Nature of Cu Interstitials in Al₂O₃ and the Implications for Filament Formation in Conductive Bridge Random Access Memory Devices

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ABSTRACT

Resistive random access memory (RRAM) is a prime candidate to replace Flash memory. Of the two classes of RRAM, conductive bridge RAM (CBRAM) is favoured over that based on filaments of oxygen vacancies because of its larger on/off resistance ratio. The nature of the filament in Cu/Al₂O₃-based CBRAM is analysed using density functional theory. The defect and binding energies of Cu interstitials and clusters in Al₂O₃ are calculated. The binding energy per Cu interstitial is shown to significantly increase with increasing Cu coordination, whereas the binding per oxygen vacancy only slightly increases with vacancy concentration. This explains why metal filaments in CBRAM devices tend to be denser than oxygen vacancy filaments. Using three different filament models, we discover that the strong binding between Cu interstitials drives filament formation, resulting in Al ions being driven out of the Cu-rich environment. This leads to the formation of densely packed metallic Cu filaments with bonding similar to Cu metal, as confirmed by electronic structure calculations.

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1. INTRODUCTION

New nonvolatile memory technologies with higher speed, retention time and endurance are needed to replace FLASH memory. One such technology is resistive random access memory (RRAM) devices as a result of their simple metal-insulator-metal (MIM) structure, fast operation, low power consumption, high endurance and excellent scalability¹⁻⁷. In addition, RRAM also have the advantage of the conductance being controlled by migrating atoms not electrons. Atoms are less self-repulsing than electrons⁸ and as the mass of an atom is much larger than the mass of an electron, the conducting filaments are more stable⁹. However, their commercial uptake depends on a more detailed understanding of the defect processes, switching mechanisms and filament formation in these new systems.

Conductive bridge random access memory (CBRAM) is one of two types of RRAM¹⁰. The basic structure and switching process of a typical CBRAM device are illustrated in Fig. 1. Essentially, a CBRAM device consists of an electrochemically active top metal electrode (usually Cu or Ag) and an inert bottom electrode (e.g. Pt). The two electrodes are separated by a solid electrolyte (e.g. Al₂O₃). When a positive voltage bias is applied to the active electrode, the metal atoms become oxidised (e.g. Cu \rightarrow Cu^{z+} + ze⁻, z = 1,2) and it is generally believed that they drift through the electrolyte to the inactive metal electrode where they are reduced (e.g. Cu^{z+} + ze⁻ \rightarrow Cu, z = 1,2). This cation transport creates a conducting filament which grows backwards towards the active metal electrode and makes the low resistive state (LRS) in the device^{1,2}. Applying a negative voltage to the active electrode dissolves the filament and restores the high resistive state (HRS). CBRAM devices have several advantages over typical oxygen vacancy-based RRAM devices⁵. RRAMs based on oxygen vacancies tend to have smaller R_{ON}/R_{OFF} ratios, whereas CBRAMs can have very large R_{ON}/R_{OFF} ratios (>10⁶)⁴. For the same number of defects in a filament, Cu-filaments in CBRAM devices are narrower, and thus reach larger resistive states⁵.

Al₂O₃ is a valuable material capable for nonvolatile memories^{3,11,12} due to its CMOS compatibility⁹, large band gap, low leakage current and stability of its amorphous phase to high temperatures¹³⁻¹⁵. Al₂O₃ has a number of different phases with quite different electrical properties, band gaps and local structures^{13,16}. Here, we use Θ -Al₂O₃ to represent the amorphous phase of Al₂O₃, to save computational time, because it possesses a similar short-range order, mass density and band gap to amorphous and liquid Al₂O₃¹⁷. Another option would have been to use the γ phase, which also shows structural similarities to amorphous Al₂O₃¹⁷, however it should be noted, we would still expect to see similar Cu interstitial

behaviour and results had we chosen this Al_2O_3 phase. The development and properties of a variety of Al_2O_3 -based CBRAM devices, many of which also feature Cu metal as the active electrode, have been reported in the literature^{1-7,18-20}.

While there are numerous density functional theory (DFT) studies of intrinsic and extrinsic defects in the various phases of Al₂O₃, few have been in placed in the context of CBRAM devices. Most consider only local-density methods such as the local density approximation (LDA) or generalised gradient approximation (GGA), which underestimate the band gap by 2-3 eV for Al₂O₃ phases,¹³ leading to errors in the defect transition levels. There are two DFT studies of the doping of Al₂O₃ with Cu interstitials. Sankaran *et al.*²¹ used the GGA to compute the injection energies of Cu in α -Al₂O₃. They found that Cu can be exothermically injected in the 1+ or 2+ oxidation states. Xu *et al.*⁹ used GGA to study the formation and conduction of Cu filaments in α -Al₂O₃. Cu substituting for Al in the α and Θ phases of Al₂O₃ has also been considered using the LDA and GGA²². In an excellent study by Pandey *et al.*²³, both DFT and molecular dynamics were used to analyse the nature of Cu interstitials in Al2O₃ and SiO₂. There results were placed in the context of CBRAM devices and a variety of important thermodynamic, kinetic and electronic properties were calculated. They found significantly reduced formation energies for Cu interstitials as a result of the metal-insulator interfaces and showed the importance of Cu-Cu interactions in these systems.

