

XAS Studies of Chemical Bonding of Nitrogen and Oxygen Atoms in Ti/Zr/Hf High-K Gate Dielectrics

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Abstract. Near edge x-ray absorption spectroscopy (NEXAS) has been used to study bonding in Ti/Zr/Hf (hereafter TM) Si oxynitrides and silicates. Comparisons between O K₁ and N K₁ spectra are particularly informative since O and N anti-bonding molecular orbitals (MO) display distinct features from nearest- and next-nearest-neighbor TM and Si atoms. MO TM-atom spectral features are qualitatively different in TM silicates and Si oxynitrides. NEXAS studies of TM silicates identify chemical phase separation (CPS) into TM-dioxides and SiO₂ for annealing to 900°C.

Keywords: transition metal dielectrics, transition metal silicates, transition metal Si oxynitrides, near edge absorption spectroscopy, spectroscopic ellipsometry, remote plasma enhanced chemical vapor deposition.

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INTRODUCTION

Hf and Zr oxide high-k gate dielectrics have emerged as leading candidates for introduction in advanced Si devices. Nanocrystalline films of HfO₂ with physical thicknesses greater than 3 nm have intrinsic defects associated with O-atom vacancies clustered along internal grain boundaries [1]. These defects have been associated with asymmetric trapping of holes and electrons injected from Si substrates. This has revitalized interest in non-crystalline high-k gate dielectrics. Previous studies have shown that Zr(Hf) silicates, (Zr(Hf)O₂)_x(SiO₂)_{1-x}, are non-crystalline as-deposited, and chemically phase separate (CPS) into SiO₂ and Zr(Hf)O₂ after annealing to temperatures of 800–900°C [2]. This has stimulated research in the post-deposition nitridation remote plasma processing, to inhibit CPS [3]. This processing did indeed increase stability, but has not as yet been commercialized. This paper approaches nitridation of silicates from different route: the direct deposition of pseudo-ternary Ti/Zr/Hf (IVB transition metals, TMs) Si oxynitride alloys by remote plasma-assisted chemical vapor deposition, RPECVD [4]. Coupled with soft x-ray absorption spectroscopy for identifying the electronic structure, this research i) demonstrating chemical stability and ii) identified, via resonant absorption, the local bonding coordination of the IVB TM atoms.

SAMPLE PREPARATION

Thin films of pseudo-ternary IVB TM Si oxynitrides such as (ZrO₂)_x(SiO₂)_y(Si₃N₄)_{1-x-y}, were grown on Si substrates at 300°C by RPECVD by plasma excitation of He/O₂ and delivering active O-species to the deposition chamber into which the Si and IVB TM sources gases, silane, SiH₄, and TM t-butoxides, respectively, were injected, and isolated by gas flow from back-streaming into the plasma region. Alloy compositions were determined by Rutherford back-scattering, RBS, which was used to calibrate online Auger electron spectroscopy, AES, as a secondary chemical characterization. In addition to RBS and AES, additional studies were made using Fourier transform infra-red, FTIR, and derivative x-ray photoelectron spectroscopy, DXPS, studies of the O 1s core level at ~530 eV to establish the stability of these ternaries alloys with respect to CPS at temperatures between 900 and 1100°C.

These studies identified two qualitatively different ternary alloy regimes with markedly different properties [4]. Each of these alloy types had approximately equal concentrations of SiO₂ and the IVB TM oxide. The group that exhibited CPS by both FTIR and DXPS, had relatively low concentrations of Si₃N₄, < 20%, or 1-x-y ~ <0.2, with higher and ~ equal concentrations of SiO₂ and the IVB TM oxide, > 40%, or x-y >0.40. For this group, the as-deposited films

had a single DXPS O 1s feature, whilst films annealed at temperatures $>900^{\circ}\text{C}$ had two features indicative of CPS into nanocrystalline ZrO_2 and noncrystalline SiO_2 . In contrast the O 1s XPS spectrum for a film in the second group with a higher Si_3N_4 concentration, ~40% and, ~30% SiO_2 and ZrO_2 , also displayed a single feature as-deposited; however in contrast, this feature narrows rather than splits after annealing to temperatures $>900^{\circ}\text{C}$ (see Fig. 2). A single feature is indicative of a unique bonding environment for O-atoms that includes both Si and the group IVB TM atom. NEXAS spectra for Ti Si oxynitride alloys are used to illustrate the local bonding arrangements of Ti atoms in as-deposited and annealed films, and in particular to establish the unique aspects of the bonding in the high Si_3N_4 content films. Some important NEXAS results are discussed for the Zr Si oxynitrides, primarily to establish relationships between crystal field (CF) d-state energy splittings for different Zr bonding coordinations [5].

