Structure and charge transport of amorphous $Cu$-doped $Ta_2O_5$: An \textit{ab initio} study

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In this paper, we present \textit{ab initio} computer models of $Cu$-doped amorphous $Ta_2O_5$, a promising candidate for Conducting Bridge Random Access Memory (CBRAM) memory devices, and study the structural, electronic, charge transport and vibrational properties based on plane-wave density functional methods. We offer an atomistic picture of the process of phase segregation/separation between $Cu$ and $Ta_2O_5$ subnetworks. Electronic calculations show that the models are conducting with extended Kohn-Sham orbitals around the Fermi level. In addition to that, we also characterize the electronic transport using the Kubo-Greenwood formula modified suitably to calculate the space-projected conductivity (SPC). Our SPC calculations show that $Cu$ clusters and under-coordinated $Ta$ adjoining the $Cu$ are the conduction-active parts of the network. We also report information about the dependence of the electrical conductivity on the connectivity of the $Cu$ sub-matrix. Vibrational calculations for one of the models has been undertaken with an emphasis on localization and animation of representative modes.

I. INTRODUCTION

Novel non-volatile memory devices are an area of active inquiry. Research on ferroelectric random access memory (FeRAM) and magnetoresistive random access memory (MRAM) have been limited due to underlying technological and scalability problems. Meanwhile, study of non-volatile memory, based on electrically switchable resistance or resistive random access memory (ReRAM), has gained considerable interest. The first studies of such resistive switching was reported in the 1960’s and was based on oxides in a metal-ion-metal (MIM) framework with formation/dissolution (SET/RESET) of filament electrochemical in nature. Amongst ReRAM’s, electrochemical metallization mechanism (ECM) or conductive bridging random access memory (CBRAM) which utilizes the electrochemical dissolution of an active electrode material such as $Cu$ or $Ag$ for SET/RESET mechanism has shown particular promise. In CBRAM, transition metals in their ionic state are converted to a conducting filament by applying a suitable electric field, which upon reversal, destroys the filament resulting in a resistive state. Several possible candidates for solid electrolytes have been studied elsewhere. Amorphous tantalum pentoxide/amorphous tantalum ($a-Ta_2O_5$) has been investigated as a possible candidate for memory devices, anti-reflection coatings and optical waveguides due to its high dielectric constant, high refractive index, chemical and thermal stability. $Cu$-doped $a-Ta_2O_5$ shows promising properties for CBRAM based memory devices.

Several experiments as well as calculations have been carried out to understand conduction mechanisms in $Ta_2O_5$ materials. In these studies, $Ag$, $Cu$, $Pt$ metals were used as electrodes while in one $Xiao$ et al. used $Cu$ nanowires of different diameters inserted into the low density $Ta_2O_5$ host to study transport and electronic properties of $Ta_2O_5$ as an electrolyte. These papers indicate that metal filaments are responsible for conduction. It has been reported that conduction paths in different electrolytes differ qualitatively. Metals such as $Cu$ form clusters, leading to a conducting filament in oxides, while no such clustering is observed in chalcogenide based electrolyte. Since a complete investigation of $Cu$-doped $Ta_2O_5$ has not yet been reported, we provide here a thorough investigation amid growing research to test its candidacy as a possible electrolyte for CBRAM technologies.

In this paper, we investigate the structural, electronic and lattice dynamics of amorphous $Cu$-doped $a-Ta_2O_5$. We provide insights into structural properties and coordination statistics, electronic and vibrational properties, and visualize conduction/current paths by computing the space-projected conductivity (SPC). We elucidate the atomistic mechanisms of phase segregation and track the emergence of $Cu$ clusters as
the melt cools. The rest of paper is organized as follows. In section II, we discuss the computational methodology used to generate our models. This is followed by validation of the generated models with particular attention to the structural, electronic, vibrational, and thermal properties in section III. In Section IV we present the conclusions of our work and future research directions.

