to fixing atoms, which can cause significant issues when constructing the interface system. The smallest cluster satisfying these requirements contains 276 atoms. It reproduces the bulk DoS around the Fermi level and the geometry (< 1 % deviation with respect to the periodic GB) as shown in Figure 3. This cluster is then used to explore the connection schemes between TiN and a hydroxylated SiO<sub>2</sub> surface as discussed below in section 2.3.



Figure 3: The smallest free standing cluster a) 276 atom TiN cluster, and b) associated DoS. Ti is represented by light blue spheres, and N by grey. From both a geometric and electronic perspective, the 276 atom cluster is the smallest cluster that reproduces the bulk grain boundary.

### 2.2 SiO<sub>2</sub> models

We construct models of bulk a-SiO<sub>2</sub> and hydroxylated surface before turning to modelling TiN GB/a-SiO<sub>2</sub> interfaces and diffusion of oxygen ions through the combined system.

#### 2.2.1 SiO<sub>2</sub> bulk

In common with previous studies, the a-SiO<sub>2</sub> periodic cells are prepared from a 216 atom cell of  $\beta$ -cristobalite using a melt/quench procedure and the molecular dynamics LAMMPS code<sup>63</sup> with the ReaxFF force field.<sup>64</sup> We used a cooling rate of 1 K/ps as described by El-Sayed *et al.*<sup>33,34,64</sup> and Patel *et al.*<sup>24,25</sup> The lattice vectors and ion positions of the obtained structures were then relaxed using DFT implemented in CP2K<sup>51,53,54,65,66</sup> with the PBE0-TC-LRC functional (with exchange truncation radius of 2 Å).<sup>52</sup> All calculations were performed at the  $\Gamma$ -point with a converged plane wave cutoff of 600 Ry. This approach produces a-SiO<sub>2</sub> cells with a mean density of 2.2 gcm<sup>-3</sup> in excellent agreement with the experimental density.<sup>67</sup> The HOMO-LUMO separation is 8.6 eV on average, a small underestimation with respect to the experimental band-gap (8.9 eV).<sup>68</sup> Migration energy barrier calculations used the CI-NEB, with 5 images along the band, with a convergence criteria of 0.01 eV / Å.

#### 2.2.2 SiO<sub>2</sub> surface

The experimental devices are fabricated in ambient conditions necessitating the modelling of hydroxylated a-SiO<sub>2</sub> surfaces. There is a wealth of previous literature concerned with tackling just this problem.<sup>69–75</sup> Here we use the approach given by Emami *et al.*<sup>76</sup> as they show excellent agreement between the experimental and the theoretical surface OH concentration. These cells are particularly large, varying between 2000 - 3000 atoms, with the simulation cells used for production containing 2953 atoms. Calculations of this size are resource intensive, and to reduce the costs as much as possible we used the PBEsol functional. The rest of the computational parameters are the same as for the bulk a-SiO<sub>2</sub> (Figure 4). These surface cells are then used as the a-SiO<sub>2</sub> side of the a-SiO<sub>2</sub>-TiN interface.



Figure 4:  $a-SiO_2$  hydroxylated surface in a) plan, and b) projection, illustrating the roughness inherent in the amorphous surface. Si is represented by dark blue spheres, H white, and O by red.

To facilitate the analysis of the results for oxygen incorporation energies and migration barriers we also employ a crystalline SiO<sub>2</sub> model to give context to the a-SiO<sub>2</sub> calculations. To achieve that, a hydroxylated  $\alpha$ -cristobalite (c-SiO<sub>2</sub>) [202] surface was constructed. This termination was selected to give an appropriate Si-OH concentration for comparison with a-SiO<sub>2</sub> systems allowing the effect of the amorphization to as much as possible be divorced from the effect of the interface. These systems are calculated with the same parameters as the a-SiO<sub>2</sub> surface slabs using the CP2K code.

### 2.3 Constructing TiN-SiO<sub>2</sub> interface systems

To model an a-SiO<sub>2</sub>-TiN system a cluster based approach is employed to mimic the method of growth while exploring the effect of the connection scheme on the interface properties. The TiN clusters employed are described in section 2.1.2 and the a-SiO<sub>2</sub> surface in section 2.2.2.