The concept of binding or condensation of defects into filaments has been previously considered for oxygen vacancies in TiO_2^{24} , HfO_2^{25} and $Al_2O_3^{26}$ using local-density methods. It was found that chains of oxygen vacancies (representing the filaments) had negative (favourable) binding energies of around -0.6 and -0.3 eV for their neutral and singly positively charged states, respectively. In contrast, doubly charged vacancies, the binding was unfavourable, meaning that isolated defects are preferred. This raises a question, if there is strong binding between oxygen vacancies in RRAM materials and it plays an important role in filament formation, then why are metal filaments denser in CBRAM materials? This is a point we return to when considering the binding of Cu atoms in Al_2O_3 .

To correct for the problems associated with local-density methods, we use the screened exchange (sX) functional for the calculation of defect formation energies, charge transitions (i.e. the Fermi energies where a change in defect charge state occurs) and electronic structures. The sX functional has been successfully applied to many semiconducting and insulating oxide materials^{7,13,27,28-31}. For Al₂O₃, sX has been shown to accurately reproduce the band gaps and band structures for the α , Θ and amorphous phases^{13,27}. A major advantage

of the sX functional compared to local-density methods is the replacement of all LDA exchange with a Thomas-Fermi screened Coulombic exchange potential²⁹. The local exchange and correlation functionals underlying the LDA and GGA cause spurious self-interaction which increases the energy of occupied states and decreases the energy of unoccupied states, whereas the exchange potential is self-interaction free. This results in more accurate defect formation energies and charge transition levels.

2. METHOD

All calculations were completed using the CASTEP plane-wave density functional theory code³². The sX calculations were completed using norm-conserving pseudopotentials for Al (3s2 3p1), O (2s2 2p4) and Cu (3d10 4s1), which were generated by the OPIUM method³³. A plane-wave cutoff energy of 780 eV was used. The Thomas-Fermi screening length was set to 2.48 Å⁻¹, as this value has been previously shown to be effective for $Al_2O_3^{34}$. To calculate the preferred interstitial sites and the binding energies, we used GGA calculations with ultrasoft pseudopotentials and the Perdew-Burke-Ernzerhof (PBE) functional³⁵. Valence electrons in these calculations were described by a plane-wave basis set with an energy cutoff of 500 eV. Defect calculations were completed using an 120 atom supercell consisting of 1 x 3 x 2 unit cells of 20 atoms. The internal geometry was relaxed within both sX and GGA using a single k-point $(1/4 \ 1/4 \ 0)$ and a 2 x 2 x 2 k-point mesh, respectively. The total energy convergence tolerance was 0.000005 eV/atom, the max ionic force tolerance was 0.05 eV/Å, the max ionic displacement tolerance was 0.003 Å and the max stress component tolerance was 0.1 GPa. While these parameters were easy to achieve for single interstitials, for clusters and filaments, several hundreds of optimization steps were required and the force and stress convergence had to be relaxed in some cases. The energy tolerance was always maintained at the same value. Full cell geometry optimization was applied in all cases.

The defect formation energy, H_q , as a function of Fermi energy (ΔE_F) from the valence band edge (E_V) and the relative chemical potential ($\Delta \mu$) of element α , can be calculated from the total energies of the defective supercell (E_q) and the perfect supercell (E_H) using the following formula:

$$H_{q}(E_{F},\mu) = [E_{q} - E_{H}] + q(E_{V} + \Delta E_{F}) + \sum_{a} n_{a}(\mu_{a}^{0} + \Delta \mu_{a}), \quad (1)$$

where qE_V is the change in energy of the Fermi level when charge q is added and n_{α} is the number of atoms of species α . The Cu chemical potential (μ_{Cu}) was calculated using a facecentred cubic Cu unit cell. The metal-rich (O-poor) limit is assumed in all our calculations due to the presence of the Cu metal electrode. If the O-rich limit had been assumed, then all Cu interstitial defect formation energies would be raised by 1.72 eV, which is equivalent to the sX calculated heat of formation of CuO (compared to an experimental value of -1.63 eV^{36}). The defect charge transition levels are not affected by the chemical potentials.

The binding energies, E_b , are calculated simply by comparing the sum of the defect energies for the isolated defects and the total energy for the defect cluster, this is illustrated for a Cu binding pair in the following equation:

$$E_b = H_a(\operatorname{Cu1Cu2}) - (H_a(\operatorname{Cu1}) + H_a(\operatorname{Cu2})), \quad (2)$$

where $H_q(Cu1)$ is the defect formation energy of the first isolated Cu interstitial, $H_q(Cu2)$ is the defect formation energy of the second isolated Cu interstitial and $H_q(Cu1Cu2)$ is the defect formation energy of the Cu interstitial pair. Negative binding energies are indicative of attraction between the defects, while positive values are indicative of repulsion and the preference for isolated defects.

3. RESULTS AND DISCUSSION

A. Bulk *O*-Al₂O₃ properties

The monoclinic Θ -Al₂O₃ unit cell is shown in Fig. 2. This phase is a structural isomorph of β -Ga₂O₃. The lattice parameters and angles for the Θ -Al₂O₃ unit cell calculated using sX and GGA are given in Table 1, experimental values are also given for comparison. While both functionals give a reasonable reproduction of the unit cell, sX is the more accurate of the two with only a slight underestimation in lattice parameters. The calculated lattice parameters are a significant improvement on several previous studies^{13,26,37,38}.