II. METHODOLOGY AND MODELS

We prepare two 210-atom models of a-(Ta2O5)0.80Cu0.20 cooled at different rates by utilizing melt-quenching within the ab initio molecular dynamics (AIMD) method. The initial density for both of the models was chosen to be that of amorphous tantala (ρ = 7.79 gm/cc), consistent with experimental and theoretical studies. We have performed molecular dynamics simulations using ab initio plane wave code VASP with projector-augmented wave (PAW) method and employed the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional. Due to the size of the unit cell, only the Γ-point is used for Brillouin zone (BZ) integrations. A plane-wave cut off of 500 eV, a time step of 3.0 fs and Nose’ thermostat was used to control the temperature.

A. Model I

We fabricated a starting model of 48 Ta, 120 O and 42 Cu atoms with random initial positions (with no atoms closer than 2 Å) in a cubic box of side 14.14 Å. The model was then taken through a melt quench (MQ) cycle. Firstly, the system was heated well above melting point to form a liquid at 6000 K and then equilibrated at 6000 K, cooled to 3000K in 18 ps, equilibrated at 3000K for 9ps and further cooled to 300K in 15 ps summing up for a total simulation time of 57 ps. The cell volume was relaxed to obtain zero pressure models. This zero-pressure relaxation produced a volume rise of 2.09% yielding an optimized density of 7.63 gm/cc.

B. Model II

Another melt and quench (MQ) model, with slower cooling rate around the melting point of Ta2O5, was made. This model started with the melt of Model I cooled to 3000K and was further cooled to 300K in 24ps without any intermediate equilibration. The total simulation time was 60 ps.

After dynamical arrest, conjugate-gradient relaxation was applied until the magnitude of the force on each atom was reduced to less than 0.01 eV/Å. Zero-pressure relaxation increased the volume by 2.39% and the density was optimized to 7.61 gm/cc. A third model, cooled faster than the models discussed here, has been described in the Supplementary Material, to provide some insight into the influence of the quench rate on the network topology.

For simplicity and consistency, we follow the same "color nomenclature" for the atomic species: Ta, O, and Cu atoms are colored green, red, and blue respectively.

| Model | Atom | n | n(Ta) | n(O) | n(Cu) |
|-------|------|---|-------|------|-------|
| Model I | Ta | 7.96 | 1.75 | 5.52 | 0.69 |
|       | O   | 2.44 | 2.21 | 0.00 | 0.23 |
|       | Cu  | 7.17 | 0.79 | 0.67 | 5.71 |
| Model II | Ta | 8.00 | 1.92 | 5.60 | 0.48 |
|        | O   | 2.45 | 2.24 | 0.00 | 0.21 |
|        | Cu  | 7.48 | 0.55 | 0.60 | 6.33 |

TABLE I: Average coordination number (n) and its distribution among different species. Coordination is counted only if the distance between the atoms is no more than the sum of their covalent radius within a tolerance of 0.1 Å. Covalent radii for Ta, O and Cu are taken as 1.70Å, 0.73Å, and 1.32Å, respectively

III. RESULTS AND DISCUSSION

A. Structural Properties

As shown in Fig.2, the radial distribution function for both models has a first peak at 1.95 Å, which arises from the dominant Ta-O bonds and corresponds to the Ta-O bond length. This peak is in agreement with experiments for pure a-Ta2O5 and previous DFT calculations for Cu-doped tantala as well which suggests that the introduction of Cu to the network does not significantly change the local environment around the Ta atoms, i.e. the dominance of Ta-O octahedra in the structure persists even after Cu doping. This finding is also supported by low Cu-O coordinations. Introduction of Cu, however, steals some O coordination from Ta, as seen in Table I, and these under-coordinated Ta atoms have a significant role in conduction which will be explained later.

