Extended Abstracts of the 2016 International Conference on Solid State Devices and Materials, Tsukuba, 2016, pp727-728

PS-4-03

Ab-initio modeling of Conductive channel in Cu – Al_2O_3 conductive bridge RRAM

James A Dawson[1], John Robertson [1]

[1] Engineering Dept,
Cambridge University, Cambridge CB2 1PZ, UK
Phone: +44-1223-748331 E-mail: jr@eng.cam.ac.uk

Abstract

The narrower, more conductive channel of Cu-based CB-RRAM compared to the channel in Oxygen vacancy based Ox-RAM is shown by ab-initio simulations to arise from the higher Cu-Cu coordinations and tighter bonding, than between the equivalent vacancy clusters.

1. Introduction

There is a rapid development of non-volatile semiconductor based memory technologies such as Resistive random access memory (RRAM) to complement Flash memory. There are two main classes of RRAM, one based on oxygen vacancies in oxides such as HfO_2 (Ox-RRAM), and one based Cu filaments or 'conductive bridges' in an oxide host such as amorphous (a-)Al_2O_3 (CB-RRAM). OX-RRAM has the advantage than it uses well known CMOS compatible oxides like HfO_2. However, OX-RRAM has a relatively small ON / OFF resistance window. The ON and OFF states are characterized by resistance distributions that overlap at the 3σ level (σ being the variance of this distribution.) In contrast, CB-RAM contains Cu, but has a much wider ON/OFF window, so the distributions do not overlap [1,2]. Belamonte [3] noted that CBRAM had a denser filament.

It is therefore of interest to understand the nature of the conductive filament in each case, using ab-initio atomic simulations. We recall that Kamiya et al [4,5] considered the pairing attraction between two O vacancies in HfO_2, Al_2O_3 and TiO_2 to understand filament formation in oxides. We find that the Cu filament in CBRAM is denser because of the much higher Cu coordination numbers and stronger Cu-Cu bonding in the CBRAM case. Previous analyses by other groups [7-9] was less detailed.

2. Methods

The calculations use the plane wave, pseudopotential code CASTEP. We first study the energetics and defect energy levels of Cu interstitials in amorphous (a-) Al_2O_3 network. We use the θ-Al_2O_3 polymorph to represent a-Al_2O_3, as it has a similar density, coordination and band gap. We then consider the binding between two Cu atoms and Cu atom clusters, as a function of separation and coordination.

3. Results and Discussion

We first evaluate the energies of single Cu^+ ions at various interstitial sites in the Al_2O_3. We find three main low energy sites, as denoted in Fig. 1. Fig. 1 shows the defect formation energy of Cu ions at these sites as a function of the Fermi energy referred to the valence band maximum, for the PBE exchange correlation functional. The Cu^{1+} state is seen to be the most stable site for most E_F. We then recalculated this for the I_9 site in the screened exchange hybrid functional which corrects the GGA band gap error, Fig. 2. E_F in this diagram gives the work function of metallic Cu, referred to the vaccum level by the known electron affinity of Al_2O_3. Fig 3 shows the partial density of states (PDOS) of isolated Cu sites in the different charge states. They are insulating.

Fig. 4 shows the binding energy of two Cu interstitials as a function of their separation in the Cu^0, Cu^+ and Cu^{2+} states. We see that there is strong binding for the Cu^0 state. The bond length in metallic Cu is 2.50 Å for reference.

Fig. 5 shows the binding energy between a Cu site increasing from 2 atoms to ever large clusters of a chain then a rod, for each charge state. It compares this with the case of O vacancies in TiO_2 [4] or HfO_2. In the O vacancy case, two open-shell V^+ vacancy sites bind together to form a 'covalent bond', with paired electrons. This is then a closed shell, so pairs have little more binding to make larger clusters. In contrast, for Cu^0 sites, the Cu-Cu bonding is of metallic character. This has longer range, and does not saturate at a coordination number of 2, but continues to increase, with an example in Fig 7. Thus, the Cu filament can bond as in metallic Cu, and form a long, dense rod. Thus, for a given ON current (compliance), the filament is denser and narrower, giving a higher ON/OFF ratio, as seen experimentally [3].

3. Conclusions

Based on atomic simulations, it is argued that the stronger, longer range and higher coordinated bonding between Cu sites than O vacancies makes for a d, narrower denser filament, leading to higher ON/OFF ratio.

Acknowledgements

We thank EPSRC for funding.

References

[1,A Calderoni, et al, Microelec Eng 147 145 (2015)
[2] S Clima et al, IEEE ED Let 36 769 (2015)
[3] A Belmonte, R Degraeve, A Fantini, G Jurczuk, L Goux, App Phys Lett 104 233508 (2014)
[4] K Kamiya, et al, App Phys Lett 100 073502 (2012)
[5] K Kamiya, et al, Phys Rev B 87 155201 (2013)
[6] X Xu, J Liu, M P Anantram, J Appl Phys 166 163701 (2014)
[7] S Pandey, R Meade, G Sandhu, J App Phys 117 054504 (2015).
[8] S Clima et al, Phys Stat Sol RRL 8 501 (2014)
[9] L Fu et al, J Mater Chem 1 14592 (2013)

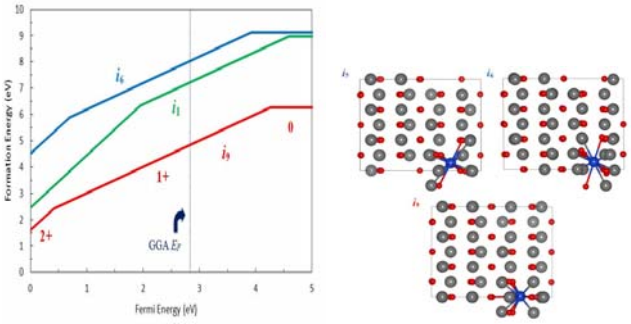

Fig. 1. Defect energy vs. Fermi energy for Cu at 3 different interstitial sites, in PBE.