The partial density of states (PDOS) for Θ -Al₂O₃ calculated using sX is also plotted in Fig. 2. We obtain band gaps of 6.51 and 5.05 eV using the sX and GGA functionals, respectively. As expected, the value from sX is in much better agreement with the experimental value of 6.20-6.50 eV^{40,41}, although it is somewhat smaller than the values of 6.58 and 6.80 eV previously calculated by the sX and Heyd-Scuseria-Ernzerhof (HSE06) functionals^{13,42}, respectively. The band gap for Θ -Al₂O₃ is significantly lower than that of α -Al₂O₃ (8.80 eV⁴¹) because it is less dense with lower coordination numbers, which in turn means a smaller band

gap⁴³. The valence band of Θ -Al₂O₃ is mostly made up of O 2p states with high effective mass, whereas the conduction band consists mostly of Al 3s and 3p states.

B. Lowest energy Cu interstitial sites

Before using the sX functional to calculate the defect formation energies and change transitions of the Cu interstitials, we must first identify the numerous possible doping sites and identify the lowest energy ones. In a high symmetry crystal structure, there usually exists unoccupied high symmetry Wyckoff positions which can be easily tested to identify the lowest energy interstitial sites. However in a low symmetry structure like Θ -Al₂O₃, this is more complicated. In a study of β -Ga₂O₃, the topology of the electron density was used to locate some potential interstitial sites⁴⁴. As the electron density is a positive definite function, which peaks at the nuclei and decays exponentially away from the nuclei, the minima sites of electron density with smaller short-range repulsion will indicate potential interstitial sites, see REF. 44.

As β -Ga₂O₃ is a structural isomorph, we can test the same identified starting interstitial positions and then allow geometry optimisation to find the actual optimised positions for Θ -Al₂O₃. Given the computational expense of sX calculations, we search for low energy sites using GGA calculations. The Wyckoff positions and atomic coordinates of ten possible Cu interstitial sites are given in Table 2, along with their GGA defect formation energies and charge transition levels at each site. In addition, Fig. 3(a) shows the Cu interstitial defect formation energies for three selected sites, relative to the valence band maximum (VBM), plotted against Fermi energies of up to 5 eV in agreement with the GGA determined band gap. The relevant Fermi level in the cell is determined by the work function of the top Cu electrode (-4.65 eV)⁴⁵. The results confirm that Cu can exist in three charge states, and that of these, 1+ is the most stable over the largest range of *E_F*. For the operating Fermi level, the majority of migrating Cu ions in a Cu/Al₂O₃-based CBRAM are in the 1+ state, not the 2+ state.

It is clear from Table 2 that there is a significant energy difference between the most and least stable interstitial sites. The highest defect energy for a neutral Cu interstitial (9.12 eV) is found at the i_6 site and the lowest energy (6.27 eV) is found at (0.26,0,0.01) from the starting position of i_9 . It is noteworthy that the two lowest energy sites, i_5 and i_9 , are also the two lowest energy sites calculated for oxygen interstitials in β -Ga₂O₃⁴⁴, suggesting that the local structure of these sites is energetically beneficial for both cation and anion interstitials. A

previously GGA calculated defect formation energy for a neutral Cu interstitial in α -Al₂O₃ of 7.92 eV⁹ is remarkably close to our average neutral Cu interstitial formation energy of 7.96 eV. Similar to our results, a large range of formation energies (5.4–6.9 eV) was also observed for Cu-doping in amorphous Al₂O₃⁴⁶, although only Cu substitutionals were considered.

C. Structure analysis of Cu interstitials

We now focus on the local structure of some of the least and most stable interstitial sites, namely i_5 , i_6 and i_9 , to identify the structural effects of Cu doping and the reason for the large range of formation energies. The local structures of the three doping sites calculated by GGA are illustrated in Fig. 3(b), and Table 3 details the bond lengths and atomic displacements for neutral Cu dopants at these sites. For the average bond lengths and atomic displacements, only ions in the first coordination sphere of 3 Å of the Cu dopants are considered as these ions are most affected by the introduction of the Cu interstitial.

Cu ions at the i_5 and i_6 sites are coordinated to six oxygen and six Al ions, while at the i_9 site, the Cu ion is coordinated to seven oxygen and six Al ions. While the coordination of each site is similar, the bonding and perturbation to surrounding ions is very different between the two low energy sites, i_5 and i_9 , and the high energy site, i_6 . The shortest Cu-O and Cu-Al bonds and small atomic displacements for the lowest energy sites are very similar, explaining why their formation energies are also similar. The average Cu-O bond length for i_9 is 0.1 Å larger than for i_5 and i_6 because of the extra coordinated oxygen ion, which has a longer bond compared to the coordinated anions. For the i_6 site, the shortest Cu-O and Cu-Al bonds are shorter than for the more stable sites and the average atomic displacement is much higher for both oxygen and Al ions. Thus, the i_6 site is a small interstice and the least stable for Cu-doping. While a shorter Cu-O bond is favoured Coulombically, a bond length of 1.80 Å is actually shorter than in CuO (1.95 Å) and Cu₂O (1.84 Å⁴⁷), suggesting Cu-doping here would significantly strain the lattice.