The Ta-Ta correlations also remain unaffected by Cu doping but a strong peak, at 2.48Å, in the Cu-Cu correlations suggests the formation of Cu clusters in the system, as seen in Fig[1], which can be attributed to the ionicity of the Ta-O bonds that drives the Cu-atom to cluster. Previously, clustering of Cu in ionic host (a-Al2O3) has been reported[4]. This strong Cu-Cu correlation suggests that Cu-atoms preferentially bond with themselves, consistent with the coordination statistics. In contrast, zirconia-doped tantala shows no Zr clustering and, the metal atoms distribute themselves homogeneously with no metal-metal pair closer than 2.9 Å[14]. It is quite interesting that our calculations “naturally” produce connected Cu "wires" that are extended in space (considering the periodic boundary conditions), not by modeler’s “installation”, but as a direct and unbiased consequence of the melt-quench simulations themselves.

Two peaks are worth mentioning in the Ta-Ta correlation: the first at around 3.3Å, and the second around 3.8Å, firstly
FIG. 1: (a) The structure of Model I (a) and Model II (b) consists of tantalum atoms bonded to 5, 6 and 7 oxygen atoms to form a mixture of edge-sharing, corner-sharing and face-sharing polyhedra and a connected subnetwork of Cu atoms. The Cu network grows in the interstitial space between Ta-O polyhedra. Cu, Ta and O atoms are shown in blue, green and red, respectively and the same "color nomenclature" will be used throughout the paper.

FIG. 2: Pair distribution function for Model I (solid line) and Model II (dotted line). The total pair distribution function (g(r)) is almost the same for both the models. There is, however, a slight change in the Cu-Cu and Cu-O partial correlations.

because they provide an idea of the how the Ta-O octahedra are connected, and secondly because they are implicated in mechanical loss for Laser Interferometer Gravity Wave Observatory application. The former comes from the joint contribution of face and edge-shared octahedral connection while the latter derives from the corner-shared connection of the octahedra.

The coordination statistics of the models in Table I largely serve to validate the findings of the RDF and the correlations between different species. It also suggests that, as we lower
the cooling rate, the Cu -Cu coordination increases while the Cu -O coordination decreases. This implies slower cooling rates produce better Cu clusters with O being pushed away from them.

To compare the Cu -Cu and the Cu -O environment and its evolution during the melt and quench process in our models, we calculate, at each step, the following quantities:

\[
d_{\text{CuCu}} = \frac{1}{3N_{\text{Cu}}} \sum_{i=1}^{N_{\text{Cu}}} \sum_{j=1}^{3} |\vec{R}_{\text{Cu},i} - \vec{R}_{\text{Cu},j}| \tag{1}
\]

\[
d_{\text{CuO}} = \frac{1}{3N_{\text{Cu}}} \sum_{i=1}^{N_{\text{Cu}}} \sum_{j=1}^{3} |\vec{R}_{\text{Cu},i} - \vec{R}_{\text{O},j}| \tag{2}
\]

The sum over \(j\) runs over three nearest \(\text{Cu}\) in the first equation and over three nearest \(\text{O}\) in the second. The scatter plots in Fig. 3 show how these distances change as we cool the melt. This plot clearly shows that as we reduce the cooling rates, the \(\text{O}\) and \(\text{Cu}\) atoms move apart. Furthermore, the details of the change in the bonding environments of the atoms and the phase segregation of \(\text{Cu}\) atoms in the network during the melt and quench process has been discussed with animations in the Supplementary Material. There, we provide a visualization of the network formation process, and observe the exclusion of \(\text{Cu}\) as the host \(T_{\text{a2O}_5}\) network, rendering the \(\text{Cu}\) becomes atomus non grata in or near the \(T_{\text{a2O}_5}\) regions. The main “takeaway” from Fig. 3 is that the more extended cooling produces a more compact \(\text{Cu}\) cluster for Model II (hence the extended right “leg” on the right side of the “ballerina plot” of Fig. 3b compared to Fig 3a). This suggests that slower cooling rates create \(\text{Cu}\) clusters that are as compact as possible, and minimize \(\text{Cu}\) cluster surface area exposed to the \(T_{\text{a2O}_5}\) host. Of course this hints at a propensity to form crudely spherical clusters, though our simulations are too small to prove this assertion.