XAS SPECTROSCOPIC STUDIES

O K_1 and N K_1 edge NEXAS spectra for high Si_3N_4 content Zr Si oxynitrides are consistent with 4-fold

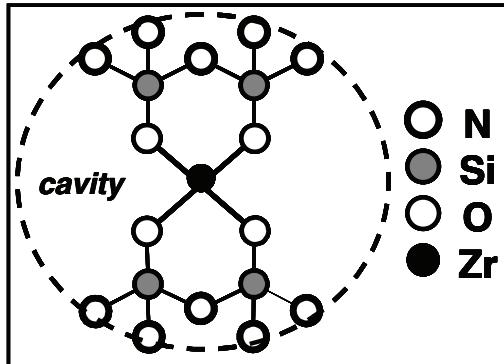


FIGURE 1. Schematic representation of local bonding arrangement in optimized Zr Si oxynitride alloy with ~33-40 % Si_3N_4 , and 30-33 % SiO_2 and ZrO_2 .

coordinated Zr with O nearest-neighbors [5]. The primary evidence for this are differences in the CF splitting of the Zr $4d_{3/2}(\text{E}_g)$ and $4d_{5/2}(\text{T}_{2g})$ states in these films is ~2.2 eV, but 4.8 eV in Y_2O_3 stabilized cubic ZrO_2 , and ~3.6 eV monoclinic ZrO_2 . These CF splitting differences are consistent with a 4-fold coordination of Zr in the Zr Si oxynitride, 8-fold in the Y-stabilized cubic zirconia Si, and 7-fold in the monoclinic ZrO_2 . The CF splitting ratios between 8 and 7-fold Zr, and 4-fold Zr are to zeroth order expected to be 2 and 1.75, compared with the experimentally-observed ratios of 2.2 ± 0.2 , and 1.60 ± 0.2 . O-atom and N-atom bonding the Zr Si oxynitrides is qualitatively similar to Si_2ON_2 , but with

the O-atom bonding groups clustered to encapsulate the Zr atoms in tetrahedral arrangements [4] as shown in Fig. 1. This encapsulation prevents CPS.

The dependence on bonding coordination of the Si_3N_4 content is best illustrated by considering the Ti L₃, O K₁, and epsilon 2 (ϵ_2) spectra in Figs. 3(a), (b) and (c) for Ti Si oxynitrides. Of particular significance is the correlation between the Ti d-state features in the O K₁ edge, and in the ϵ_2 spectrum extracted from spectroscopic ellipsometry studies of band edge transitions. The Ti d-state and O and N features in the do not overlap in O K₁ NEXAS spectra (not shown). In a low Si_3N_4 Si oxynitride alloy, $(\text{TiO}_2)_{0.16}(\text{SiO}_2)_{0.42}(\text{Si}_3\text{N}_4)_{0.42}$, the Ti atom coordination, obtained from d-state CF and is 4-fold as deposited, and increases to 6-fold after chemical phase separation into SiO_2 and nanocrystalline TiO_2 . This coordination difference is established on the basis of studies for low TiO_2 content as-deposited Ti silicate alloys, and nanocrystalline TiO_2 . The ratios of the CF splittings in these films that undergo CPS is 1.53, and is approximately equal to coordination ratio of 6/4 = 1.5 [5]. In contrast, the coordination of Ti in as-deposited and annealed high Si_3N_4 content (>33%) alloys is the same as-deposited and after 900°C annealing. By comparison with the low TiO_2 content Ti silicates, and the results presented above, the coordination of Ti is 4-fold both as-deposited and annealed (900°C) in a Ti Si oxynitride with 40% Si_3N_4 , and equal TiO_2 and SiO_2 concentrations of ~30%.

DISCUSSION

A schematic representation of the local bonding in the group IVB TM atoms in the optimized TM Si oxynitrides has been presented in Fig. 1. The application of bond constraint theory, BCT, to this bonding group includes broken bending constraints on the Si atom, and yields an average number of bonding constraints per atom, C_{av} ~3.05, for an alloy with equal concentrations of Si_3N_4 , SiO_2 and the TM elemental oxide, e.g., ZrO_2 . Alloys with C_{av} in the range between 2.9 and 3.2 generally form intermediate phases in which defects and defect precursors are minimized making them ideal candidates for device applications. C_{av} increases modestly to ~3.15 when the Si_3N_4 concentration is increased to 40%, and the SiO_2 and TM elemental oxide concentrations are reduced proportionally to ~30%. This higher Si_3N_4 content creates regions of local rigidity associated with the Si_3N_4 alloy fraction being greater than the SiO_2 fraction. However, this local rigidity cannot percolate throughout the sample, and does not change the intermediate phase properties of these alloys. The bonding arrangements in these alloys results from a