A series of interface models are constructed based upon a geometric descriptor. The initial input geometries are then relaxed allowing the descriptor to be refined and the energetic ordering understood. Small scale tests of TiN-SiO<sub>2</sub> systems have confirmed that the strongest interface binding interaction was due to the formation of Ti-(OH)-Si units. This is in line with previous observations for both the oxidation of the TiN surface, and the modeling of the extended TiN / oxide interfaces.<sup>77–79</sup> For interfaces derived from non-hydroxylated surfaces there is a secondary Si-N interaction, which is significantly weaker than the Ti-O interaction but can still be an important part of the interface binding mix. In the case of hydoxylated surfaces the Si-N interaction is negligible: as each surface Si is fully coordinated there are no available Si sites, hence forming Si-N units is sterically problematic. The initial geometric descriptor was therefore selected to maximize the number of Ti-(OH)-Si units. To achieve this, a grid based method was employed based upon cubic symmetry of TiN cluster, which is then tessellated over the a-SiO<sub>2</sub> surface until a Ti-(OH)-Si unit is formed. This then forms a node, around which point the cluster is allowed to rotate and tilt with a tolerance of  $\pm 10^{\circ}$ and a cluster-surface separation of  $2.5 \pm 0.5$  Å, to find the unique interface configurations (maximizing the number of Ti-(OH)-Si units) at each node. The tolerances are all system specific and were guided after extensive testing. This approach leads to exhaustive sampling of the a-SiO<sub>2</sub> substrate, as every surface OH is used as a node. It generates a large number of initial structures that need to be screened for duplicates and grouped efficiently, this is achieved using methods based upon those of Fu et al.<sup>80</sup> and Krizhevsky et al.<sup>81</sup> The initial models with the highest number of Ti-(OH)-Si units then undergo geometric relaxation with CP2K as detailed below.

The suitability of the geometric descriptor to reproduce the interface binding energy was tested, the 8 interface groups (10 models in each group) with the largest number of Ti-(OH)-Si units are geometrically relaxed with PBEsol. The energy comparison is included in Figure S2 in the ESI, and shows an excellent correlation between the initial geometry (number of Ti-(OH)-Si units) and the interface binding energy. A secondary comparison is then made between the offset between the valence band maximum (VBM) of a-SiO<sub>2</sub> and the Fermi level of TiN, as this value is well known from experimental studies (4.2 eV<sup>58</sup>), and is important in describing the charge transfer behaviour in the system.

Choosing an appropriate density functional for a metal/insulator system such as the one studied here is nontrivial. In particular, using the PBE0-TC-LRC hybrid functional to describe TiN leads to non-metallic behaviour *via* the opening of the band-gap. Likewise PBEsol underestimates the band-gap of a-SiO<sub>2</sub> by  $\approx 3$  eV. This presents a quandary as to whether it is best to accept a compromise that results in non-metallic TiN, or an underestimation of the a-SiO<sub>2</sub> band-gap. Our choice is guided by the fact that the electron transfer from the oxygen interstitial to TiN is of primary interest. Therefore how well each functional describes the offset between the Fermi level of TiN and the valence band of a-SiO<sub>2</sub> as well as the DoS around the Fermi level is of paramount importance. It turned out that PBEsol reproduces the experimental band-offset relatively well and preserves the metallic nature of TiN. Hence all of the interface calculations were performed with the PBEsol functional and the converged parameters from the surface cells using the CP2K code.

We note that the band offset strongly depends on the TiN-SiO<sub>2</sub> separation, and only those interfaces with the maximum number ( $\approx 15$ ) of Ti-(OH)-Si units reproduce the experimental values. The binding between the TiN and SiO<sub>2</sub> is primarily facilitated by the formation of Ti-(O/OH)-Si units as shown in Figure 5. There are a range of Ti-(O/OH)-Si interactions varying by the degree of deviation between the ideal extended lattice position of TiN and the site the OH is able to occupy. The O-H bond length acts as a good proxy for the strength of this interaction, the stronger the Ti-OH interact the more the O-H bond is extended. Once the O-H separation increases to over 1.4 Å, an interface NH unit spontaneously forms at the expense of the original OH unit (shown in Figure 5a). Conversely, as the Ti-(OH)-Si interaction weakens, either as the result of strain or distance, the O-H bond shortens toward the non-interacting O-H bond length(shown in Figure 5c). In general, approximately 25 % of the interface Ti form a strong interaction liberating H (Figure 5a), an additional 25 % of the Ti sites form a weak interaction with OH (Figure 5b/c). This leaves an interface where  $\approx 50$  % of the Ti sites are undercoordinated and could be potential O<sub>i</sub> incorporation sites. It is important to note that after relaxation some of the N-sites at the interface are decorated with H. It is entirely possible that this bound H can interact with O<sub>i</sub> to generate interface OH / H<sub>2</sub>O. For the purpose of this work this type of H-interaction is neglected, with the focus being the initial transport of O to the interface and beyond.

