Qualitative Differences Between Conduction Band Edge Excitonic States and Electron Tapping in (i) SiO$_2$ and (ii) Si$_3$N$_4$ and Si Oxynitride Alloy Films

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1. Introduction
The performance and reliability of a gate dielectric, (i) non-crystalline SiO$_2$, Si$_3$N$_4$, or Si Oxynitride alloy, or (ii) a high-$\kappa$ 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) SiO$_2$, and (ii) Si$_3$N$_4$ and Si oxynitride alloys, (Si$_3$N$_4$)$_x$(SiO$_2$)$_{1-x}$, that provide an explanation for differences in trapping and trap-assisted (TAT). Differences between symmetries of band edge states in SiO$_2$ 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 SiO$_2$ is explained by many-electron theory applied to Si-atom “d-like states” [1] These states participate in O 2$p\pi$ to Si 2$p\sigma$ 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 SiO$_2$ unique reliability properties.

2. Experimental Procedures
Five nm thick films of SiO$_2$, Si$_3$N$_4$ 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 non-crystalline SiO$_2$ and crystalline Si [2]. The band edge states in these two materials that comprise the Si-SiO$_2$ 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 SiO$_2$ that has been annealed at ~950°C. There is a one-to-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 SiO$_2$. 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 band-gap, $E_g$, 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 SiO$_2$ 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-SiO$_2$ gate stack structures. In contrast, the combination of $E_g$ symmetries for band edge ZrO$_2$ and HfO$_2$ 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 ZrO$_2$ and HfO$_2$ MOS structures [3].

Figures 3 and 4 indicate respectively, (i) O K band edge spectra of non-crystalline Si$_3$N$_4$, and expanded scale plots of the negative ion states of (ii) Si$_3$N$_4$ and (ii) a (Si$_3$N$_4$)$_{0.5}$(SiO$_2$)$_{0.5}$ 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 SiO$_2$ and Fig. 3 for Si$_3$N$_4$ 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 Si$_3$N$_4$, and Si oxynitride alloys including compositions both SiO$_2$-rich and Si$_3$N$_4$-rich as well. It is significant to note that the final state for the N-atom “p$\pi$ to p$^*$” transition is at an energy that is between the band edge excitonic states of Si$_3$N$_4$ 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 Si$_3$N$_4$ dielectric thin films by promoting TAT and/or Poole Frenkel transport. The final state symmetry of the N-atom p to p* 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-vacancy negative ion states, and extending to Si oxynitride alloys as well.

4. Summary of Significant Results

The different symmetries of A$_{1g}$ excitonic states at the SiO$_2$ 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 $E_g$ symmetry of ZrO$_2$ and HfO$_2$ band edge states, and O-vacancy 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 to p* 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 Si$_3$N$_4$ and extending to Si oxynitride alloys as well.

References