D. Defect energies and charge transition levels from sX

We now calculate more accurate Cu defect formation energies using sX for the two most stable sites. Table 4 displays the calculated sX defect formation energies and charge transition levels for Cu-doping at the i_5 and i_9 sites. These values are also plotted against the Fermi energy in Fig. 4(a) and band diagrams (Fig. 4(b)) using the sX results are also constructed. The relevant Fermi level of the cell, which is controlled by the work function of

the top Cu electrode (-4.65 eV)⁴⁵, is illustrated by the blue dashed line in Fig. 4(a). For the band diagrams in Fig. 4(b), the energies are aligned to the vacuum level using the experimental electron affinity of Al_2O_3 (2.5 eV⁴⁸) and the Fermi level of the top electrode metal (Cu) is also plotted.

Perhaps the most important feature of Fig. 4(a) is that Cu⁺ again dominates over most of the E_F range, with the neutral and 2+ charge states seen for only a small range of E_F , near the conduction band minimum (CBM) and VBM, respectively. For the 1+ and 2+ charge states, the formation energy is lowered using sX, compared to the GGA, which is common for donor defects when moving from local density methods to hybrid functionals. The formation energy for neutral Cu interstitials remains relatively unchanged when comparing sX and GGA. Fig. 4 also shows that at the operating E_F , as determined by the Cu electrode, lies well within the 1+ range. This is important for CBRAM application as the positively charged Cu ions ensure controlled drift under the switching field which could potentially increase switching speed and endurance, as opposed to oxygen vacancies in Al₂O₃ which have been shown to be neutral or negatively charged at the operating E_F^{49} . In addition, the formation energies calculated in this work for Cu interstitials are comparable to the values calculated for oxygen vacancies in Al₂O₃ with sX¹³, suggesting that there are no strong energetic penalties for Cu insertion.

E. Electronic structures from sX

In addition to calculating the defect formation energies of the Cu interstitials, we also analyse the effect on the electronic structure of Θ -Al₂O₃ by producing PDOS for the local structure around the Cu interstitials in all three charge states. As the PDOS for Cu interstitials at the *i*₅ and *i*₉ sites are similar, we only discuss the results for the *i*₉ site here. Fig. 5 shows the sX calculated PDOS for Cu interstitials and their bonded ions (within 3 Å) at the *i*₉ site in the three possible charge states. For each PDOS plot, the Θ -Al₂O₃ band gap is significantly reduced by the introduction of Cu 3d and 4s/4p states to the valence and conduction bands, respectively. In the case of the 3d states, they are mostly mixed with O 2p states with the formation of some covalent bonding. Similar Cu/O hybridisation was found for sX calculations of CuAlO₂ and it was also shown to dominate the upper valence band⁵⁰. For the neutral Cu interstitial, the band gap is reduced to ~1.5 eV and a strong defect peak is produced at the VBM. When an electron is removed to form Cu⁺_i, the band gap actually increases to over 3 eV. Upon removing another electron, Cu_i^{2+} is formed and a small defect state is produced at 2 eV above the VBM. This defect state is the result of d-d octahedral splitting as Cu^{2+} has a d⁹ electron configuration and is therefore susceptible to Jahn-Teller distortion. This was also found for Cu-doped amorphous $Al_2O_3^{46}$. Similar effects occur for transition metal-doped Θ - $Al_2O_3^{22}$ and Cu-doped ZnO⁵¹.

F. Cu cluster formation

We now use GGA to calculate the binding between Cu defects and attempt to answer the previously posed question of why do the metal filaments in CBRAM devices tend to be denser than the oxygen vacancy filaments in RRAM devices? Table 5 and Fig. 6 show the binding energies (per interstitial) between pairs of Cu interstitials located at the four lowest energy sites (i_5 , i_7 , i_8 and i_9) in the three possible charge states. The interatomic distances quoted refer to the starting distances between the interstitials before any optimisation.

Clearly, for most cases, the binding is negative which suggests that Cu defect condensation is favourable in Al₂O₃. As expected, the binding energies for neutral and doubly charged Cu interstitials are generally strongest due to their unpaired electrons. However, there are also significant binding energies for most Cu⁺ pairs. Binding between closed-shell d¹⁰ Cu⁺ ions has received significant interest in the fields of coordination complex chemistry⁵² and solid state physics^{53,54}. The only occurrences where binding is not present is for charged Cu pairs with significant distances between them (> ~4 Å). The strongest binding is seen for the *i*₇-*i*₈ pair, which is likely to be a result of the fact that the distance between this pair is closest to the Cu-Cu bond distance in Cu metal (2.56 Å)⁵⁵. For single Cu interstitials, we have shown that Cu⁺ dominates over the *E_F* range, however, as we can see from these binding energy calculations that when considering Cu clusters and indeed filaments, metallic Cu is energetically preferred.

For comparison, we also calculated the binding between oxygen vacancy pairs in the same charge states as for Cu interstitials. The energies were calculated using nearest neighbour oxygen vacancies, in order to maximise the interactions. We obtained binding energies (per oxygen vacancy) of -0.12, -0.40 and 0.22 eV for the neutral, 1+ and 2+ charge states, respectively. These values are in excellent agreement with previous LDA calculations on α -Al₂O₃²⁶. Reasonable agreement is also achieved with values calculated previously for TiO₂²⁴ and HfO₂²⁵, and the general trend for adhesion of the neutral and 1+ charge states and

isolation for the 2+ charge state, is also replicated. These calculations alone suggest that the binding between Cu interstitials is overall stronger than the binding between oxygen vacancies. However, to confirm this we also consider the binding of larger clusters.