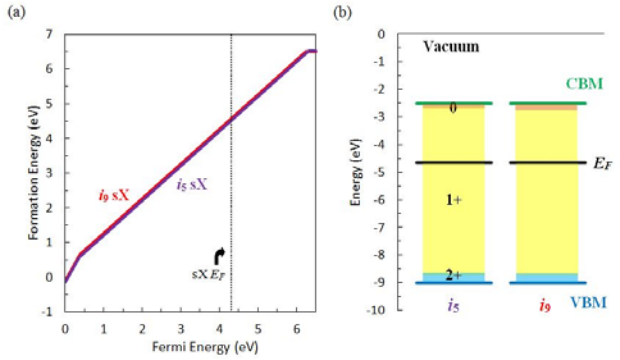

Fig. 2. Defect energy vs. Fermi energy in SX, for different Fermi energies, refered to vacuum level.

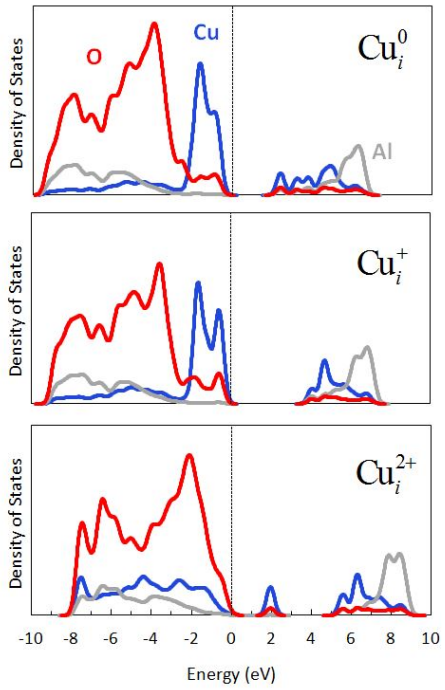

Fig. 3. PDOS of Cu0, Cu+ and Cu2+ states of isolated Cu sites in Al2O3.

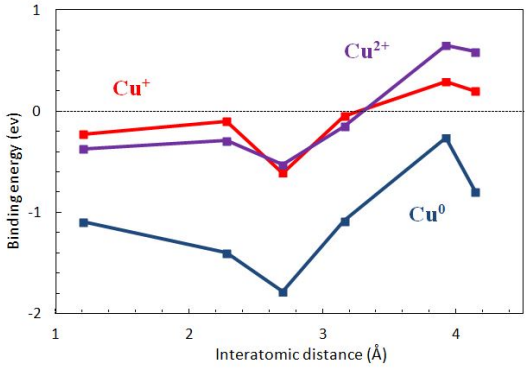

Fig. 4. Binding energy between pairs of Cu sites vs separation, for different charge states.

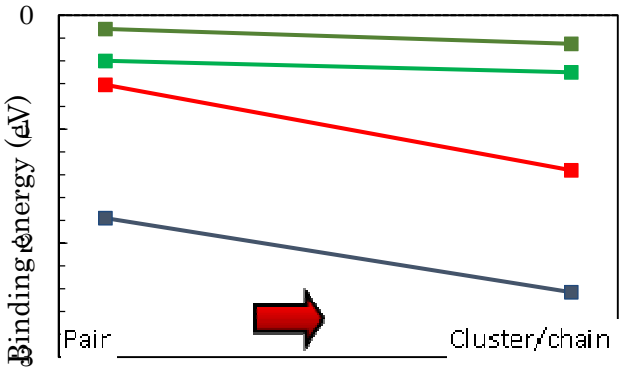

Fig. 5. Binding energy of Cu sites compared to O vacancies, for increasing clustering.

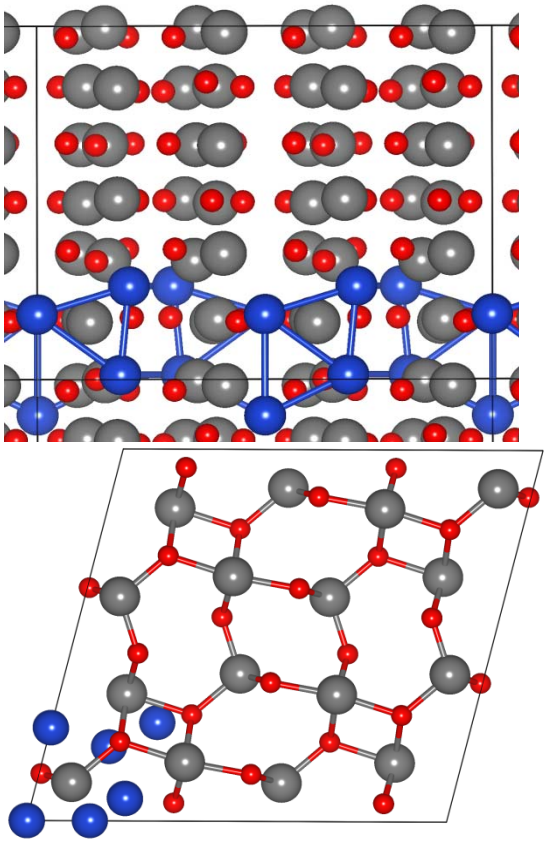

Fig. 6. Top and side view of a model Cu filament through the Al2O3 host. Cu=blue, Oxygen =red, Al=grey.