In addition to the band offset reproducing the experimental values, the DoS around the Fermi level of TiN shows the same character as is present in the periodic GB and the freestanding cluster. These factors taken together give confidence that the interfaces produced well describe the experimental interface and with the caveats already discussed will act as the test system to probe the effect of the interface on  $O_i^{2-}$  migration and incorporation.

### 3 Results and Discussion

The results of experimental work are discussed in great detail in the works of Mehonic et  $al.^{5}$  and Munde  $et al.^{31}$  and additional experimental details focused on the interface are provided in the electronic supplementary material (ESI, Figure S1). The TEM and EELS data presented in ESI illustrate the movement of oxygen to the interface post forming. The incorporation of oxygen in TiN at the interface is most evident from the O-K edge (Figure S1b). In the pristine device there is no observable oxygen signal, whereas on forming there is an appreciable oxygen signal. These results, however, give no information on how the oxygen is incorporated at the interface.



Figure 5: Schematic view of the interface binding modes between TiN and SiO<sub>2</sub> a) shows the strongest Ti-O interaction where the H is lost to a neighboring N site. b) Shows the case where the Ti is shared by two Si-OH groups where the interaction is considerably weaker than in a), the OH bond typically extends but remains intact. Finally, c) shows the weakest binding, the interaction is charge-diplole in nature and shows no significant perturbation of the OH bond (< 0.1(5) Å). Each of the inset pictures shows and examples of the various types in the relaxed interface systems. Ti is represented by light blue spheres, N by grey, Si by bright blue, and O by red.

To provide further understanding of the experimentally observed oxygen incorporation in the the TiN/a-SiO<sub>x</sub> system, the interface effect and the subsequent oxygen migration through the TiN are simulated below. A schematic picture of the O<sub>i</sub> incorporation and migration paths is shown in Figure 6. Firstly, the O<sub>i</sub> migration through the a-SiO<sub>2</sub> bulk to the interface is investigated in section 3.1 at different depths (represented by numbers 2-6 in Figure 6). Having arrived at the interface, the O<sub>i</sub> diffusion on the interface plane, or the SiO<sub>2</sub> surface, represented by 0-1 in Figure 6 is then discussed in section 3.2. Finally, the O<sub>i</sub> diffusion through the TiN bulk and GB and the effect of N vacancies are studied (section 3.3). For completeness, both oxygen interstitials and oxygen substitutional defects in TiN are included, with the effect of distance from the interface (1-TiN, 2-TiN, and 3-TiN in Figure 6b) taken into account.



Figure 6: a) Schematic view of the  $O_i$  interstitial incorporation and migration which is being investigated in this work. b) shows the sites that are referred to in the text, the depth profile of the indicated sites in c-SiO<sub>2</sub> is used to group the interstitials / barriers in a-SiO<sub>2</sub>.

### 3.1 Oxygen interstitial diffusion in $a-SiO_2$

The mechanism of  $O_i$  formation and subsequent diffusion in the bulk a-SiO<sub>2</sub> has been described extensively in the previous works.<sup>5,6,35</sup> This work provides increased sampling of the barriers described in the previous studies. The calculations have been performed in accordance with the previous studies of Gao *et al.*<sup>35</sup> with the models refined by Patel *et al.*,<sup>24,25</sup> as described in section 2. The comparison between the barriers calculated with PBEsol and PBE0-TC-LRC provides the important link between the previous bulk results and interface systems. Including better statistics allows the range of barriers for interstitial migration to be described more accurately.

The results reported in ref.<sup>35</sup> predict an average migration barrier of 0.2 eV for  $O_i^{-2}$  diffusion in a-SiO<sub>2</sub>. Here we used both the PBE0-TC-LRC and PBEsol functionals to perform an exhaustive sampling (total of 1080 calculations) within 5 a-SiO<sub>2</sub> cells (mean density 2.2 gcm<sup>-3</sup>) to allow the spread of barriers to be estimated. These calculations well reproduce the previous results<sup>35</sup> giving a mean barrier height of 0.24 ± 0.09 eV for PBE0-TC-LRC and

 $0.29 \pm 0.11$  eV for PBEsol. The distribution of barrier heights for both PBE and PBE0 are included in the ESI Figure S3. The similarity of the barriers gives confidence in the ability of the PBEsol functional to reproduce the migration barriers of the  $O_i^{-2}$  in the interface system.