For this purpose, we simulated clusters of six Cu interstitials and six oxygen vacancies, respectively. For the Cu interstitial clusters, we consider all the possible configurations for the seven lowest energy sites, an example configuration is shown in Fig 7(a). For the oxygen vacancies, we use the same oxygen vacancy chain model as used previously for HfO₂²⁵, which is in essence, a chain of six nearest neighbour oxygen vacancies which represents an ordered conductive filament, corresponding to the ON state, as shown in Fig. 7(b). It must be noted that these models are very simplistic representations of the actual filaments in RRAM/CBRAM devices, however, they are more than sufficient in providing us with an idea of the binding of these defects at the atomic level. The GGA binding energies for these clusters with defects in the neutral and 1+ charge states are given in Table 6 and plotted in Fig. 7(c). Fig. 7(c) also compares the binding energies of the defect pairs and clusters/chains. Defects in the 2+ charge state were also considered, but unfortunately, because of the high charge, achieving convergence was difficult or impossible. This is not a significant issue, as we have already shown that doubly charged oxygen vacancies do not bind and we do not predict that the binding energy behaviour of Cu²⁺ clusters will be dramatically different from the neutral or singly charged species.

The most obvious feature of the results in Table 6 and Fig. 7(c) is the significant difference in binding energy between Cu interstitials and oxygen vacancies. Considering only defect pairs, the binding energies (per defect) for Cu interstitials and oxygen vacancies were comparable, although the binding energies for neutral Cu interstitials were stronger than for the other species. However, the difference for clusters is far larger, suggesting that the adhesion of Cu defects is considerably stronger than the adhesion of oxygen vacancies. Furthermore, by comparing the data for defect pairs and clusters, it is clear that defect coordination plays the key role in defect clustering. For the oxygen vacancies, there is only a small increase in binding (0.13 and 0.10 eV for V_0^0 and V_0^{1+} , respectively) for the transition from defect pairs of defect pairs joining together, singly positively charged oxygen vacancies will easily pair up, but when these now doubly charged pairs attempt to join other pairs to form larger clusters, there is significant repulsion, whereas Cu interstitials with longer range chemical interactions, continue to increase their stability by forming larger

clusters. However, these results raise an important question, if the binding between Cu defects is stronger than that between oxygen vacancies, then why are deeper reset states obtained experimentally in the literature for CBRAM compared to vacancy-based RRAM? What makes it easier to break Cu-Cu bonds and dissolve the Cu-filaments? While the answer is not entirely clear, it has been reported that the deeper HRS levels in CBRAM devices are accounted for by the increased probability of particle removal in these systems⁵. This is a topic that requires further study.

These results suggest that the vacancy-vacancy coordination number is lower than the Cu-Cu coordination number. This is an important point, especially when considering filament formation, as the number of Cu defects increases, the already large energetic gain for defect adhesion increases faster, whereas for oxygen vacancies, the energy gain is limited. This concept was also tested for larger Cu clusters of eight and twelve and similar behaviour was found. Furthermore, it has also been reported that the metal-insulator interfaces in these devices further reduce the formation energies of Cu occupation, as they effectively act as thermodynamic driving forces for the Cu defects²³. In the same study, it was confirmed that the Cu formation energy further decreases with increasing Cu concentration in such structures.

We have highlighted some of the differences between the behaviour of Cu and oxygen vacancy clusters, and when we consider these results in terms of RRAM/CBRAM filament formation, it is apparent why Cu filaments are denser than oxygen vacancy filaments in Al₂O₃. However, what is the actual structure of these Cu filaments, and how does their formation influence the neighbouring Al and oxygen ions?

G. Cu filament models

In order to analyse Cu filament structures and their influence on the surrounding atoms in the Al₂O₃ electrolyte, we consider three structurally different Cu filament models. Fig. 8 shows the starting and unoptimised structures of these three filament models. Filament 1 consists of 8 Cu atoms running along the *c*-axis of the supercell with Cu-Cu separations of 2.81 Å. Filament 2 consists of 12 Cu atoms along the *c*-axis with Cu-Cu separations of 1.98 Å. Finally, filament 3 is made up of 8 Cu atoms along the *b*-axis with Cu-Cu distances of 2.18 Å. The starting positions of the some of the Cu atoms in these filaments are structurally unfavourable with several very short Cu-O and Cu-Al distances, however, by optimising the

three different models, we can observe how the Cu atoms rearrange themselves in order to form the lowest energy structures and what happens to the surrounding Al and O atoms. The results presented here are for neutrally charged filaments. Similar structures were also found for charged Cu interstitials and we have already shown that strong Cu-Cu binding exists in all three of the possible charge states. To further confirm our previous results, we calculated the Cu binding energy of filament 2. This filament was chosen as it has the most Cu atoms. We recorded an energy of -2.97 eV per Cu atom, this value is lager than the values obtained for Cu-Cu pairs and Cu clusters, and as a result, confirms our finding that Cu-Cu interactions become more favourable with increasing Cu concentration.