B. Electronic Properties

To understand the electronic structure of the models, we examine the total density of states (DoS), partial DoS and inverse participation ratio (IPR). These calculations not only help us check the validity of the model, but can also be used for a priori information to model amorphous material. The plot of the DoS in Fig. 4 reveals that both models have states around the Fermi level with extended Kohn-Sham orbitals indicating conducting behavior. Since the host \((T_{\text{a2O}_5})\) is an insulator with a band gap of 4.22 eV, we see that the introduction of \(\text{Cu}\) to the network closes the gap by inducing impurity bands spread throughout the entire host \((T_{\text{a2O}_5})\) gap. This is corroborated by the fact that the states near the Fermi level arise from the \(\text{Cu}\) -3d orbitals hybridized mainly with \(\text{Ta}\) and small contributions from \(\text{O}\) orbitals, as seen in the partial DoS plots in Fig.4.

Our calculations show that the states near the Fermi level arise mostly due to \(\text{Cu}\) and \(\text{Ta}\) and a small contribution from \(\text{O}\). The occurrence of \(\text{Cu}\) clusters in the \(T_{\text{a2O}_5}\) host suggest that the \(\text{Cu}\) -clusters and \(\text{Ta}\) atoms near them form the conduction-active parts. In order to study the details of the states near the Fermi level, we plot the species-projected DoS averaged over three states above and below the Fermi level,

\[
\mathcal{I}(\psi_n) = \frac{\sum_i |a_{n,i}^d|^4}{\left(\sum_i |a_{n,i}^d|^2\right)^2}
\]

with \(a_{n,i}^d\) being the contribution to the eigenvector \(\psi_n\) from the \(i^{th}\) atomic orbital \((s, p, d)\) as obtained from VASP.
FIG. 4: Electronic density of (Kohn-Sham) states, Inverse Participation Ratio and projection onto atomic species for Model I (a) and Model II (b) with black vertical drop lines indicating Fermi level. The insets show a magnified version of the DoS contributions from each species near the Fermi Level.

FIG. 5: Electronic DoS averaged over three bands below (a) for Model I and (c) for Model II) and above ((b) for Model I and (d) for Model II) the Fermi level. The size of the atoms is proportional to their contribution to the total DoS. Colors as in Fig. 1.

In physical terms, IPR of electronic states is a measure of localization: localized state having high IPR value (ideally
equal to $I = 1$) while a completely extended state having a value of $(1/N)$, i.e. evenly distributed over $N$ atoms. Near the Fermi level, we observe low IPR indicating delocalized states and conducting behavior of the models.

### 1. Space Projected Conductivity

The density of states provides some hints about the species contributing near the Fermi-level; however, the conduction also depends upon the localization of their electronic states and momentum matrix elements between Kohn-Sham states near the Fermi level. Recently, we have developed a spatial decomposition of the Kubo-Greenwood formula that provides information about conducting paths in real space. By introducing a discrete grid in space, we show that the quantity:

$$\zeta(x) = \left| \sum_x \Gamma(x,x) \right|$$

provides such information at the spatial grid point $x$ and for which:

$$\Gamma(x,x') = \sum_{ij\alpha} g_{ij} \xi_{ij}^\alpha(x) (\xi_{ij}^\alpha(x'))^*.$$  \hspace{1cm} (4)

We have used this approach to describe transport in a solid electrolyte material[11] and $Cu$-doped $\alpha$-alumina[32]. In a mixed (insulating/conducting) system like ours only a few eigenvectors of $\Gamma$ characterize essentially all conduction in the system.

