Conducting-Bridge Memory



Spatial Projection of Electronic Conductivity: The Example of Conducting Bridge Memory Materials

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Conducting bridge random access memory materials have special promise for FLASH memory, other applications beside, and also special potential for continued miniaturization. They are electronic materials of unique flexibility. Here, we offer new models of Cu-doped alumina, and reveal qualitative differences in the behavior of transition metal ions in chalcogenide and oxide hosts, showing that Cu clusters in an amorphous alumina host, in contrast with chalcogenides in which the metal atoms do not cluster. We further elucidate the processes of electron transport. To determine these, the Kubo– Greenwood formula is cast in a form to enable the estimate of a spaceprojected conductivity. The method reveals those parts of the networks that may conduct a current (or absorb radiation at frequency ω).

Some leading contenders for next generation non-volatile computer memory depend on manipulation of electrical conduction. Among these, conducting bridge random access memory (CBRAM) and phase change memory (PCM) materials are examples. In this article, we discuss the atomistic conduction mechanisms in two CBRAM materials^[1]: a-(GeSe₃)_{0.75}Ag_{0.25} and a-Al₂O₃:Cu. We show that the chalcogenide and oxide stories turn out differently, with Cu or Ag clustering in the oxide and dissolving in chalcogenides. To more deeply understand these phenomena and to grasp the atomistic electronic conduction mechanisms in these materials, we identify and quantify conducting structures in materials. The compositions discussed

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in this paper are relevant for both scientific studies of these materials, and some devices in use and/or development.

We begin by creating supercell models $a-Al_2O_3$, of $(a-Al_2O_3)_{0.9}Cu_{0.1}$ and (a-Al₂O₃)_{0.8}Cu_{0.2} consisting of 200 atoms. The bulk density of $3.175 \,\mathrm{g \, cm^{-3}}$ is taken for a-Al₂O₃. Due to a lack of experimental data, we refer to ref. [2] to make an initial guess of bulk density of $3.7 \,\mathrm{g}\,\mathrm{cm}^{-3}$ $(3.9 \,\mathrm{g}\,\mathrm{cm}^{-3})$ for 10% (20%) Cu models, respectively. We perform ab initio molecular dynamics simulations using $VASP^{[3]}$ and projector-augmented wave (PAW)^[4,5] potentials within the local density approximation.^[6] A plane wave cutoff energy of 420 eV and Γ -point Brillouin zone (BZ)

sampling was used. The time step was 1.5 fs, and the temperature was controlled by a Nosé-Hoover thermostat. The models were prepared using the melt-quench scheme^[7] starting with random initial configurations at 3500 K. After annealing the initial configurations for 7.5 ps at 3500 K, we cool each model to 2600 K at a rate $0.27 \,\mathrm{K}\,\mathrm{fs}^{-1}$ and equilibrate for 10 ps at this temperature. Each model is then quenched to 300 K at the same cooling rate $0.27 \,\mathrm{K}\,\mathrm{fs}^{-1}$ and equilibrated for another 10 ps. We performed zero-pressure relaxation for these equilibrated models and obtained optimized densities of 3.75 and 3.99 g cm⁻³ for the 10 and 20% Cu-doped models. The a-(GeSe_3)_{0.75}Ag_{0.25} model discussed in this work is a 100-atom cubic cell, reported in ref. [8].

In **Figure 1**, we illustrate the radial distribution functions of pure alumina and two Cu-doped alumina models, and compare to experiment^[9] for the undoped case. In contrast to the more covalent silver-doped chalcogenides,^[10] there is an obvious proclivity for Cu to cluster in alumina, as seen in **Figure 2**. For the 20% Cu cluster, the clustering leads to a narrow space-filling conducting path described below, whereas for 10% the path is broken, and states near the Fermi level are somewhat localized. Pure alumina has an LDA (Γ -point) gap of 4.0 eV. States near the Fermi level in the 20% Cu-doped system are fairly extended originate mostly from Cu.

