# Exploring the atomic structure of copper-doped Gd<sub>2</sub>O<sub>3</sub> for the conductive bridging RAM technology

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## Abstract

In this study we model the active layer of a conductive-bridging RAM (CBRAM) at the atomic scale. We concentrate our efforts onto a cubic gadolinium oxide  $c-Gd_2O_3$  doped with a copper atom coming from an electrode (copper-rich) by a redox mechanism. Using ab initio simulations, the formation enthalpies and the specific electronic states related to neutral and charged Cu interstitials are computed, relative to the level of injection of the electrons provided by the electrodes. A scenario is then proposed for the resistive switching of this type of CBRAM.

# 1. Introduction

Among resistive RAM technology, one of the most promising candidates is the conductive-bridging random access memory (CBRAM) due to its high scalability, its long retention time (~ 10 years), and its low power consumption. Practically, it consists of a dielectric sandwiched between two metallic electrodes and acting as a solid electrolyte. One of the electrodes possesses redox properties, allowing for the diffusion of metallic cations inside the dielectric, up to the point of resistive switching. Therefore, the main hypothesis that underlies CBRAM function is the electrochemical formation and dissolution of a conduction path, (a nanometric metallic filament), between the two electrodes allowing to flip between low and high resistance states. However, the true nature of this filament is of unknown composition and shape. Here, we have used electronic structure simulations applied to a copper-doped  $c-Gd_2O_3$ , contributing to better understanding of the CBRAM's physics.

## 2. Computational details and methodology

Ab initio calculations have been performed using density functional theory  $(DFT)^{[1,2]}$  thanks to the simulation tool Siesta<sup>[3]</sup> (linear combination of atomic orbitals). Electron-ion core interactions have been treated using norm-conserving pseudopotentials. Local spin density approximation (LSDA) is used, completed by the on-site coulomb corrections method (LSDA+U)<sup>[4]</sup> for strongly correlated 4f levels of Gd. Within this formalism, U and J represent the Coulomb and exchange parameters, respectively. The values U=6.7 eV and J=0.7 eV have been chosen for Gd levels according to the study of Kurz and al.<sup>[5]</sup>.

For all the calculations, a polarized double- $\zeta$  basis (DZP) with an energy shift of 50 meV combined with a mesh cutoff of 300 Ry were used for the self-consistent

convergence of the electronic wave-functions. A Monkhorst-Pack scheme<sup>[6]</sup> was used for the Brillouin zone sampling 3x3x3 and all the structures have been optimized until the forces and the stress become smaller than 0.05 eV/Å and 200 MPa respectively.

For this work we focus only onto the cubic structure  $c-Gd_2O_3$  which is one of the two most stable forms at room conditions<sup>[7,8,9]</sup>.  $c-Gd_2O_3$  belongs to the space group Ia-3 which is usually described as an oxygen defective fluorite-type (a quarter of anionic sites is empty).  $Gd^{3+}$  cations occupy equivalent sites 24d and 8b and the oxygen anions occupy the 48e sites<sup>[10]</sup>, leading to 16  $Gd_2O_3$  formula per cell<sup>[11]</sup>. After structural optimization of bulk material, the obtained relaxed structure is used to investigate the features of defective materials at the chemical bonding scale.

# 3. Results

# Geometry optimization

Table I shows the obtained results with LSDA and LDSA+U compared to experiment. As expected, the LSDA+U results are in better agreement with the experiment for cell parameter and material density. The electronic gap of 2.7 eV in LSDA is also slightly improved in LSDA+U at 3.5 eV mainly due to better localization of 4f states, but still underestimated by approximately 2 eV.

Table I: c-Gd<sub>2</sub>O<sub>3</sub> relaxed structural parameters

Structural parameters	Exp. Values	LSDA	LSDA+U
a (Å)	$10.81^{[10]}$	11.17	10.67
		(+3%)	(-1%)
Volume	$1262.9^{[10]}$	1394.9	1213.2
$(Å^3)$		(+11%)	(-4%)
Density	7.66 <sup>[12]</sup>	6.91	7.94
$(g/cm^3)$		(-10%)	(+4%)
Gap (eV)	5.3 <b>-</b> 5.6 <sup>[13]</sup>	2.7	3.5

## **Formation enthalpies**

Using,

$$\Delta H_{f} = U(Gd_{2}O_{3}) - 2.U(Gd) - \frac{3}{2}U(O_{2(g)})$$
(1)

the calculated formation enthalpy  $\Delta H_f$  of c-Gd<sub>2</sub>O<sub>3</sub> is -19.60 eV in good agreement with the experimental value of -18.86 eV<sup>[14]</sup> per formula unit.