The SPC for both models is visualized as a grayscale plot in Fig.6. The figure shows that connected $Cu$ atoms form primary sites of conduction as expected. However, some $Ta$ atoms, which are near the $Cu$ atoms also contribute significantly to the electronic conduction. A detailed analysis of the bonding environment of these $Ta$ atoms show that they are under-coordinated with oxygen, i.e. have less than (or equal to) five $O$ bonds, a result that in agreement with previous works on non-stoichiometric tantala[33]. A detailed discussion of the bonding environment and the coordination statistics of these $Ta$ atoms has been made in the Supplementary Material. Furthermore, slower cooling rates produces higher $Cu$-$Cu$ coordination and better connectivity, thereby enhancing conductivity. There is a factor of about 5 higher conduction in Model II than Model I, presumably because of the small “neck” interlinking $Cu$ in Model I.

### C. Vibrational Properties

#### 1. Vibrational Density of States

The vibrational density of states (VDOS) provides key information about local bonding environments in amorphous solids and serves as a test to validate a model[34]. Model I was well relaxed, and the lattice vectors were simultaneously relaxed to attain zero pressure, which of course produces a slightly non-orthogonal supercell. We displaced each atom...
in six directions ($\pm x, \pm y, \pm z$) by ($\sim 0.015$ Å), and after each of these small displacements, forces were computed on all atoms, to obtain the force constant matrix, and dynamical matrix. Classical normal modes were computed from the dynamical matrix by direct diagonalization. The VDOS is defined as:

$$g(\omega) = \frac{1}{3N} \sum_{i=1}^{3N} \delta(\omega - \omega_i)$$  \hspace{1cm} (6)$$

with $N$ and $\omega_i$ representing the number of atoms and the eigenfrequencies of normal modes, respectively. To determine the elemental contribution to the VDOS, we computed species projected VDOS defined as:

$$g_\alpha(\omega) = \frac{1}{3N} \sum_{i=1}^{N_\alpha} \sum_n |e^{\alpha}_n|^2 \delta(\omega - \omega_n)$$ \hspace{1cm} (7)$$

$|e^{\alpha}_n|^2$ are the eigenvectors of the normal modes and $N_\alpha$ is total number of atoms of $\alpha$ species. These species-projected VDOS must satisfy the relation $g(\omega) = \sum\alpha g_\alpha(\omega)$.

As seen in Fig.7 (left panel), the VDOS is peaked at $\sim 105 \text{cm}^{-1} \approx 13 \text{meV}$, a peak arising due to the mixing of vibrational motion of Ta and Cu atoms. Partial VDOS plot (right panel) shows that Ta - and Cu - vibrations are both peaked at $\sim 105 \text{cm}^{-1}$ while the O atoms do not contribute to low frequency vibrations as significantly as the other species. However, at frequencies above $\sim 400 \text{cm}^{-1}$, VDOS contributions arise mainly from the O -atoms, with no mixing, which can be ascribed to the low atomic mass of O compared to Cu - and Ta - atoms. In the intermediate region (200 cm$^{-1}$ - 320 cm$^{-1}$), vibrations arise from combined contributions of all atomic species. Animations of selected modes are provided in the Supplementary Material. Mode mixing and cross-talk between the phase-separated regions are features of these an-

FIG. 7: (a, top panel) Total vibrational density of states for the Cu - doped Ta$_2$O$_5$ (Model I) and the magnitude of normalized eigenvectors averaged over atomic species ($|u_i^j|^2$) in (a, bottom panel). A transition is seen at frequency $\sim 270 \text{cm}^{-1}$ where the Oxygen atoms start dominating the vibrational spectrum. The total vibrational localization (IPR) in (a, top panel) shows that phonons modes are mostly extended with few localized modes appearing at higher frequencies. The yellow circles show IPR that indicates localization of vibrational eigenmodes. (b) We plot species-projected VDoS and VIPR of our Model I. We observe that oxygen dominates the higher frequency range and the Cu sub-network modes are mostly extended in nature.
imotions.