### 3.2 Oxygen interaction with the $TiN-SiO_2$ interface

The interface calculations were performed on both  $\alpha$ -cristobalite and the a-SiO<sub>2</sub> cells as described in section 2. The crystalline system gives a baseline for the a-SiO<sub>2</sub> to be compared with, while maintaining the same interface hydroxyl concentration. Initially, the interstitial incorporation as a function of layer distance from the interface (0-6 in Figure 6b) is explored with incorporation energies and geometries considered. These stationary points are then linked *via* NEB trajectories to describe how the barriers for O<sub>i</sub><sup>-2</sup> migration change approaching the interface.

### 3.2.1 O<sub>i</sub><sup>-2</sup> incorporation

In common with the bulk,  $O_i^{2}$  incorporates at the split interstitial site in a "diamond" configuration as described in ref.<sup>35</sup> The z-dimension of both the crystalline and the amorphous cells were selected to give bulk like behaviour at the cell center. This was judged based upon the defect-free geometric and electronic structure, and geometries and incorporation energies of the oxygen interstitial, as outlined in section 2.3. The incorporation energies are reported relative to the bulk (average bulk value for a-SiO<sub>2</sub>) with negative values representing favorable incorporation with respect to the bulk, and *vice versa* (Table 1). There is an added complication inherent in the amorphous cells as the clear layers of the crystal are lost. This makes the selection of those barriers that make up a particular layer nontrivial, in this case the depth profile of the crystalline system is used as a reference for the amorphous system. To describe the range of incorporation energies, 30 calculations were performed in each layer. The full set of distributions are included in the ESI Figure S4.

It is clear from Table 1 that the presence of the interface facilitates the incorporation

Table 1: The incorporation energy for the  $O_i^{-2}$  interstitial as a function of depth below the interface for the c-SiO<sub>2</sub> ( $\alpha$ -cristobalite) and a-SiO<sub>2</sub>. The incorporation energies in eV are referenced to the bulk interstitial, the standard deviation ( $\sigma$ ) is reported for the amorphous interstitials in a given layer. The numerical positions are shown in Figure 6b.

Layer	$c-SiO_2$	a-SiO <sub>2</sub> ( $\sigma$ )
0	-2.85	-2.50(0.2)
1	-1.49	-1.70(0.5)
2	-1.05	-0.90(0.6)
3	-0.29	-0.50(0.4)
4	-0.27	-0.35(0.1)
5	-0.20	-0.29(0.2)
6	0.00	-0.05(0.3)

of the  $O_i^{-2}$ , with the incorporation energies rapidly decreasing as the interface is approached (layers 1-6 in Figure 6b). The same trend is apparent in both the c-SiO<sub>2</sub> and a-SiO<sub>2</sub>, although in the amorphous case there is a greater spread of values associated with each layer. This spread is in response to the greater variety in geometry and ring flexibility as the interface is approached. It is important to note, however, that the sampling in the case of the a-SiO<sub>2</sub> system is far from complete, so the range should be treated as indicative only.

There were no stable minima identified in the layer directly below the interface in either of the systems, with interstitials placed within this region relaxing to form interface structures. Furthermore, no stable minima were identified using a series of manual scans of the energy surface, giving confidence that this effect is not an artifact of the minimizer selected, and is common to both the crystalline and the amorphous system. It is, however, important to note that the sampling of the amorphous interface was not exhaustive, so metastable near interface O configurations cannot be entirely ruled out. The final two interstitial configurations (0 & 1 in Figure 6b) relate to  $O_i$  incorporated at the interface to form a Si-O-Ti unit with undercoordinated Ti ions (Figure 7). These structures represent an oxidation of the interface as shown in Figure 7.

From these calculations, a quandary arises: in the bulk regime (section 3.1 and Table 1 layer 6) the  $2e^{-}$  of the  $O_i^{-2}$  are localized on the interstitial site in anti-bonding oxygen p-states,<sup>35</sup> however, at the interface these electrons have been lost to the TiN electrode and



Figure 7: A schematic view of O incorporation at the TiN / SiO<sub>2</sub> interface a) shows the deprotonated form and b & c) shows the protonated form of O incorporation. The inset pictures show the O incorporation at the interface, in the two configurations.

