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Interfacial growth in HfO_xN_y gate dielectrics deposited using $[(\text{C}_2\text{H}_5)_2\text{N}]_4\text{Hf}$ with O_2 and NO

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The interface growth by oxygen diffusion has been investigated for 5 nm thick HfO_xN_y gate-quality dielectric films deposited on Si(100) by low-pressure pulsed metalorganic chemical vapor deposition. Analysis by x-ray photoelectron spectroscopy of the films deposited using the precursor tetrakis (diethylamido) hafnium with O_2 showed that the films contained 4 at. % nitrogen. This increased to 11 at. % N when NO was used as the oxidant. Significant growth of the interface layer was observed for films exposed to air at ambient temperature and lower rates of growth were observed for vacuum annealed films and those with the higher N content. For films annealed in O_2 at temperatures in the range 600–900 °C, the activation energies of the interfacial growth were 0.36 and 0.25 eV for N concentrations of 11 and 4 at. %, respectively. The results were interpreted in terms of atomic oxygen formation in the bulk and reaction at the interface. The increase in N incorporation from 4 to 11 at. % increases the crystallization temperature from between 500 and 600 °C to between 600 and 700 °C. © 2003 American Institute of Physics.

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Hafnium oxide has proven to be one of the most promising candidates to replace SiO_2 as the gate insulator in sub-0.1- μm complementary metal oxide semiconductor (CMOS) devices due to its relatively high dielectric constant and thermodynamic stability when in direct contact with Si.^{1,2} However, the high oxygen diffusion rate through hafnium oxide,³ which results in the ready formation of interface layers, and a low crystallization temperature⁴ remain concerns. The incorporation of Si to form silicates with a higher crystallization temperature has been investigated but silicon/hafnium ratios as high as 9 may be required,⁵ resulting in a significant reduction in the dielectric constant over that of pure HfO_2 . The incorporation of N rather than Si may ultimately result in a better tradeoff between dielectric constant and crystallization temperature. Even low concentrations of nitrogen may significantly reduce the diffusion of B or the formation of an interface layer when MOS structures are exposed to oxygen.⁶

In this letter, hafnium oxynitride films deposited by metalorganic chemical vapor deposition (MOCVD) using the amide precursor tetrakis (diethylamido) hafnium (TDEAH), $[(\text{C}_2\text{H}_5)_2\text{N}]_4\text{Hf}$, are described. The growth of an interfacial layer during air exposure and after annealing in O_2 was analyzed by x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM).

p-type Si(100) substrates with a resistivity of 0.01–0.02 Ωcm were given a HF-last RCA clean just prior to their

introduction into an ultrahigh vacuum system which comprises a low-pressure MOCVD system, an *in situ* XPS system, and a rapid postdeposition annealing (PDA) chamber. A 0.1 M solution of TDEAH dissolved in the octane was introduced with Ar carrier gas into the CVD chamber with the vaporizer and gas distribution system held at 150 °C. Si substrates were held at a temperature of 400 °C during deposition, and the oxidant gas, either O_2 or NO , was introduced into the CVD chamber at a pressure of 11 mTorr through a separate gas introduction ring. The oxidant was introduced for 5 min prior to film deposition with the substrate held at 500 °C, resulting in the formation of a buffer layer. XPS showed these films to be ~0.4 nm thick with the approximate composition of SiO_2 or SiON , depending on whether the oxidant was O_2 or NO , respectively. Separate precursor and oxidant pulses were employed during the deposition of 5 nm thick films with intervening nitrogen flushing steps to minimize carbon contamination. XPS analysis was performed *in situ* with all peaks referenced to the Si 2p substrate peak at 99.4 eV.

Figure 1(a) shows the N 1s XPS spectrum of a film deposited using NO as the oxidant. The peak at 396.0 eV was attributed to N–Hf bonds in the bulk of the film [the N 1s (N–Hf) peak]. Since the films were relatively thick, the peak at 398.3 eV was attributed to N–C bonds⁷ [the N 1s (N–C) peak] arising from residual precursor on the surface rather than N–Si bonds at the interface. Most of the N 1s (N–C) peak vanished after mild sputtering in an *ex situ* XPS system. As shown in Fig. 1(b), the O 1s peak could also