Before discussing the structural effects on the surrounding Al_2O_3 lattice, we first analyse the structures of the filaments themselves in Fig. 8. In filament 1, due to the Cu interstitials being reasonably well separated, the optimised structure of the filament is not dramatically different from the starting configuration and is the simplest structure of the three models. The filament is almost two-dimensional with only very slight Cu deviations along the *a*-axis. While the *b* and *c* lattice parameters of the supercell experience small increases (-2 Å) after optimisation, the *a* length increases by 1.2 Å, which is primarily a result of the Al ions being pushed away from the filament, as discussed shortly. From the starting Cu-Cu distance of 2.81 Å, several shorter Cu-Cu bonds of 2.54 Å are formed. This distance is almost same as the 2.56 Å Cu-Cu bond in Cu metal, suggesting the formation of Cu metal-like environments, consistent with the strong binding observed for this separation in the previous section.

The Cu interstitials are more closely packed in filament 2 and this results in a more complex, low energy structure. During the optimisation, the Cu ions spread out as much as possible, while still retaining a highly ordered three-dimensional structure. One third of the Cu ions retain their position, while the other two thirds are displaced along the *a*-axis in opposite directions. Similar behaviour also occurs along the *b*-axis. This causes a significant increase in the *a* and *b* cell lengths of 2.08 and 0.38 Å, respectively. The optimised Cu-Cu bonds are all between 2.28 and 2.60 Å, which again reinforces the argument that despite the low compressibility of the Al₂O₃ host, dense Cu metal-like clusters can form within the filament.

Like filament 1, filament 3 contains 8 Cu interstitials; however as they are stacked along the shorter b lattice parameter, their starting Cu-Cu interatomic distance is significantly shorter. Similar to filament 2, the Cu ions move away from each other during optimisation, forming an ordered three-dimensional filament, almost comparable to a double helix

structure. Somewhat surprisingly, this filament causes the largest expansions of 2.26 and 0.20 Å in the *a* and *c* directions, respectively. This can again be explained by the significant structural rearrangements undergone by the neighbouring Al and O ions, as discussed shortly. All the optimised Cu-Cu bonds are between 2.27 and 2.69 Å, close to the 2.56 Å bond in Cu metal. These results illustrate that although it is not possible to form perfect Cu metal clusters, due to the starting positions of the Cu ions and the surrounding structure of Al and O ions, the Cu ions still try to arrange themselves in the lowest energy configuration by forming as many strong Cu-Cu interactions as possible, regardless of whether the starting Cu-Cu distance is longer or shorter than the value in the metal. In all of these three filament models, and in the study of binding energies, there is strong evidence of the formation of Cu-Cu bonding and interactions in these clusters and filaments, similar to that in Cu metal.

To confirm the metallic nature of these filament models, we analyse their electronic structures by producing PDOS plots, as was completed for single Cu interstitials in Section 3E. As the plots are similar for all three models, only the results from filament 3 with neutral Cu interstitials are presented and discussed here. Fig. 9 shows the GGA calculated PDOS for the filament 3 model. In Fig. 5, it was observed that the introduction of Cu to Al_2O_3 resulted in the reduction of the band-gap and the creation of mid-gap defect states, the results presented in Fig. 9 are a significant extension of this. As a result of the metallic Cu 3d and 4s states, there is now no band-gap present in the material due to the large number of localised states. The closure of the band-gap illustrates the metallic character of the filament. Significant Cu/O hybridisation is again also present. Furthermore, in the models of Pandey *et al.*²³, a three orders of magnitude increase in the electronic transmission was explicitly observed due to aggregation of Cu ions in the insulator. In conjunction with our own results, the production of this conducting pathway provides strong evidence for metallic Cu filaments in these devices.

Now that we better understand the structure and metallic nature of these Cu filaments, we can investigate their impact on the host material. The starting and optimised structures of the three filament models are again shown in Fig. 10, however, the structural consequences of the filaments on nearby Al and O ions are more clearly visible. It is clear from all three of the filaments, that the Al and O ions undergo significant structural rearrangement during optimisation. One of the first things to note is that there are no Al or O ions within the Cu filaments, meaning that very Cu-rich environments are formed within the Al₂O₃ electrolyte. Overall, our analysis reveals that any Al ions in the vicinity of the filaments get pushed out,

while the surrounding O ions can maintain their relatively short distances to the filaments, although there is of course still some substantial movement for O ions with very short Cu-O distances before the optimisation.

The extent of Al ions being forced out is reflected by the fact that there are no Cu-Al distances under 2.3 Å in these structures, which is remarkable considering the volume that these Cu filaments occupy in the Al₂O₃ lattice. In fact, there are only a few Al ions within 2.5 Å of the Cu filaments. This effectively means that there is a large part of each supercell that is Cu-rich and Al-deficient. In contrast, there are numerous Cu-O bonds of less than 2 Å in the cells and closer to ~2.5 Å, we see the formation of partial, distorted CuO₆ octahedral units. If we consider the optimised filaments at a basic level, they can almost be described as layered structures, consisting of Cu-rich metallic-like areas coordinated to surrounding O ions, which are in turn coordinated to the Al ions.