are delocalized. The question is at which point this charge transfer occurs and can any useful information be extracted from the above static calculations to answer this question. This is important as the  $O_i^0$  has far higher migration barriers (> 1 eV). Therefore, if the electrons are lost at some distance from the interface, the mobility of the  $O_i$  is dramatically reduced. There are a number of challenges inherent in accurately describing the  $O_i$  charge transition levels (CTL), in this case a hybrid functional such as HSE06 or PBE0 is required to have confidence in the quantitative validity of the values calculated.<sup>33,35</sup> Even when hybrid functionals are deployed there is still a significant disagreement between the values calculated dependent on whether the functional has been fitted for Koopmans compliance, band-gap, or the stock values used. In the case of the interface system, hybrid functionals are not an option, as highlighted in section 2, giving an inappropriate description of the TiN. While absolute values for the CTL are beyond the methods deployed here, it is still possible to extract general trends. The (0/-2) CTL is at  $\approx 3.0$  eV above the VBM of a-SiO<sub>2</sub> in the bulk like regime. This value increases to 3.9 eV as the interface is approached (layer 6 - 2), which still sits below the Fermi level  $E_F$  of TiN (at 4.2 eV) and, with caveats highlighted above, at

any distance the interstitial would be in the -2 charge state at this level of theory.

### 3.2.2 O<sub>i</sub> migration

The previous section deals with the thermodynamic picture of  $O_i$  migration and demonstrates a strong drive for  $O_i$  to move from the bulk of the oxide to the interface. To elucidate this picture further, an understanding of the barriers involved in the migration is required, in essence connecting the minima described above.

Table 2: The migration barriers, in eV for  $O_i$  as a function of distance below the surface, the standard deviations ( $\sigma$ ) are included for the amorphous systems. The numerical positions are shown in Figure 6b and the trajectories are formed by connecting the indicated points.

Layer	$c-SiO_2$	a-SiO <sub>2</sub> ( $\sigma$ )
6-5	0.24	0.21 (0.09)
5-4	0.20	0.20(0.11)
4-3	0.14	$0.10 \ (0.06)$
3-2	0.12	$0.10 \ (0.05)$
2-1	0.09	$0.05 \ (0.05)$
1-0	1.5	1.55(0.26)

From Table 2 it is clear that the same trend as was observed for the incorporation energies (table 1) persists for the migration barriers – in both cases the presence of the interface facilitates the incorporation of the O<sub>i</sub>. The migration barriers in both the crystalline and the amorphous SiO<sub>2</sub> show the same trends with the bulk barriers being reduced from 0.24 and 0.21 eV, respectively. This trend is valid for migration in SiO<sub>2</sub>, but once the O is incorporated at the interface forming a Si-(O)-Ti unit and effectively oxidizing the interface, the barrier for migration along the interface is always in excess of 1 eV in the most strained configuration, with an average migration barrier of  $\approx 1.5$  eV. This allows the oxidation of the interface observed *via* TEM and EELS to be understood, as upon forming the O<sub>i</sub> moves from the bulk to the interface, leading to the observed oxidation of the interface. The structural rearrangement upon electroforming is presented in ref<sup>5</sup> and shows there is a widespread rearrangement of the oxide as the conductive filament is formed of correlated V<sub>O</sub>. This process leads to a reduction of the oxide in the vicinity of the filament and the release of O<sub>i</sub>, which is driven by the field to the top electrode where oxidation of the TiN occurs as shown in Figure S1 of the supplementary information.

We would like to stress that the results of this work are limited to consideration of  $O_i$  incorporation in the low concentration limit representing the situation at the start of the forming process. Further study is required to understand how the incorporation of  $O_i$  is facilitated after the initial interface oxidation.

### 3.3 O<sub>i</sub> in the bulk TiN grain boundary

#### 3.3.1 Oxygen incorporation in GB

Following the treatment of the  $SiO_2$  portion of the system, the bulk TiN picture is first considered before the effect of the interface on the O incorporation is explored. Previous studies<sup>57</sup> have shown that O<sub>i</sub> incorporation is not favoured in TiN bulk, therefore only the GB system and substitutional sites are considered for O incorporation (Figure 2). Before considering diffusion of oxygen in the grain boundary, the possible configurations of the TiN GB containing an oxygen atom need to be defined.

Two variants of O incorporation are considered, with the oxygen atom occupying either an interstitial ( $O_i$ ) or a substitutional ( $O_N$  or  $O_{Ti}$ ) site. In the case of interstitial, O is placed inside the GB channel and located either in the atomic plane or between the planes. Two stable O interstitial configurations were identified and are shown in Figure 8. The in-plane configuration (left column Figure 8) is energetically more favorable than the inter-plane (right column Figure 8), with a calculated energy difference of 0.39 eV. Henceforth, any discussion of the O interstitial configuration will refer to this lowest energy in-plane configuration.