2. Localization of vibrational modes

While the VDOS is an observable that can be measured almost directly from inelastic neutron scattering experiments, the localization of these vibrations are not easily observable. To study the localization of vibrational modes in the Cu-doped $Ta_2O_5$, we calculate the vibrational IPR, the vibrational analogue of the electronic IPR, from the eigenvectors as shown in Equation 8:

$$V(\omega_n) = \frac{\sum_{i=1}^{N} |u_{ni}|^4}{\left(\sum_{i=1}^{N} |u_{ni}|^2\right)}$$

where $(u_{ni})$ is displacement vector of $i^{th}$ atom at normal mode frequency $\omega_n$.

A small value of VIPR indicate evenly distributed vibration among the atoms while higher values imply only a few atoms contributing at that particular eigenfrequency. We have plotted the total VIPR in Fig.7. Low values of VIPR below ~ 300 cm$^{-1}$ suggest that the vibrational modes are completely delocalized/extended. Above 300 cm$^{-1}$, we observe higher VIPR. To provide visual insight to the spread of vibrations over atoms and localization of some vibrational modes, suitable animations and explanations of some normal modes has been provided in the Supplementary Material.

To investigate the relation between the vibrational localization and atomic species, we evaluate contribution to VIPR from each atomic species, commonly called species-projected VIPR\textsuperscript{[2]}\textsuperscript{[23]} These projections sum up to the total VIPR, i.e. satisfy the relation:

$$V(\omega_n) = V_{Ta}(\omega_n) + V_{O}(\omega_n) + V_{Cu}(\omega_n)$$

and is shown on the right panel of Fig. 7. The species-projected VIPR calculations suggest that low frequency modes arise mainly from $Ta$ - and $Cu$ -atoms while the high frequency vibrations come mostly from the $O$ -atoms which can be attributed to the atomic masses of the species. Higher values of partial VIPR are seen at higher frequencies. Therefore, the high frequency modes are localized on a few $O$ atoms in the network while the low frequency modes are spread among larger number of $Ta$ and $Cu$ atoms. The quantity plotted in the bottom left panel Fig. 7 is the squared-magnitude of normalized eigenvectors summed across the atomic species for all the normal modes. The scatter plot and the partial VDOS plots suggest that the $Ta$ - and $Cu$ -atoms participate almost equally in the low frequency vibrations.

IV. CONCLUSIONS

We describe the atomistic process of phase segregation of $Cu$ in $a$-$Ta_2O_5$. The $Cu$ did not significantly alter the $Ta$ -$O$ bonding but instead phase separated, forming $Cu$ clusters. Models made with a slower cooling rate revealed significantly better (denser) clustering than the one with faster cooling rate. These clusters, along with the neighboring under-coordinated $Ta$ atoms, form a conducting path in the network which is in agreement with previous literature, though presented in novel way in this paper, and not relying only on the Kohn-Sham states near the Fermi level, but also the momentum matrix elements, a legacy of the current-current correlation functions of Kubo. All this lends significant insight into an important CBRAM material.

It is interesting to speculate on what would happen in larger models and different cooling rates. We might expect to see Cu blobs in the network, possibly spatially separated but potentially interconnected by some other conducting fabric, perhaps Cu nanowires (of essential interest of course for CBRAM applications). While direct simulations like this one is computationally impossible for so large a system, it provides potentially useful a priori information for modeling employing simpler interatomic interactions. Electronic DoS calculations show that $Cu$ -doping closes the gap in the DoS of pure $a$-$Ta_2O_5$ with extended Kohn-Sham orbitals around the Fermi level. Vibrational modes at low frequencies are shared among many $Ta$ and $Cu$ atoms while those at high frequency are quite localized and come only from $O$ atoms.

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