For a-(GeSe₃)_{0.75}Ag_{0.25} the Ag dissolves uniformly into the matrix^[11] and when the Ag ions are well separated (in the homogeneous state of the material), it is semiconducting. Separate calculations have shown that Ag clusters in a-Al₂O₃ as Cu does. The inference then is that the highly ionic alumina host induces the transition metal clustering. It seems likely that this is just due to the large energy penalty for homopolar bonds for



r[Å]





Figure 1. Left: Radial distribution for alumina and experiment.^[9] Right: Radial distribution functions g(r) for Cu-doped alumina. The peak near 2.44 Å is due to Cu–Cu correlations.

r[Å]

such an ionic system. Thus, in crude terms, the primary role of electrochemical manipulation of the materials is to connect (break) conducting filaments in chalcogenides (oxides). The qualitative difference in ion solubility between the chalcogenide and oxide host must affect ion trap-release dynamics, device response to radiation, and electronic characteristics. The alumina-based materials have been carefully studied experimentally, including even the morphology of an electro-chemically induced filament.^[12]

To determine the space-projected conductivity (SPC), we use the Kubo–Greenwood formula (KGF),^[13] which is suited for density-functional simulations of materials with its singleparticle Kohn–Sham orbitals and energies.^[14] The KGF has been exploited in tight-binding and DFT computations of conductivity of liquids and solids,^[15] and may be employed with better (post-DFT) estimates of excited states.^[16] The idea is to spatially decompose the KGF in terms of Kohn–Sham orbitals in real space. We describe two ways to achieve this, one directly from the KGF, and the other in terms of the eigenvectors of a Hermitian matrix described below.

The KGF estimates the AC conductivity (for frequency ω and Bloch vector **k**) as

$$\sigma_{\mathbf{k}}(\omega) = \sum_{i,j} g_{ij}(\mathbf{k}, \omega) \sum_{a} \left| p_{ij}^{a} \right|^{2}$$
(1)

In the shorthand notation of Equation (1), we averaged over diagonal elements of the conductivity tensor (a = x, y, z), *i* and *j* index Kohn–Sham orbitals $\psi_{i,\mathbf{k}}(x)$ with associated energies $\varepsilon_{i,\mathbf{k}}$, p^a is the momentum operator (for direction *a*) and



Figure 2. Cu atoms (blue), O (red), and Al (gray) in $(a-Al_2O_3)_{0.9}Cu_{0.1}$ (left) and $(a-Al_2O_3)_{0.8}Cu_{0.2}$ (right). Note that the Cu clusters in the oxide matrix. Periodic boundary conditions are employed throughout.

 $g_{ij}(\mathbf{k},\omega) = 2\pi e^2 \left[f_i(\mathbf{k}) - f_j(\mathbf{k}) \right] \delta(\varepsilon_j(\mathbf{k}) - \varepsilon_i(\mathbf{k}) - \hbar \omega) / (3m^2 \omega \Omega),$ where Ω is the cell volume and f is the Fermi–Dirac distribution.

From this point on, we suppress the explicit dependence on **k** and ω . The matrix elements of the momentum operator are $p_{ji}^{a} = \langle \psi_{j} | p^{a} | \psi_{i} \rangle$ so that

$$\sigma = \sum_{ija} \int d^3x \int d^3x' g_{ij} \Big[\psi_j^*(\mathbf{x}) p^a \psi_i(\mathbf{x}) \Big] \Big[\psi_i^*(\mathbf{x}') p^a \psi_j(\mathbf{x}') \Big]$$
(2)

Define complex-valued functions $\xi_{ij}^{\alpha}(\mathbf{x}) = \psi_i^*(\mathbf{x})p^{\alpha}\psi_j(\mathbf{x})$ on a real-space grid (call the grid points \mathbf{x}), and suppose, for simplicity, that the grid is uniformly spaced in three-dimensional space with spacing *h*. In such a case, the spatial quadratures are easily estimated as a sum on the grid, and the operation of p^{α} is provided by finite-differences. Then the conductivity is approximated as

$$\sigma \approx h^{6} \sum_{\mathbf{x}, \mathbf{x}'} \sum_{ija} g_{ij} \xi_{ji}^{a}(\mathbf{x}) \xi_{ij}^{a}(\mathbf{x}')$$
(3)