For substitutional oxygen incorporation, an O can occupy either a nitrogen  $(O_N)$  or titanium  $(O_{Ti})$  site. There are three different possibilities for each of these cases, as there are three different layers in GB at which oxygen can substitute (see Figure 2 for notations). The energy differences and relative formation energies for each of these substitutional oxygen configurations are presented in Table 3, whereby the oxygen substitutional configurations



Figure 8: Illustration of the stable configurations of oxygen in TiN GB. The left column shows the in-plane configuration, the right column shows the inter-plane configuration. Ti is represented by light blue spheres, O by red, and N by grey. The numbers next to the Ti-O bonds indicate bond length in units of Å.

within each sublattice can be directly compared to one another.

 $E_i - E_0$  in Table 3 shows the energy difference between configurations with the O in the i-th layer and in the 0-th layer on the same sublattice. A negative  $E_i - E_0$  indicates an energy decrease when going from the 0-th layer to the i-th layer. From Table 3, it is clear that  $O_N$  preferentially occupy the 0-th layer, whereas  $O_{Ti}$  is most energetically stable in the 2-nd layer.  $\Delta E$  (Table 3) show that  $O_N$  in layer 0 is the most energetically favorable configuration for O in TiN GB. Formation of  $O_{Ti}$  requires a significant energy, and hence  $O_{Ti}$ is not considered further. Having calculated the preferred oxygen position in TiN GB, the segregation of oxygen into the GB is described by the segregation energy ( $E_{seg}$ ) according to equation 2:

Table 3: The energy difference  $(E_i - E_0)$  and the relative formation energy  $(\Delta E)$  for the various configuration of substitutional oxygen defects in TiN GB. All values are in units of eV.

Layer	$E_i - E_0$	$\Delta E_{N-poor}$	$\Delta E_{stoichiometric}$
N sublattice $(O_N)$			
0	0	-1.8	-0.45
1	0.26	-1.55	-0.20
2	0.53	-1.27	0.08
Ti sublattice $(O_{Ti})$			
0	0	6.18	4.83
1	-2.12	4.06	2.70
2	-2.89	3.29	1.94

$$E_{seg}(\text{Bulk}_{\text{sub}} \to \text{GB}_{\text{sub}}) = [E(\text{TiN}_{\text{GB}}\text{O}_{\text{sub}}) - E(\text{TiN}_{\text{GB}})] - [E(\text{TiN}_{\text{Bulk}}\text{O}_{\text{sub}}) - E(\text{TiN}_{\text{Bulk}})],$$

$$E_{seg}(\text{Bulk}_{\text{int}} \to \text{GB}_{\text{int}}) = [E(\text{TiN}_{\text{GB}}\text{O}_{\text{int}}) - E(\text{TiN}_{\text{GB}})] - [E(\text{TiN}_{\text{Bulk}}\text{O}_{\text{int}}) - E(\text{TiN}_{\text{Bulk}})],$$

$$E_{seg}(\text{Bulk}_{\text{sub}} \to \text{GB}_{\text{int}}) = [E(\text{TiN}_{\text{GB}}\text{O}_{\text{int}}) - E(\text{TiN}_{\text{GB}})] - [E(\text{TiN}_{\text{Bulk}}\text{O}_{\text{sub}}) - E(\text{TiN}_{\text{Bulk}})] - \mu_N,$$

$$E_{seg}(\text{Bulk}_{\text{int}} \to \text{GB}_{\text{sub}}) = [E(\text{TiN}_{\text{GB}}\text{O}_{\text{sub}}) - E(\text{TiN}_{\text{GB}})] - [E(\text{TiN}_{\text{Bulk}}\text{O}_{\text{int}}) - E(\text{TiN}_{\text{Bulk}})] + \mu_N.$$
(2)

Here,  $E(\text{TiN}_{\text{GB}})$  is the energy of the pure TiN GB,  $E(\text{TiN}_{\text{GB}}O_{\text{sub(int)}})$  is the energy of the TiN GB with O in the substitutional (interstitial) position,  $E(\text{TiN}_{\text{Bulk}})$  is the energy of the pure bulk TiN, and  $E(\text{TiN}_{\text{Bulk}}O_{\text{sub(int)}})$  is the energy of the bulk TiN with an O in the substitutional (interstitial) position. Equation 2 accounts for the fact that oxygen can occupy both interstitial and substitutional positions in GB as well as in the bulk. Table 4 shows the results of calculations of  $E_{seg}$  for various configurations. The negative sign of  $E_{seg}$ means that the segregation of oxygen to the GB is favorable. In general, Table 4 shows that oxygen segregates to the TiN GB.