For the study of Cu-doped  $Gd_2O_3$ , a copper atom was introduced in the unit cell of c- $Gd_2O_3$  followed by relaxation of forces only. Two different interstitial sites

have been simulated near to 24d and 8b Gd sites respectively. No noticeable differences have been seen for these two locations. Using the first interstitial position, the neutral and charged defects have been studied. By employing,

$$\Delta H_{f} = U \Big( Gd_{2}O_{3} : Cu^{+q} \Big) - U \Big( Gd_{2}O_{3} \Big) - U \Big( Cu_{(s)} \Big) + q.\mu_{e}$$
(2)

the formation enthalpies of defects have been evaluated against  $\mu_e$  the chemical potential of the electrons. This quantity varies between the valence maximum (VBM) and the conduction band minimum (CBM) of Gd<sub>2</sub>O<sub>3</sub> and is associated to the level of injection of electrons inside the CBRAM. Results obtained are shown in Fig. 1 the most stable state is Cu<sup>+</sup> (orange line) for a large window centered onto mid-gap injection conditions, followed by Cu<sup>-</sup> (blue line) for reduction conditions or Cu<sup>++</sup> (red line) for oxidation conditions. Due to coulomb repulsion, above a certain amount of copper inside Gd<sub>2</sub>O<sub>3</sub>, the Cu<sup>0</sup> species will be favored, visualized by the downward shift of the black line.



Fig. 1 Formation enthalpies of Cu-doped c-Gd<sub>2</sub>O<sub>3</sub> (left panel); interstitial position of Cu<sup>+</sup> inside c-Gd<sub>2</sub>O<sub>3</sub> (right panel): gadolinium green, oxygen red, copper yellow.

#### **Density of states**

The electron density of states of Cu-doped c-Gd<sub>2</sub>O<sub>3</sub> obtained in LSDA+U are shown in Fig. 2. The copper interstitial introduces electronic states inside the forbidden gap of c-Gd<sub>2</sub>O<sub>3</sub>: Cu<sup>0</sup> shows half-filled states with 4s<sup>1</sup> type at ~1 eV below the conduction band, Cu<sup>+</sup> has empty states of 4s<sup>0</sup> type at the edge of the conduction band, while Cu<sup>-</sup> leads to two states filled at ~1.5 eV (4s<sup>2</sup>) below the conduction band.

#### 4. Discussion and conclusion

These elemental results allow us to draw a functional scheme, Fig. 3 during the SET operation, interstitials copper are emitted from the anode (due to oxidation), generating mainly  $Cu^+$  which is thermodynamically favoured inside the dielectric. Close to the cathode,  $Cu^+$  should be reduced into  $Cu^-$ , but above a certain concentration, the repulsive Coulomb interaction will favor  $Cu^0$ . Driven by the electric field, one can also deduced that not only the Cu+ diffusion will be enhanced, but that electrons could tunnel by a trap assisted mechanism between the  $Cu^{-70}$  and  $Cu^+$  states, through  $Gd_2O_3$ .



Fig. 2 Density of states of Cu-doped c-Gd<sub>2</sub>O<sub>3</sub>, spin-polarized. VB and CB are the valence and conduction band respectively. The pristine c-Gd<sub>2</sub>O<sub>3</sub> is in black. For Cu<sup>0</sup> (top left) and Cu<sup>-</sup> (top right) the dashed line delimitates the filled levels from the empty ones. Cu<sup>++</sup> and Cu<sup>+</sup> (bottom left) are shown together (Cu<sup>+</sup> in magenta, Cu<sup>++</sup> in turquoise). Only the Cu<sup>+</sup> 4s states are shown on bottom right to distinguish them from the CB.



Fig. 3  $Cu^+$  diffusion from anode to cathode inside  $Gd_2O_3$  accompanied with electron hopping at +2V polarization.

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