Table 7 shows the average atomic displacements for Al and O ions in the three filament models. These averages were calculated using ions in the direct vicinity of the Cu filaments, as these ions are more likely to be the most affected the filaments. We analysed the displacements of the ten closest Al ions and the ten closest oxygen ions for all three models. Perhaps the most important aspect of these displacement results is that unlike for the single Cu interstitials, discussed previously, the average Al displacements are now larger than the average O displacements. This fact gives further evidence of Al ions being forced away from the Cu environments. In addition, the largest single displacements were observed for Al ions, Al displacements of 1.15, 1.30 and 1.25 Å were found for filaments 1, 2 and 3, respectively. Significant O ions displacements are also observed during the formation of these Cu filaments, however, most of these are a result of very close Cu-O distances before optimisation.

Now that we have established the energetics and stabilities of various Cu species in Al_2O_3 , we can relate our results to the processes shown in Fig. 1. Overall, as generally surmised in experiment, the Cu defects at the interface become oxidised and migrate through the electrolyte, forming stable clusters. As our calculations show, the 1+ state is active over the majority of the Fermi energy range, with a mixture of 1+ and 2+ migrating Cu ions being likely in the electrolyte. The strong Cu-Cu bonding leads to the formation of clusters and then filaments, producing a stable LRS. Such stable LRS states have also been reported previously for SiO₂ and Al_2O_3 using DFT²³. They reported activation energies of 1.6–1.8 eV for

retention loss. When the filament does dissolve, the Cu ions dissociate and their charge states change, resulting in the return to the HRS.

4. CONCLUSIONS

Using GGA and sX calculations, we have calculated the energetics, local and electronic structures, and binding of Cu interstitials in Al_2O_3 . On the basis of structural analysis and defect formation and binding energies, new insights into metallic filament formation in CBRAMs have been achieved.

We have shown how the adhesion of Cu interstitials can lead to filament formation, and how this influences the local structure of Al_2O_3 . As individual Cu interstitials begin to form larger clusters, nearby Al ions are forced away, leading to the creation of Cu filaments with properties similar to those of Cu metal. This explains how such tightly packed metallic filaments can form in a host system that is as strong and dense as Al_2O_3 . The binding energy per Cu in Cu pairs and clusters has been shown to be significantly stronger than the binding energy per oxygen vacancy, and this difference is further amplified with increasing Cu coordination, as opposed to the binding per oxygen vacancy, which only slightly increases with vacancy concentration. These results help to explain why metal filaments in CBRAM devices tend to be denser than oxygen vacancy filaments in RRAM devices, as determined experimentally. Cu filaments are shown to be energetically stable with significant internal Cu interactions and Cu-O bonding. These results provide fundamental insight into the chemistry and physics of Cu/Al₂O₃ CBRAM cells that until now have been unavailable.

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TABLES

Table 1. Calculated and experimental lattice parameters and angles for Θ -Al₂O₃.

	a (Å)	b (Å)	<i>c</i> (Å)	β (deg)
sX	11.73	2.90	5.59	104.01
GGA	11.93	2.94	5.66	104.05
Experiment ³⁸	11.80	2.91	5.62	103.80

Table 2. Sites considered for Cu interstitials in Θ -Al₂O₃ and the respective formation energies (ΔH) and charge transition levels relative to the valence band maximum (VBM) calculated using GGA. All energies are in eV. The two lowest energy sites are highlighted.

Site	Position	Coordinates	$\Delta H(Cu_i^0)$	$\Delta H(Cu_i^+)$	$\Delta H(Cu_i^{2+})$	ε(2+/1+)	ε(1+/0)
i_1	$2a, C_{2h}$	(0,0,0)	8.98	4.39	2.44	1.95	4.59
i_2	$2b, C_{2h}$	(0,0.5,0)	8.18	3.56	2.27	1.29	4.62
i ₃	$2c, C_{2h}$	(0,0,0.5)	9.02	4.41	2.59	1.82	4.61
i_4	$2d, C_{2h}$	(0,0.5,0.5)	8.09	3.47	2.80	0.67	4.62
<u>i</u> 5	<u>4e, C_i</u>	(0.25,0.25,0)	<u>6.48</u>	<u>1.89</u>	<u>1.55</u>	<u>0.34</u>	<u>4.59</u>
<i>i</i> ₆	$4f, C_i$	(0.25,0.25,0.5)	9.12	5.20	4.50	0.70	3.92
<i>i</i> 7	$4i, C_s$	(0.076,0.5,0.046)	8.08	3.58	2.27	1.31	4.50
<i>i</i> ₈	$4i, C_s$	(0.098,0.5,0.532)	7.20	2.87	1.88	0.99	4.33
<u>i9</u>	<u>4<i>i</i>, C</u> _s	<u>(0.317,0,0.121)</u>	<u>6.27</u>	<u>2.01</u>	<u>1.59</u>	<u>0.42</u>	<u>4.26</u>
<i>i</i> ₁₀	$4g, C_s$	(0,0.039,0)	8.20	3.56	2.44	1.12	4.64

Table 3. Bond length and atomic displacement data for the first coordination sphere (within 3 Å) of neutral Cu dopants at three interstitial sites. All measurements are in Å.