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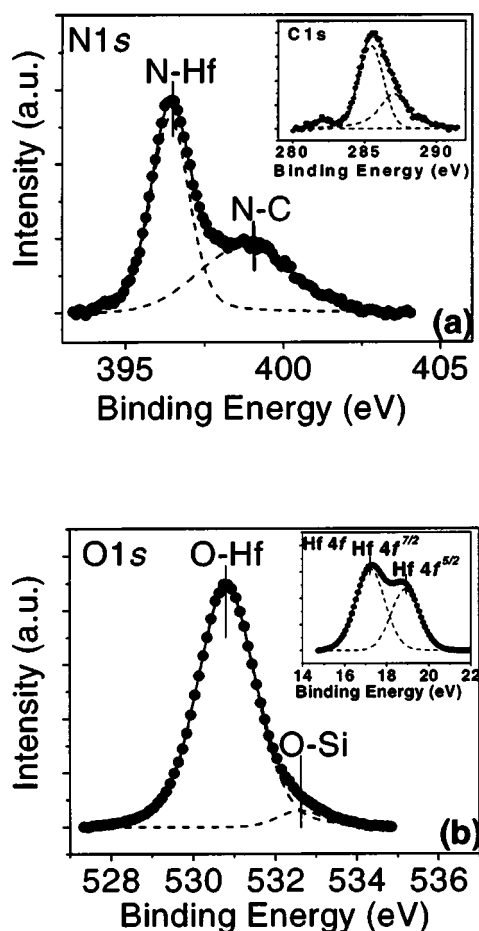


FIG. 1. (a) N 1s and C 1s (inset) XPS spectra of HfO_xN_y film deposited with NO oxidant. The closed circles are measured data, dashed lines are fitted peaks, and solid line is the sum of all fitted peaks; (b) corresponding O 1s and Hf 4f spectra (inset).

be fitted with two peaks, the O 1s (O–Si) component at 532.4 eV attributed to oxygen bonded to Si in an interfacial layer, and the O 1s (O–Hf) peak at 530.5 eV due to oxygen bonded to Hf in the deposited layer. Using standard sensitivity factors for the O 1s (O–Hf), N 1s (N–Hf), and Hf 4f peaks, the average nitrogen composition was 11 at. % for the films deposited with NO gas and 4 at. % for those deposited with O_2 .

The existence of N–Hf bonds in the bulk of the films is also evident from the positions of the Hf 4f^{7/2} peak shown in the inset of Fig. 1(b). This peak is at 17.9 eV for HfO_2 films⁸ and 15.3 eV for $\text{HfN}_{1.9}$ films.⁹ Nitrogen bonding results in a shift to lower energy for the Hf 4f doublet and an increase in the area ratio of the Hf 4f^{7/2} and Hf 4f^{5/2} components from the ideal value of 1.4, since the Hf 4f^{5/2} component shifts in the direction of the Hf 4f^{7/2} component. The area ratio is 1.66 and 1.46 for the films deposited using NO and O_2 , respectively, while the corresponding positions of the Hf 4f^{7/2} peak energy are 17.0 and 17.3 eV, consistent with previous work.⁶

The Si 2p peak was fitted with three components, two comprising the standard Si 2p^{3/2–1/2} doublet from the substrate, and the Si 2p (bonded) peak due to silicon bonded at the interface. The energy separation between the substrate and bonded Si peaks, $\Delta\text{Si } 2p$, was lower for the films deposited with NO (2.5 eV) than the ones deposited with O_2 (3.1

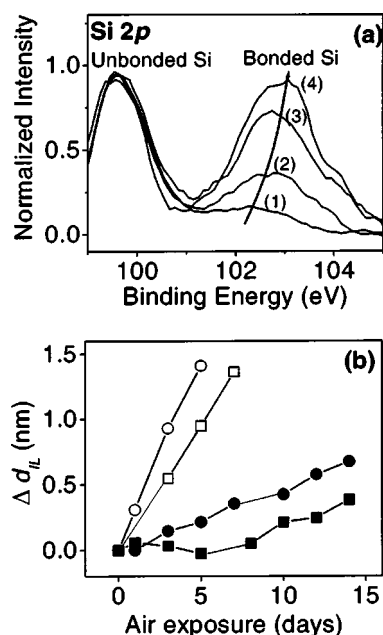


FIG. 2. (a) Si 2p XPS spectra of HfO_xN_y film deposited using O_2 after exposure to air for (1) 20 min, (2) three days, (3) five days, and (4) seven days. (b) Increase in nominal thickness of interface layer, Δd_{IL} , with air exposure: Closed (open) symbols are for films with (without) vacuum PDA: (●), (○) 4 at. % N, (■), (□) 11 at. % N.

eV). This indicates the presence of N at the interface for the former films, although the presence of Hf or suboxide bonding near the interface cannot be ruled out.

