Qualitative Differences Between Conduction Band Edge Excitonic States and Electron Tapping in (i) SiO_2 and (ii) Si_3N_4 and Si Oxynitride Alloy Films

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1. Introduction

The performance and reliability of a gate dielectric, (i) non-crystalline SiO₂, Si₃N₄, a Si Oxynitride alloy, or (ii) a high- κ transition metal oxide are determined by band edge intrinsic bonding states, intrinsic bonding defects and macroscopic strain. This paper addresses significant differences between band edge excitonic states in (i) SiO₂, and (ii) Si₃N₄ and Si oxynitride alloys, (Si₃N₄)_X(SiO₂)_{1-X}, that provide an explanation for differences between symmetries of band edge states in SiO₂ and transition metal oxides also explain differences in TAT injection from negatively biased n-type Si substrates.

A connection between (i) strain-reducing medium range order (MRO), and (ii) nano-scale separation into *hard-soft* mixtures in non-crystalline SiO₂ is explained by many-electron theory applied to Si-atom "d-like states" [1] These states participate in O $p\pi$ to Si d π back-donation, yielding shortened Si-O bond-lengths and MRO atom-pair correlations. These bonding interactions identify a coherence length of ~1 nm associated with *hard* 6-member rings encapsulated by *compliant* or 5- and 7-member rings into a nano-grain *hard-soft* nano-structure, reducing macroscopic strain and giving SiO₂ unique reliability properties.

2. Experimental Procedures

Five nm thick films of SiO₂, Si₃N₄ and Si oxynitride alloys were remote plasma deposited on nitrided superficially oxidized Si(001). These films were annealed in Ar at a temperature of ~950°C. Si L_{2,3}, and O and N K edge spectra were obtained by X-ray absorption spectroscopy (XAS) at the Stanford Synchrotron Research Lightsource (SSRL).

3. Experimental Results

Figure 1 compares the Si $L_{2,3}$ spectra of noncrystalline SiO₂ and crystalline Si [2]. The band edge states in these two materials that comprise the Si-SiO₂ interface are "s-like" non-degenerate A_{1g} states. Figure 2 is the 2nd derivative spectrum of the band edge states in non-crystalline, thin film plasma deposited SiO₂ that has been annealed at ~950°C. There is a oneto-one correspondence between the energy differences

in eV units of band edge states as determined by visible and vacuum UV spectroscopies, and in the O K edge spectra [1]. An X-ray energy of 529.25±0.1 eV corresponds to an energy of 8.9 eV for the band-gap of non-crystalline SiO₂. In order of decreasing X-ray energy, and as marked in Fig. 2, the features in the O pre-edge derivative spectra correspond to: i) the bandgap, E_g , ii) two bound excitons, E_2 and E_1 , iii) negative ion states between 529.1 and 527.4 eV, and iv) four intra-d state transitions for the O-atom vacancy defect represented by a high-spin d^2 state. The symmetries of these states are indicated using the Tanabe-Sugano diagrams. The combination of the localized A_{1g} excitonic states at the SiO₂ band edge, and the A_{1g} and T_{2g} symmetries of unoccupied negative ion states of O-vacancy defects does not support radiative decay into the negative ion states. This is why TAT processes have not been reported for negatively biased n-type Si in Si-SiO₂ gate stack structures. In contrast, the combination of E_g symmetries for band edge ZrO₂ and HfO₂ states, and A_{1g} and T_{2g} symmetries for unoccupied negative ion states of O-vacancy defects favors radiative decay into the negative ion states. This accounts for the TAT processes initiated by electron injection from n-type Si substrates that have been reported for ZrO₂ and HfO₂ MOS structures [3].

Figures 3 and 4 indicate respectively, (i) O K band edge, and pre-(band0 edge states of non-crystalline Si₃N₄, and expanded scale plots of the negative ion states of (ii) Si₃N₄ and (ii) a (Si₃N₄)_{0.5}(SiO₂)_{0.5} Si oxynitride alloy that has been used as alternative gate dielectric in the first eight to ten years of the 21st century. There is a significant qualitative difference between Fig. 2 for SiO₂ and Fig. 3 for Si₃N₄ that is related to the difference in the number of p electrons in the ground states of O- and N-atoms, four for O, and five for N. This correlates with the singly occupied $2p\pi$ state that gives rise to sharp spectral feature at 400 eV in Si₃N₄, and Si oxynitride alloys including compositions both SiO2-rich and Si3N4-rich as well. It is significant to note that the final state for the N-atom " $p\pi$ to $p\pi$ " transition is at an energy that is between the band edge excitonic states of Si₃N₄ and Si oxynitride alloys, and the negative ion states associated with N-vacancy defects in these dielectrics. This difference in the ordering of electronic states manifests itself in Si₃N₄ dielectric thin films by promoting TAT and/or Poole Frenkel transport. The final state symmetry of the N-atom $p\pi$ to $p\pi^*$ transition provides a transport channel between the "s-like" symmetry of the band edge states, and the even symmetry of the negative ion states. In addition, it is likely that this state plays a role in the Negative Bias Temperature Instability that is much stronger in N-containing dielectrics than SiO₂.

4.Summary of Significant Results

The different symmetries of A_{1g} excitonic states at the SiO₂ band edge, and O-vacancy A_{1g} and T_{2g} unoccupied negative ion states effectively prevents injection into these negative ion states suppressing trap-assisted tunneling (TAT). The combination of E_g





Fig. 3. N K edge and pre-edge spectra - Si₃N₄.

symmetry of ZrO_2 and HfO_2 band edge states, and Ovacancy A_{1g} and T_{2g} symmetries favors TAT for electron injection from n-type Si substrates [3]. The differences in O and N-atom p-states (4 vs. 5) results in a N-atom $p\pi$ to $p\pi^*$ transition sandwiched between the "s-like" symmetry of band edge states, and the even symmetry of N-vacancy negative ion states. This provides a "pathway" for TAT processes, well known in Si₃N₄ and extending to Si oxynitride alloys as well.

References

[1] J.L. Whitten et al., J. Vac. Sci. Technol. B 20, 1710 (2002).

[2] F. deGroot and A. Kotani, Core Level Spectroscopy of Solids (CRC Press, Boca Raton, 2008).

of transition metal ions, (Academic Press, New York, 1970). [3] G. Lucovsky et al., Solid State Electronics 53, 1273 (2009).



Fig. 2, Pre-edge O K spectra for nc thin film SiO₂.



Fig. 4. Expanded x-axis N K pre-edge spectra.