

Chemical Bonding Self-Organizations in Non-crystalline Hf Si Oxynitride Dielectrics: Low Direct Tunneling and Defect Levels Comparable to SiO₂

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1. Introduction

The dielectric in production for advanced Si CMOS devices is a Si oxynitride alloy with approximately equal concentrations of SiO₂ and Si₃N₄ [1]. This alloy has a dielectric constant, $\kappa \sim 5.5$, and combined with an SiON interface allows EOT scaling to ~ 1.1 - 1.2 nm before direct tunneling becomes too high for mobile devices. Zr or Hf silicates were proposed as replacements for Si oxynitrides [2]; however, these alloys are unstable with respect to chemical phase separation (CPS) into SiO₂, and ZrO₂ or HfO₂ [3]. This paper identifies a narrow composition range for pseudo-ternary Hf Si oxynitride alloys that are stable against CPS to temperatures $>1000^\circ\text{C}$, have dielectric constants ~ 10 to 12 , tunneling leakage $<10^{-7}$ A-cm⁻² 1 V above V_{fb} , and defect levels and reliability comparable to SiO₂ [4]. This paper demonstrates that these electrical properties derive from strain reducing *chemically self-organized* bonding arrangements with length scale of ~ 0.8 nm, with a *percolation* of these strain reducing bonding arrangements throughout the entire thin film thickness.

2. Suppression of CPS in Hf Oxynitrides

Hf oxynitrides have been prepared by remote plasma assisted CVD onto on Si(100) substrates with SiON interfacial layers (EOT ~ 0.35 nm). Stability with respect to CPS for Hf Si oxynitride alloys with \sim equal concentrations of SiO₂ and HfO₂, and with different Si₃N₄ concentrations of $\sim 20\%$ and 40% has been detected by differentiation of O 1s X-ray photoelectron spectra (XPS). Alloys with $< 35\%$ SiO₂ display CPS with SiO₂ and HfO₂ spectral features. Alloys with a Si₃N₄ content increased to ~ 35 to 45% show a single feature in the differentiated O 1s XPS spectra indicating stability against CPS to $\sim 1100^\circ\text{C}$.

3. Spectroscopic Studies

Conduction band states have been studied by near edge X-ray absorption spectroscopy (NEXAS) and visible vacuum UV spectroscopic ellipsometry (vis-VUV-SE), and valence band states by soft-X-ray photoelectron spectroscopy (SXPS). Crystal field (C-F) splittings between Hf 5d E_g and T_{2g} states are ~ 2.2 eV indicating Hf atoms are four-fold coordinated in as-deposited and annealed 40% Si₃N₄ content films. This is in contrast the a C-F splitting of ~ 4 eV for 7-fold coordinated Hf in thin film HfO₂ with a monoclinic primitive unit cell.

Comparisons between conduction and valence band edge epsilon 2 (absorption) spectra for Ti Si oxynitrides with $\sim 16\%$ and 40% Si₃N₄ indicate significantly reduced densities of band edge defects for the 40% alloys. These

alloys, as well as Zr and mixed Hf,Ti Si oxynitrides display bonding properties similar to Hf Si oxynitrides such as the SXPS valence band spectra in Figs. 1(a) and (b). These spectra indicate an order of magnitude difference in valence band defects: significantly lower for the 40% Si₃N₄ composition than for the 16% Si₃N₄ composition.

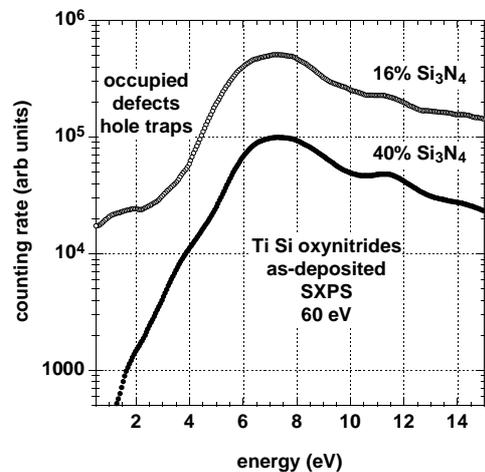


Fig. 1. SXPS valence band spectra Ti Si Oxynitrides comparing band edge defects for 16 and 40% Si₃N₄ alloys.

4. Electrical Measurements

Fig. 2(a) shows leakage current versus applied voltage for Si substrate injection of electrons in MOSCAPS with as-deposited Hf Si oxynitride dielectrics fabricated on n-type Si substrates with Al gate electrodes ($V_{fb} \sim 0.0$ V). Fig. 1(b) displays leakage current for $V_g - V_{fb} = 1$ V, versus Si₃N₄ content for \sim equal SiO₂ and HfO₂ content. There is a significant reduction in leakage for a narrow range of compositions at $\sim 40\%$ Si₃N₄.

Figs. 3(a) and 3(b) compare C-V traces for 18% and 40% Si₃N₄ with \sim equal SiO₂ and HfO₂ content. The V_{fb} voltage indicated a fixed interfacial charge $<10^{11}$ cm⁻² for the 40% alloy, and a positive fixed charge $\sim 0.5 \times 10^{12}$ cm⁻² for the 18% alloy. The frequency dispersion of the C-V characteristics is different between 1 MHz and 100 kHz indicating a D_{it} level $\sim 10^{12}$ cm⁻² for substrate hole injection or the 18% alloy, and $>10\times$ lower for the 40% alloy.

Total-dose X-ray irradiation response of low- and high-Si₃N₄ content Hf Si oxynitrides has been compared with SiO₂ devices, and devices with Hf-based dielectrics [5]. The low level of hole trap generation in the high-Si₃N₄ content Hf Si oxynitride films was comparable to SiO₂

devices confirming the validity of the chemical bonding analysis presented below. In contrast, there is significant electron trapping in HfO₂ devices.

