Filament Formation by Cu and Ag Ions for Memory Applications Utilizaing Oxide Dielectrics With Pre-existing Vacated O-atom Sites

Zhichun Zhang¹, Evan J. Katz¹, Daniel Zeller², Gerald Lucovsky^{*},² and Leonard F. Brillson¹

*^{,2}North Carolina State University, Depart. of Physics

2401 Stinson Drive, Raleigh, North Carolina 27695-8202, USA

Phone: +01-919-515-3938, E-mail: lucovsky@ncsu.edu

¹Department of Electrical and Computer Science, Ohio State University, Columbus, Ohio 43202, USA

1. Introduction and Background

Memory cells based on formation of Cu and Ag filaments in SiO₂ have been proposed [1]. This paper demonstrates that pre-existing defects in SiO₂ and GeO₂, as well as transition and rare earth lanthanide atom dielectrics are vacated O-sites, and play an significant role in filament formation. Two theory-based models have been proposed for the electronic structure O-vacancy states. The Robertson and Shlugger groups have used density functional theory (DFT) based models, identifying singlet O-vacancy (V_O), and interstitial O-atoms (I_O) states in the band gap [2]. Lucovsky and co-workers have applied two-electron Tanabe-Sugano [T-S] diagrams [3] to the two Si(Ge) states with d-symmetries projecting into the defect site [4]. This model predicts singlet states and triplet terms using a calculation



Fig. 1. O K pre-edge spectrum for b-Lu₂O₃.



Fig. 2. O K pre-edge spectrum for GeO₂.

based on vacated O-sites. When the distance between the

bordering atoms is increased the exchange energy is decreased as these atoms relax to make the ground state energies ~equal [4]. Experimental detection of single and triplet states in O K pre-edge spectra is presented and assigned to vacated O-atom sites [4,5]. This theoretical approach supported by experiment identifies problems with DFT methods applied to strongly correlated d-states as in Ref. 6.

2. Experimental Results: XAS and CLS Spectroscopy Figures 1 and 2 are O K pre-edge spectra for (i) bixbyite structured b-Lu₂O₃ [5], and thin film non-crystalline GeO₂ prepared by remote plasma procresses. [4]. The b-Lu₂O₃ spectrum includes over-lapping singlet state and triplet term features, each with a spectral width equal to a ligand field splitting (Δ LF) = 2.4±0.1 eV. There are four negative ion states at higher photon energies [5]. As noted above, singlet and triplet features are present in the same spectrum when the respective ground state energies are the same [4]. Singlet final states are atom-symmetry specific, but singlet and tripplet terms within the ligand-field split regimes are not. This accounts for four, rather than two negative ion states in b-Lu₂O₃ [5].

Figure 2 is the O K pre-edge for GeO₂ film anealed to a temperature 0f 700 °C that promotes release of O-atoms, and is extended to include ground state features. Energy differences between the band-gap singlet feature (9.7±0.15 eV) and other singlet states are included for comparisions with the cathoduluminesce (CLS) spectrum in Fig. 3. Based on comparisons between O K pre-edge spectra for GeO2 (Fig. 2) and SiO_2 (Fig. 4), the features in these spectra are assigned to process-induced, pre-existing defects. This includes structural relaxations increasing the Ge-Ge and Si-Si distances into a regime in which the singlet and triplet ground energies are the same. Plots in Fig. 5 are obtained from ab initio calculations using an embedded cluster with an O-atom removed from a network site. The two bordering Si- or Ge- atoms each have a single dangleing bond. The total energy includes a contribution from spin entropy; i.e. a total four singlet and triplet spin-degeneracies.

Figure 3 presents a the CLS optical emission spectrum for the GeO₂ film in Fig. 2. The emission spectrum markers, [1],....[5], are centered at energy differences determined from the corresponding arrows between singlet features in Fig. 2. The relative energies of singlet features in the pre-edge spectrum of an SiO₂ film annealed at 950°C in Fig. 5, and for the GeO₂ film in Fig. 2 are about the same. This is because respective band-gaps, E_g . and ligand field splittings, Δ LF, are very nearly the same to within ±0.3 eV. Ultra-Violet and X-ray photoelectron spectrscopy studies

(UPS and XPS) of valence bands of high-к dielectrics



Fig. 3. CLS optical response vs photon energy.



Fig. 4. O K pre-edge spectrum for SiO₂.





indicate two band edge ground state features, scaling in amplitude with single features in O K pre-edge spectra [7].

3. Summary

O K pre-edge spectra in transition metal (TM) TmO₂ and

 Tm_2O_3 oxides [5], non-crystalline SiO₂ and GeO₂ [4], LaMnO₃, LaTiO₃, SrTiO₃, and TiO₂-based alloys are qualitatively and quantitatively similar. All spectra have both singlet states and triplet terms, ordered as in T-S diagrams. This also includes multiplicities in negative ion states scaling with multiple valence states. UPS and XPS valence band spectra indicate singlet and triplet state features. These results are consistent with assignment of pre-edge features in oxide dielectrics to pre-existing defects introduced during deposition and/or annealing. Comparisons between films of SiO₂ annealed as different temperatures indicate stronger singlet state features with increasing temperature.

Why do DFT calculations only introduce singlet features, and why is the energy separation between negative O-vacancy states and ground states smaller than in XAS spectra? Bersuker states in Ref. 6: "It is shown that the claims that density functional theory (DFT) can handle orbitally degenerate states are ungrounded." "The constraint search formulation of DFT allows one to determine a set of densities and eigenvalues" that "are neither observables, nor can they be used to solve the system of coupled equations for the nuclear motions to obtain observables, as in the wave function presentation." Observables include triplet terms, and energy differences between singlet states as well, including band gap energies. It is important to recognize the energy distribution of singlets and triplets in T-S diagrams is always plotted as a function of the effective ligand field splitting demonstrating the importance of valence band molecular orbitals as obtained symmetry-adapted linear combinations (SACLs) of atomics states [3].

Proposed memory structures based on filamentary formation by Ag and Cu ion transport into and through SiO₂ films. Itt is important to understand the nature of pre-existing vacated O-atom sites, that can become bonding sites for Ag and Cu ions in filament formation [1]. The electrical conductivity through the filaments is dependent on the ion charge states; this is obtained by analysis of $L_{2,3}$ spectra.

Acknowledgements

One of the authors (GL) acknowledges discussions with Professors D.E. Aspnes and J.L. Whitten, and B. Papas, a postdoctoral fellow, all at NC State University. Support from the NSF and DTRA is acknowledged. The Lu₂O₃ sample was deposited by the group of Dr. H. Kurtz at AMO located at RWTH in Aachen DE. XAS measurements were made at soft X-ray beam-lines at SSRL in Menlo Park, CA.

References

- [1] R. Waser, et al., Adv. Mater. 21, 2632 (2009).
- [2] K. Xiong. et al., Appl. Phys. Lett. 87, 183505 (2006):
- L. Gavartin, et al., Appl. Phys. Lett. 89, 082908 (2006).
- [3] F.A. Cotton, Chemical Applications of Group Theory, 2nd Ed. (Wiley Interscience, New York, 1963) Chap. 8.
- [4] G. Lucovsky, et al., Microelectron. Eng. 88 1471 (2011).
- [5] G. Lucovsky, et al., Microelectron. Eng. 88 1437 (2011).
- [6] I.B. Bersuker, J. of Comput. Chem., 18, 260 (1997).
- [7] L. Fleming, et al., J. Appl. Phys. 192, 03370 (2007).