This equation expresses the conductivity as a double spatial sum and leads us to define the Hermitian, positive-semidefinite matrix:

$$\Gamma(\mathbf{x}, \mathbf{x}') = h^6 \sum_{ija} g_{ij} \xi^a_{ji}(\mathbf{x}) \xi^a_{ij}(\mathbf{x}')$$
(4)

and it follows from Equation (3) that $\sigma = \sum_{\mathbf{x},\mathbf{x}'} \Gamma(\mathbf{x}, \mathbf{x}')$ as $h \to 0$. Equation (4) suggests a means to spatially decompose the conductivity. We take the SPC to be $\zeta(\mathbf{x}) = |\Sigma_{\mathbf{x}'} \Gamma(\mathbf{x}, \mathbf{x}')|$. $\zeta(\mathbf{x})$ is of interest as it is positive, additive, and by construction indicates the conduction-active parts of the system. $\Gamma(\mathbf{x}, \mathbf{x}')$ decays for large $|\mathbf{x} - \mathbf{x}'|$. The physical reason is cancellation due to loss of correlation for $|\mathbf{x} - \mathbf{x}'| > \delta$,^[17] where δ is a system-dependent length. This is reminiscent of Kohn's "principle of nearsightedness,"^[18] developed for the density matrix. In fact, for qualitative structure of SPE, the positive diagonal approximation $\Delta(\mathbf{x}) = \Gamma(\mathbf{x}, \mathbf{x})$ yields results virtually identical to ζ . See the left panel of **Figure 3**.

Since Γ is Hermitian, it is natural to diagonalize it. Its eigenvalue problem reads: $\Gamma |\chi_{\mu}\rangle = \Lambda_{\mu} |\chi_{\mu}\rangle$, for which $\mu = 1$, n_g . n_g is the number of points in the spatial grid (thus for example, $n_g = n^3$ for *n* points in each Cartesian direction in 3D). Diagonalization provides a spectral representation: $\hat{\Gamma} = \sum_{\mu} |\chi_{\mu}\rangle \Lambda_{\mu} \langle\chi_{\mu}|$, from which:

$$\sigma = \sum_{\mathbf{x}} \sum_{\mu} \Lambda_{\mu} \left| \chi_{\mu}(\mathbf{x}) \right|^{2} + \sum_{\mathbf{x}, \mathbf{x}', \mathbf{x} \neq \mathbf{x}'} \sum_{\mu} \Lambda_{\mu} \chi_{\mu}(\mathbf{x}) \chi_{\mu}^{*}(\mathbf{x}')$$
(5)

Equation (5) introduces the concept of conduction eigenvalues and modes. In Figure 3 (right), we report the density of states for Γ and spatial localization of the associated $\chi_{\Lambda}(\mathbf{x})$. The eigenvectors conjugate to extremal Λ are highly extended. Few eigenvalues contribute significantly to σ , with an overwhelming accumulation of spectral weight in the density of states near $\Lambda = 0$. While the details of such spectra vary from systems like Al to c-Si, the basic form is similar (an exception being a spectral tail







Figure 3. Properties of Γ (**x**, **x**') for 10% Cu-doped model. Left: Decay of Γ matrix. Right: Spectrum of Γ and localization (inverse participation ratio)^[19] of its eigenvectors (χ).

that forms near $\Lambda = 0$ for more metallic systems). The spectral decomposition of σ of Equation (5) categorizes the conductivity into a finite and, in practice, tiny (compared to the dimension of Γ) set of conduction channels, and in practice the first few terms of Equation (5) resemble $\Gamma(\mathbf{x}, \mathbf{x})$. Because of trace invariance of Γ the first term of Equation (5) reproduces $\Delta(\mathbf{x}) = \Gamma(\mathbf{x}, \mathbf{x})$, in a similar fashion, $\Sigma_{\mu} \Lambda_{\mu} = \Sigma_{\mathbf{x}} \Delta(\mathbf{x})$.

To carry this out, we employ Kohn–Sham orbitals computed with VASP. The $\psi_{i,\mathbf{k}}(\mathbf{x})$ are obtained from the VASP WAVECAR file using a convenient code of R. M. Feenstra and M. Widom.^[20] The ξ (of Equation (3)) are obtained using central differences with $\delta r = 0.05$ Å. The KGF is evaluated in its "exact form" (Equation (8) of ref. [21]) and to estimate the SPC ζ , we adopt a discrete grid with n = 36 (dim $\Gamma = 46\,656$). Among various tests, we studied FCC Al (108 atoms and 4 k-points) and obtain a DC conductivity of 12.3×10^6 S m⁻¹, in favorable comparison with Figure 10 of ref. [21]. We select a temperature T = 1000 K for the Fermi–Dirac distribution. The exact value of the conductivity is somewhat sensitive to this choice, the SPC plots far less so.