Site	Shortest Cu-O	Average Cu-O	Shortest Al-O	Average Al-O	Average O	Average Al
	bond length	bond length	bond length	bond length	displacement	displacement
i_5	1.87	2.36	2.36	2.64	0.18	0.16
<i>i</i> ₆	1.80	2.36	2.23	2.68	0.35	0.41
i9	1.88	2.46	2.37	2.57	0.18	0.15

Table 4. Formation energies (ΔH) and charge transition levels relative to the valence band maximum (VBM) for the lowest energy Cu interstitials in Θ -Al₂O₃, calculated using the sX functional. All energies are given in eV.

Site	Position	Coordinates	$\Delta H(Cu_i^0)$	$\Delta H(Cu_i^+)$	$\Delta H(Cu_i^{2+})$	ε(2+/1+)	ε(1+/0)
<i>i</i> 5	$4e, C_i$	(0.25,0.25,0)	6.52	0.21	-0.15	0.36	6.31
İ9	$4i, C_s$	(0.317,0,0.121)	6.51	0.28	-0.10	0.38	6.23

Table 5. Binding energies (E_b) (per defect) and interatomic distances for pairs of Cu interstitials in Θ -Al₂O₃ calculated using GGA. All distances are in Å and all energies are in eV.

Interstitial pair	Distance	$E_b(\operatorname{Cu}_i^0)$	$E_b(\operatorname{Cu}_i^+)$	$E_b(\operatorname{Cu}_i^{2+})$
<i>i</i> 5- <i>i</i> 9	1.20	-1.09	-0.23	-0.37
<i>i</i> ₅ - <i>i</i> ₇	2.28	-1.40	-0.10	-0.29
<i>i</i> ₇ - <i>i</i> ₈	2.70	-1.78	-0.61	-0.53
<i>i</i> ₇ - <i>i</i> ₉	3.16	-1.08	-0.05	-0.15
<i>i</i> ₅ - <i>i</i> ₈	3.92	-0.26	0.29	0.65
i ₈ -i ₉	4.14	-0.79	0.20	0.59

Table 6. Binding energies (E_b) (per defect) for clusters of six Cu interstitials and a chain of six oxygen vacancies in Θ -Al₂O₃ calculated using GGA. All energies are given in eV.

Cluster species	E_b	
Cu ⁰ _i	-2.05 to -2.43	
Cu_i^{1+}	-1.09 to -1.36	
V_{O}^{0}	-0.25	
V_0^{1+}	-0.50	

Table 7. Average atomic displacement data for Al and O ions in close vicinity to the three filament models. All measurements are in Å.

Filament	Average Al displacement	Average oxygen displacement
1	0.52	0.41
2	0.58	0.46
3	0.67	0.47

FIGURE CAPTIONS

Fig. 1. Illustration of the structure and switching process in a CBRAM cell consisting of an active Cu electrode, an Al₂O₃ insulating layer and an inert Pt electrode. (a) OFF state, (b) switching ON, (c) ON state and (d) switching OFF.

Fig. 2. Optimised unit cell structure and PDOS for Θ -Al₂O₃ calculated by sX. The large grey spheres are Al and the small red spheres are oxygen.

Fig. 3. (a) Defect formation energies for Cu interstitials in Θ -Al₂O₃ at three selected sites calculated using GGA at the metal-rich limit. The top of the valence band is represented by a Fermi energy of 0 eV and Fermi energies of up to 5 eV are plotted, as determined by the GGA calculated band gap. (b) Optimised local structures for neutral Cu interstitials at the *i*₅, *i*₆ and *i*₉ sites in Θ -Al₂O₃.

Fig. 4. (a) Defect formation energies for the lowest energy Cu interstitials in Θ -Al₂O₃ using sX at the metal-rich limit and (b) the respective sX band diagrams with energies plotted with respect to the vacuum level and the Fermi level corresponding to the work function of Cu metal. Fermi energies of up to 6.5 eV, as determined by the experimental and sX band gap, are plotted.

Fig. 5. PDOS of Cu interstitials in three charge states and their bonded ions at the i_9 site in Θ -Al₂O₃ calculated using the sX functional. The VBM is set to 0 eV.

Fig. 6. Binding energies (E_b) (per defect) for Cu interstitial pairs as a function of interatomic distance in Θ -Al₂O₃ calculated using GGA.

Fig. 7. Unoptimised local structures for (a) an example six Cu cluster and (b) the six oxygen vacancy chain model, both in Θ -Al₂O₃. (c) Binding energies (*E_b*) (per defect) for Cu and oxygen vacancy pairs and clusters/chains in Θ -Al₂O₃ calculated using GGA. The energies plotted for the Cu binding are the largest calculated.

Fig. 8. Cu/Al₂O₃ filament models before (left) and after (right) optimisation. Unique Cu-Cu bond lengths are displayed in Å. Cu-Cu distances are all equivalent in the starting structures.

Fig. 9. PDOS of filament 3 calculated using the GGA functional. The filament is neutrally charged in the calculation.

Fig. 10. Illustrations of the effect of the Cu filaments on the surrounding Al₂O₃ lattice after optimisation. Significantly displaced Al atoms are indicated by the red dashed circles.



















Fig. 5.



Fig. 6.



Fig. 7.

Filament 1



Filament 2



Filament 3



Fig. 8.



Fig. 9.

Filament 1



Filament 2



Filament 3



Fig. 10.

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