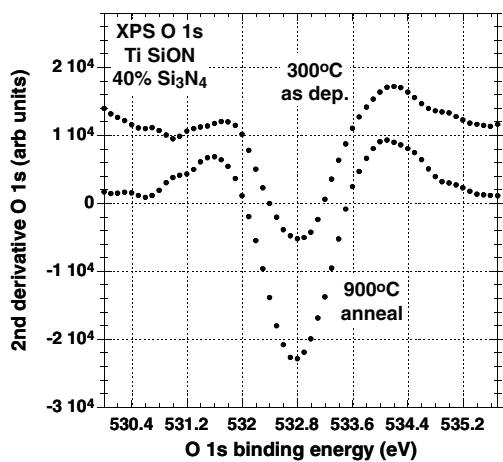


FIGURE 2. The 2nd derivative O 1s XPS spectrum for a 40 % Si_3N_4 Ti Si oxynitride. The O 1s binding energy is the same as-deposited and after the 900 °C anneal.

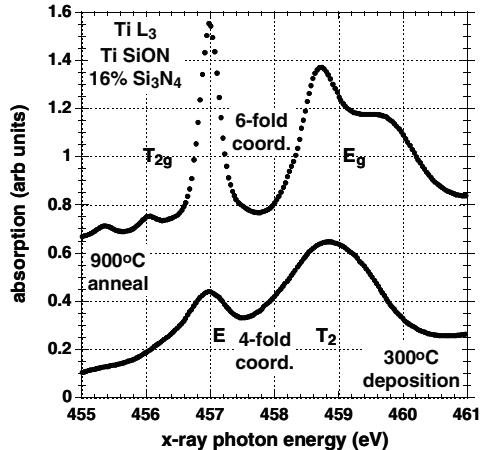


FIGURE 3(b). Ti L_3 spectrum for a 16 % Si_3N_4 Ti Si oxynitride. The $E - T_2$ splitting indicates an increase from 4-fold to 6-fold coordination of Ti after the 900 °C anneal.

chemical bonding self-organization that optimizes bonding properties, reducing configurational entropy associated with random bonding, but reducing bond strain to compensate for the entropy reduction.

In alloys which the SiO_2 and IVB TM oxide concentrations greater than the Si_3N_4 , chemical self-organizations cannot produce this tradeoff between reductions in both configurational entropy of random bonding and strain reduction, and a chemical phase separation results.

Based on the spectroscopic studies, the discussion presented above, and electrical measurements, the group IVB TM Si oxynitride high Si_3N_4 alloys provide engineering solutions for extending Si device

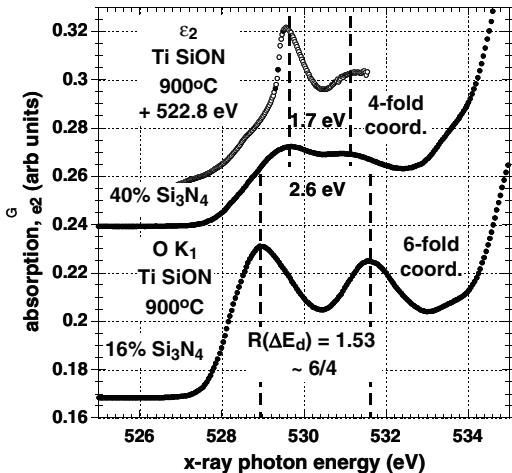


FIGURE 3(a). O K_1 spectra for 16 % and 40 %, and ϵ_2 spectrum for Si_3N_4 Ti Si oxynitrides after 900 °C anneals. The change in d-state splitting indicates a change from 4-fold to 6-fold coordination of Ti.

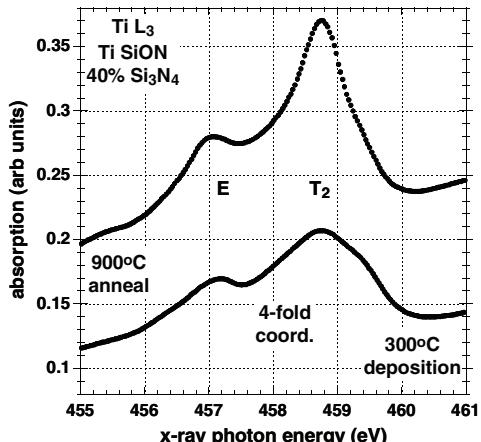


FIGURE 3(c). Ti L_3 spectrum for a 40 % Si_3N_4 Ti Si oxynitride. The $E - T_2$ splitting indicated is the same as-deposited and after a 900 °C anneal, indicating 4-fold coordination.

considerations apply to the integration of these alloys into devices with Ge and compound semiconductors.

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