Using the assumptions above, we obtained DC conductivities of 60, 1.5, 45 S cm⁻¹ for a-(GeSe₃)_{0.75}Ag_{0.25}, (a-Al₂O₃)_{0.9}Cu_{0.1}, and (a-Al₂O₃)_{0.8}Cu_{0.2}, respectively. The first two are essentially semiconductors/insulators (with gaps of about 0.4 eV, and 4.0 eV (with Cu levels), while the 20% model exhibits a more metallic mode of conduction with more banding Cu states in the host alumina gap. To graphically display the SPC ζ (**x**), we take two approaches: 1) a plot of minimal space filling path (for the ζ field) projected onto atomic sites (**Figure 4**) and 2) a direct scheme



Figure 4. Bader projection of SPC ζ (**x**) of oxides. Left: Al₂O₃:Cu, 10%. Right: Al₂O₃:Cu, 20%. The atoms with color represent the atoms with 80% of SPC.^[22] Color nomenclature is green: Cu, yellow: O, blue: Al.

indicating atom positions and in gray scale the "intensity" of ζ (**x**) (see Figure 6). In the latter case, we normalize the gray scale to either the mean or maximum of ζ (**x**). For case 2, we note that each material is normalized separately: gray scale images should not be compared (except for qualitative structure) between different materials.

In **Figure 5**, we present SPC iso-surfaces for the 20% Cudoped model obtained from Equation (5), summed over 20 and all eigenvectors. Twenty terms offers a reasonable qualitative approximation for ζ .

It is apparent that for the Cu-doped oxides that ζ is strongly associated with Cu, particularly for the 20% case. A notable number of O atoms contribute, especially in the 10% case, which is expected since in the absence of transition metals in the system, transport would occur through Kohn-Sham states near the Fermi level, built almost entirely from O p states. Al plays essentially no role in the conduction for either composition. The case of the 20% is especially interesting as a Cu cluster exists that is space-filling, when periodic boundary conditions are considered. Electronic delocalization/banding of Kohn-Sham states (mostly involving Cu) surrounding the Fermi level hint at a disordered form of metallic conduction made explicit in our analysis. As the cluster is not well connected in the 10% system, the conductivity is lower. The usual means to determine the conducting parts of a network is to just look at the Kohn-Sham orbitals near the Fermi level. This is at best qualitative, and the present work correctly includes effects stemming from the current-current correlation function, which is central to the Kubo approach to electrical transport.

For the chalcogenide (**Figure 6**, top panel), the system (with homogeneous Ag distribution) is semiconducting (albeit with a small gap compared to the alumina systems) and the Ag (green) sites are not well correlated with ζ (**x**). Instead, rather like the 10% Cu-doped oxide, the Se p states again appear, indicating hopping conduction.

Where SPC is concerned, as for any method based on KGF, thermal broadening, k-point sampling, and other details have to be treated carefully,^[21] and the method is only as good as the models and single-particle states/energies we employ. We analyzed three representative models that lend insight into the electronic processes in a significant class of electronic



Figure 5. Isosurfaces of SPC from weighted sum of eigenvectors for 20% Cu-doped alumina. Left: SPC computed from 20 eigenvectors (with largest eigenvalues), right: SPC computed from all eigenvectors. The blob volumes indicate the value of the weighted sum at the point. Left and right figures use the same isosurface cutoff. Cu atoms are shown in blue for reference.











Figure 6. Space-projected conductivity $\zeta(\mathbf{x})$ for a-(GeSe₃)_{0.75}Ag_{0.25} (top), (a-Al₂O₃)_{0.9}Cu_{0.1} (middle), and (a-Al₂O₃)_{0.8}Cu_{0.2} (bottom). O and Ge atoms are shown in red, Cu and Se atoms in blue, and Al and Ag atoms in green. The SPC at each grid point is shown in gray scale which is scaled by either the mean (Al₂O₃:Cu) or the maximum (a-(GeSe₃)_{0.75}Ag_{0.25}) value of $\zeta(\mathbf{x})$.

materials and processes. Comparison to experiment is qualitative at this point due to: 1) inadequate sampling of possible metal structures in the host and 2) incomplete treatment of electron–phonon couplings,^[23,24] now coarsely handled by broadening – $\partial f/\partial \varepsilon|_{\varepsilon_{\rm F}}$.^[25] Notwithstanding this, we offer a new tool that extends the reach of ab initio simulation, lends qualitative new insight into transport in complex materials and is easily adapted to standard codes. For a finite frequency ω , the scheme is useful to determine absorptive and transparent parts of complex materials, which might prove useful for designing waveguides, etc.

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Conflict of Interest

The authors declare no conflict of interest.

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