		$E_{seg}$
$\mathrm{Bulk}_{\mathrm{sub}} \to \mathrm{GB}_{\mathrm{sub}}$		-0.33
$\mathrm{Bulk_{int}} \to \mathrm{GB_{int}}$		-5.36
	N-poor	Stoichiometric
$\mathrm{Bulk_{sub}} \to \mathrm{GB_{int}}$	1.54	0.19
$\mathrm{Bulk_{int}} \to \mathrm{GB_{sub}}$	-7.23	-5.88

Table 4: Segregation energy  $(E_{seg})$  in eV of oxygen to the TiN GB.

#### 3.3.2 Oxygen diffusion in GB

To study the process of oxygen diffusion inside TiN it is important to consider the various potential diffusion mechanisms. Based on the results of the previous section, the simplest possible mechanism is the interstitial diffusion along the GB channel. From previous studies<sup>45</sup> it is also clear that there is an appreciable number of nitrogen vacancies in the GB. Section 3.3.1 illustrates that the oxygen prefers to occupy the substitutional positions on the N sublattice ( $O_N$ ). Therefore, it is reasonable to assume that N vacancies ( $V_N$ ) can affect the oxygen diffusion mechanism.

#### 3.3.3 Interstitial mechanism of diffusion

The simplest diffusion mechanism corresponds to the interstitial diffusion of oxygen along the GB channel with no other defects present. This mechanism is represented as the O atom in the most stable interstitial configuration (top row in Figure 8) hopping between the adjacent atomic planes. The potential energy profile for this migration is shown in Figure 9.

As can be seen, the profile has a local minimum in the middle of the reaction path. This minimum corresponds to the second stable interstitial configuration of oxygen, which is shown on the bottom row in Figure 8. The energy barrier for this migration path is 0.57 eV.



Figure 9: The potential energy profile for the migration of an interstitial oxygen atom along the GB channel.

#### 3.3.4 Interstitial mechanism in $V_N$ containing system

As TiN is known to be nitrogen deficient, it is important to consider oxygen behaviour in GB with a  $V_N$  in one of the layers (see Figure 2). Figure 10 shows the energy profiles of  $O_i$ migration through a  $V_N$  in layers 0, 1 and 2, respectively. In the case of layers 0 and 1, the oxygen migrates to a  $V_N$  site almost without a barrier and becomes trapped. The energy barrier to leaving the  $V_N$  site and reforming the  $O_i$  is 2.0 eV.  $O_i$  migration in layer 2 follows a multi-step vacancy occupation. First,  $O_i$  approaches a  $V_N$ , with an energy barrier of about 0.60 eV, and, while remaining as  $O_i$ , binds to the  $V_N$ , forming a  $V_N$ - $O_i$  defect cluster. Now the oxygen can either continue its migration as an interstitial or occupy the  $V_N$  site. The first process requires overcoming an energy barrier of about 1.0 eV (not shown here), while the energy barrier for the second process is 0.54 eV. Therefore, it is more probable that the oxygen migrates to, and henceforth occupies, the  $V_N$  site, where it subsequently becomes trapped, as the energy barrier to be overcome for leaving the vacancy site is 2.0 eV. It is interesting to note that although all the oxygen configurations in the substitutional positions, *i.e.* in the layers 0, 1 and 2, are not energetically equivalent (see Table 3), the energy profiles for migrations via these configurations are similar, and the barriers for oxygen leaving the vacancy are nearly identical. Hence, it is expected that all these paths would be responsible for O<sub>i</sub> migration in this system.



Figure 10: The potential energy profiles for the migrations of  $O_i via V_N$ . Numbers 0, 1 and 2 denote the index of the layer where  $V_N$  is located. For each of the trajectories 6 represents the  $O_i$  at the vacancy site.

#### 3.3.5 Diffusion into the TiN GB

The final part of the diffusion picture relates to the transport of the  $O_i$  into and along the grain boundary. From the section (3.2.2) the barriers for  $O_i$  migration along the interface are significant when compared to the bulk  $O_i^{-2}$ , with barriers in excess of 1 eV. These barriers reduce the probability of diffusion along the interface, acting as a vector for oxygen transport into the grain boundary. However, there is still the case of the  $O_i$  moving out of the oxide and across the interface in the vicinity of the grain boundary. In the case of SiO<sub>2</sub>, the effect of the interface is dramatic with the reduction in barriers extending a considerable distance into the oxide. The picture at the TiN side of the interface has a number of similarities and some important differences.