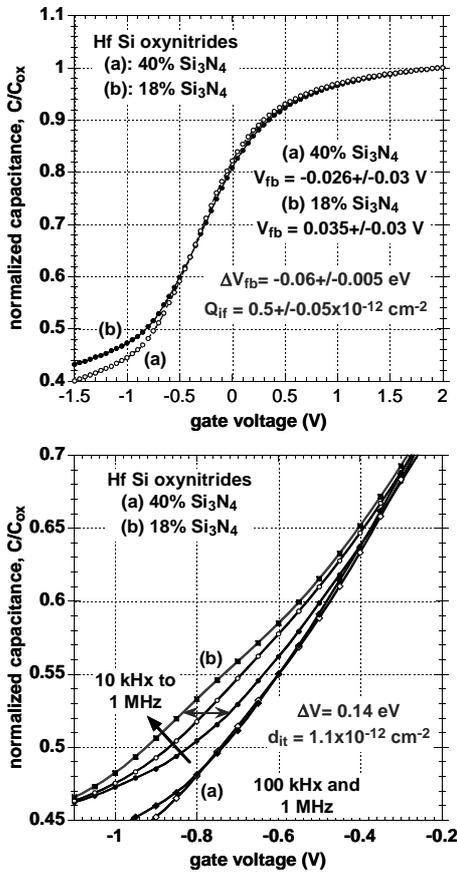


Fig. 2. (top) C-V traces at 1 MHz for Hf Si oxides. (bottom) Expand scale comparison of C-Vs for frequency dependent trapping.

5. Discussion: Chemical Bonding and Defect Reductions

Low direct tunneling currents and reduced defect densities in the ~40% Si₃N₄ content Hf,Zr,Ti and Hf,Ti alloy Si oxynitrides, as well, are the result of self-organized chemical bonding arrangements that *minimize and effectively eliminate* macroscopic strain, thereby reducing defect levels [4]. These compositions are not associated crystalline phase bonding, and occupy a very small fraction of the HfO₂, SiO₂ and Si₃N₄ ternary phase diagram. Alloys along the join-line from SiO₂ to Si₃N₄, are stable with respect to CPS, and the 50-50 alloy has extended CMOS EOT scaling beyond the performance limitations of SiO₂. Hf silicates along the join-line from SiO₂ to HfO₂ are unstable against CPS; however, HfO₂ rich alloys, e.g., 80% HfO₂-20% SiO₂ are inverted silicates with SiO₂ inclusions limiting nano-crystalline size, and thereby reducing defect levels with respect to HfO₂ through elimination of grain boundaries [3]. With the exception of alloys with 35 to 45% Si₃N₄, and ~equal SiO₂ and HfO₂ composition, all other ternary alloys are unstable against CPS, and have

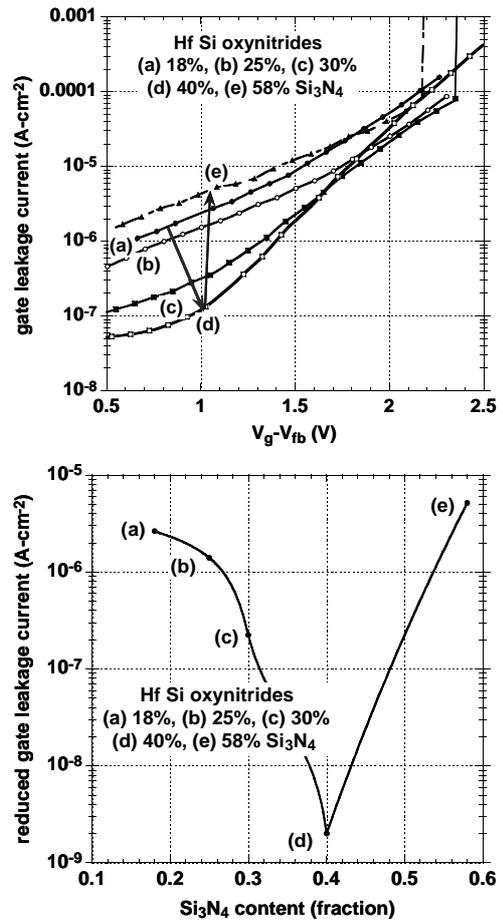


Fig. 3. (top) Gate leakage current versus $V_g - V_{fb}$. (bottom) *Normalized* gate leakage current versus Si₃N₄ content.

electrical properties after annealing. The optimal properties of the 40% Si₃N₄ content alloys derive from a reduction of bond-bending constraints on the Si atoms from symmetry reductions from T_d to C_{3v} [5], and from strings of bonds; ...N-Si-O-Hf-O-Si-N... which are at the percolation threshold of 16-17% for reduction of macroscopic strain [6], and thereby reducing defect/defect precursor levels.

The results reported in this abstract represent a comprehensive study combing film deposition, advanced spectroscopic techniques, theory and electrical measurements, and provide a firm foundation for device development. Further increases in κ to values in excess of 20 for the Hf,Ti Si oxynitride alloys are expected to be of considerable interest for mobile and rad-hard devices.

References

- [1] G. Lucovsky G, IBM J. Res. Dev. **43**, 301 (1999).
- [2] G. Wilk et al, J. Appl. Phys. **89**, 5243 (2001).
- [3] G. Lucovsky et al., Jap. J. Appl. Phys. **46** (2007) in press.
- [4] D.K. Chen, et al., IEEE Trans. Nuclear Sci. (2007).
- [5] G. Lucovsky, et al. J. Non-Cryst. Solids (2007), in press.
- [6] R. Zallen, *The Physics of Amorphous Solids* (Wiley-Interscience, New York, 1983)