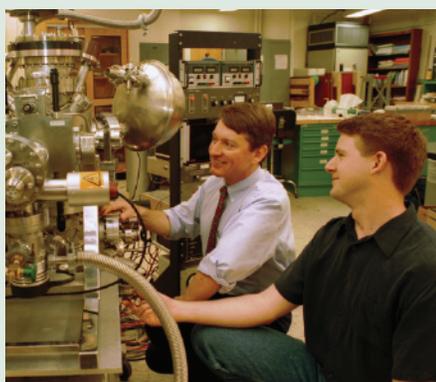


## Electronic Structure of Thin Film Silicon Oxynitrides Measured Using Soft X-Ray Emission and Absorption Spectroscopies

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*The elementally-resolved valence band electronic structure of a thin film silicon oxynitride gate dielectric used in commercial device fabrication has been measured using soft x-ray emission and absorption spectroscopies. Specifically, the valence and conduction band partial density of states in the interfacial region of both the nitrogen and oxygen states was determined. The element-specific band gap for the O 2p states was measured to be 8.8 eV in the interfacial region, similar to that of pure SiO<sub>2</sub>. However, the band gap for the N 2p states in the interfacial region was measured to be approximately 5 eV.*



Authors (from left): Kevin Smith and James Downes

The material properties of SiO<sub>2</sub> gate dielectric are crucial to the behavior of metal-oxide-semiconductor field effect transistors. SiO<sub>2</sub> possesses a relatively low dielectric constant, which leads to increased leakage currents in submicron devices. One favored replacement dielectric material currently in use is SiO<sub>x</sub>N<sub>y</sub> (silicon oxynitride). While much progress has been made in understanding both the process of oxynitride film formation and the macroscopic dielectric and device properties of these films, the basic electronic structure of the nitrogen-rich interfacial layer remains poorly understood. We have made the first direct measurement of the element-specific O 2p and N 2p valence and conduction band partial densities of states for an ultrathin commercial SiO<sub>x</sub>N<sub>y</sub> layer. The measurements were made using synchrotron radiation-excited soft x-ray emission (SXE) spectroscopy and soft x-ray absorption (SXA) spectroscopy on beamline X1B at the NSLS. SXE is a unique probe of the bulk element-specific electronic structure of solids. SXE spectra reflect the occupied valence band partial density of states (PDOS — the valence band density of states resolved into its orbital angular momentum components). SXE measurements are also element-specific and are bulk-sensitive, with a sampling depth of well over 100 nm. Finally, as a “photon in - photon out” spectroscopy, SXE can be used to make electronic structure measurements on insulating samples, such as SiO<sub>x</sub>N<sub>y</sub>. Thus, SXE is in many ways a more useful probe of buried interfaces than photoemission spectroscopy, which, as a “photon in - electron out” spectroscopy, typically measures the electronic structure of solids within less than 1 nm of the vacuum-solid interface. Our SXE measurements were made with a Nordgren-type grating spectrometer, which is the only one of its kind at the NSLS.

The silicon oxynitride samples under investigation in this study were device-grade materials, where the nitration treatment consists of annealing the pre-grown SiO<sub>2</sub> in an NH<sub>3</sub> environment at elevated temperatures. This treatment results in a non-uniform distribution of nitrogen in the layer, with preferential build-up at both the Si-SiO<sub>2</sub> interface and the outer surface.

**Figure 1** shows the N 2p PDOS for SiO<sub>x</sub>N<sub>y</sub> as measured in this experi-

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ment. Also shown are SXE spectra from bulk  $\alpha$ - $\text{Si}_3\text{N}_4$  and gas phase  $\text{N}_2$ . The ability of SXE and SXA to measure the elementally-resolved band gap in solids is immediately clear from **Figure 1**. The N  $2p$ -derived band gap for  $\text{SiO}_x\text{N}_y$  is approximately 5 eV, which is much less than the 8.8 eV for bulk  $\text{SiO}_2$ . Such elementally-resolved measurements are not possible using photoemission spectroscopy, which is the standard probe of solid-state electronic structure.

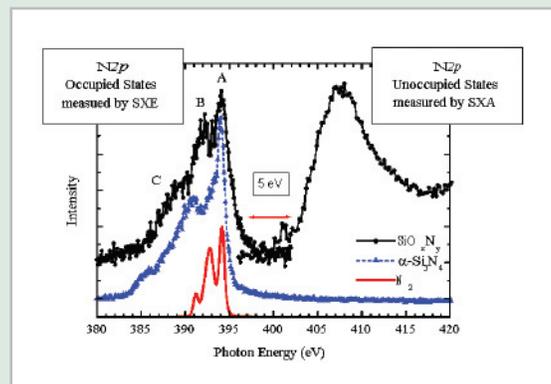


Figure 1. N K edge SXE and SXA spectra from the  $\text{SiO}_x\text{N}_y$  sample. The SXE spectrum reflects the occupied density of electronic states of N  $2p$  character, while the SXA spectrum reflects the unoccupied density of electronic states of N  $2p$  character. The  $\text{SiO}_x\text{N}_y$  SXE spectrum was obtained with an excitation energy of 435 eV. The N K edge SXE spectra obtained from  $\alpha$ - $\text{Si}_3\text{N}_4$  (G. Wiech and A. Simunek, Phys. Rev. B **49**, 5398 (1994)) and molecular  $\text{N}_2$  (Glans et al, J. Elec. Spec. Related Phenom. **82**, 193 (1996)) are also shown.