In common with the  $SiO_2$  side of the interface, no stable minima were identified directly at the interface, with the  $O_i$  placed in the first layer of the GB relaxing back towards the interface forming a strained Ti-O-Si unit. The first stable interstitial position is therefore in position 1-TiN in figure 6. This results in a long path length for the NEB trajectory. To compensate for this, the number of images along the band are increased to 11. In order to keep a consistent spacing between images, 5 images are used for the in GB diffusion, in common with the other portions of the system. The barriers for  $O_i$  diffusion along the GB are presented in Table 5.

Table 5: The migration barriers for  $O_i$  as a function of distance above the interface. The  $O_i$  starts at position 2 in SiO<sub>2</sub>. The numerical positions are shown in Figure 6b and the trajectories are formed by connecting the indicated points.

Layer	TiN / eV
4-TiN - 3-TiN	0.61
3-TiN - 2-TiN	0.56
2 - 1-TiN	0.49

It is clear from Table 5 that there is a small interface effect with the bulk migration barriers being rapidly re-established. This is in marked contrast to the  $SiO_2$  portion of the system where the interface effect is far more extended. The lack of a stable GB configuration at the interface suggests that initially the O incorporates at the undercoordinated Ti sites at the interface, thereby blocking the available sites from subsequent O<sub>i</sub> arriving at the interface. A second step can then be envisaged to involve the migration of O<sub>i</sub> along the GB, along with a number of side reactions that are to be considered in a future publication.

### 4 Conclusions

The work presented here gives an atomistic insight into the transport of  $O_i$  from the bulk of  $SiO_2$ , to the interface, and beyond through the TiN electrode in the context of electroforming of  $TiN/SiO_x/TiN$  devices. For convenience, the system has been split into three distinct regions: inside the bulk of  $SiO_2$  and TiN, and at the  $SiO_2$ -TiN interface based upon the distinctly different incorporation and migration of  $O_i$ .

In the bulk of  $SiO_2$ , interstitial migration is rapid and non-directional in the absence of any external bias, with migration occurring in accordance with the mechanism previously presented in ref.<sup>35</sup> In the presence of the forming and switching biases, the diffusion becomes directional with the O<sub>i</sub> being moved from the bulk towards the interface.

At the interface, the incorporation and migration barriers for the  $O_i$  become vanishingly small, introducing a strong thermodynamic and kinetic driver for the transport of  $O_i$  to the interface. In the low concentration limit considered here, the  $O_i$  is then incorporated at the interface forming a Ti-O-Si unit and in effect oxidizing the interface. This gives atomistic meaning to the TEM and EELS measurements observed by Mehonic *et al.*<sup>5</sup> and illustrates the significant reconstructions induced as a result of the forming process.

Finally, oxygen transport across the interface into TiN is shown to be facilitated by the presence of grain boundaries, where  $O_i$  can be initially incorporated, and eventually transported through the electrode to form the gas bubbles observed.<sup>5</sup> Alternatively, it is shown that the  $O_i$  interstitial can be favourably incorporated at  $V_N$  sites where it in essence "heals" the defective TiN lattice.

These insights allow the electroforming process and the subsequent transport of oxygen to the interface and beyond to be understood. They explain how, as a result of electroforming, the system undergoes a very significant structural changes with the oxide being significantly reduced, interface oxidized and a portion of the oxygen leaving the system. The oxygen trapped at the interface and inside the grain boundaries in TiN can take part in the reset process when the bias is reversed and recombine with some of the vacancies forming the conductive filament. The fact that the binding energy of O in Si-O-Ti units at the interface is around 1.0 eV can explain retention in the ON state of formed ReRAM devices. Whether the interface sites can store the oxygen generated during the set process of formed devices and the mechanisms of set and reset will be considered in a separate publication.

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### Supporting Information Available

Full details of the experimental interface EELS results, the calculated migration barriers with the PBE0-TC-LRC and the PBEsol functional, and the distributions of the  $O_i$  incorporation and migration energies in a-SiO<sub>2</sub> are included in the supplementary information.

The following files are available free of charge.

• TiN-ESI.pdf: Expanded experimental and theoretical results.

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## Graphical TOC Entry