Figure 2(a) shows XPS spectra of the Si 2p peak for the films deposited using O_2 , after exposure to ambient air. A significant increase of the Si 2p(bonded) and Si 2p(substrate) area ratio in the air-exposed samples was observed for both oxidant gas samples, accompanied by an increase of $\Delta\text{Si } 2p$ to the value characteristic of that for SiO_2 . This indicates that interfacial reactions occurred as previously observed in other high- k films, such as Y_2O_3 , La_2O_3 , and Sc_2O_3 .^{10–12} Previous research on the oxygen diffusion through these high- k oxides suggested that the species responsible for interfacial growth was atomic oxygen released in the film from absorbed water or molecular oxygen.¹³ Assuming that the interfacial layer is SiO_2 , a nominal interfacial layer thickness, d_{IL} , can be obtained from the Si 2p(bonded)/Si 2p(substrate) peak area ratio using the parameters of Ref. 14. The increase in d_{IL} with exposure to air, Δd_{IL} , is shown in Fig. 2(b) for films deposited using O_2 and NO, with and without a 1 s *in situ* PDA at 800 °C in a vacuum of 1×10^{-8} Torr. The results show that a higher concentration of N in the films retards growth of the interfacial layer in air. The PDA also retarded the growth of the interface layer and this can be attributed to film densification during annealing.

Interfacial growth during subsequent annealing in 1 atm of O_2 was also investigated with films deposited with O_2 and NO, with and without the vacuum PDA. O_2 annealing was done at temperatures of 600, 700, 800, and 900 °C and the growth rate $\Delta d_{IL}/\Delta t$ was determined from the change in d_{IL} after 1 min anneals. Arrhenius plots of the nominal interfacial layer thickness calculated from the XPS Si 2p spectra are shown in Fig. 3. Linear fits of the data gave activation energies of 0.25 and 0.36 eV for the films deposited using O_2

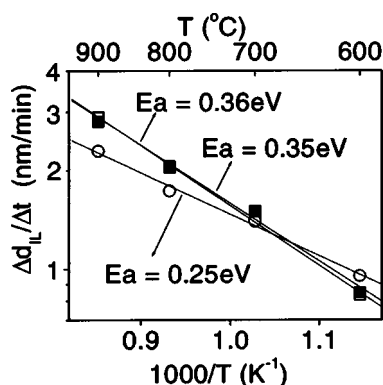


FIG. 3. Arrhenius plot for the growth of the nominal interfacial layer thickness of HfO_xN_y films annealed in O_2 at 1 atm.: (●)(●)(●) films with 4 at. % N deposited using O_2 , (□)(□)(□) films with 11 at. % N deposited using NO , (■)(■)(■) films with 11 at. % N vacuum annealed at 800 °C after deposition with NO .

(4 at. % N) and NO (11 at. % N); respectively. For the films deposited with NO there is no significant difference in activation energy for the films with and without the vacuum anneal. The higher activation energy for the film deposited with NO is likely a result of N at high- k film and the interface, reducing oxygen diffusion and the interface reaction rate. Despite the higher activation energy, the NO -deposited films have thicker interface layer at high temperature, as a result of a larger frequency factor in Arrhenius plot. This may indicate that the N sites in the bulk are more effective at converting H_2O or O_2 , providing more O which diffuses rapidly to the interface.

TEM images of the films show that the increase in nitrogen incorporation from 4 to 11 at. % increases the crystallization temperature from between 500 and 600 °C to between 600 and 700 °C, in agreement with previous observations at higher N concentrations.¹⁵

In summary, HfO_xN_y films were deposited by MOCVD using $[(\text{C}_2\text{H}_5)_2\text{N}]_4\text{Hf}$ with O_2 or NO as the oxidant. The nitrogen composition of the films deposited at 400 °C has been determined to be 11 at. % with NO and 4 at. % with O_2 . Interfacial growth during air exposure at room temperature

was attributed to absorption and diffusion of O_2 or H_2O with subsequent formation of atomic oxygen in the high- k film. It was confirmed that nitrogen incorporation and vacuum annealing at 800 °C delays the interfacial growth during air exposure. Activation energies for the interfacial growth for 1 min anneals in O_2 were 0.25 and 0.36 eV for films containing 4 and 11 at. % N, respectively. The vacuum anneal does not decrease interfacial layer growth during high-temperature oxygen anneals. N incorporation decreases the rate of interfacial growth, even at these low levels, increases the crystallization temperature of hafnium oxide films.

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