Chemical analysis of HfO$_2$/Si (100) film systems exposed to NH$_3$ thermal processing

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Nitrogen incorporation in HfO$_2$/SiO$_2$ films utilized as high-$k$ gate dielectric layers in advanced metal-oxide-semiconductor field effect transistors has been investigated. Thin HfO$_2$ blanket films deposited by atomic layer deposition on either SiO$_2$ or NH$_3$ treated Si (100) substrates have been subjected to NH$_3$ and N$_2$ anneal processing. Several high resolution techniques including electron microscopy with electron energy loss spectra, grazing incidence x-ray diffraction, and synchrotron x-ray photoelectron spectroscopy have been utilized to elucidate chemical composition and crystalline structure differences between samples annealed in NH$_3$ and N$_2$ ambients as a function of temperature. Depth profiling of core level binding energy spectra has been obtained by using variable kinetic energy x-ray photoelectron spectroscopy with tunable photon energy. An “interface effect” characterized by a shift of the Si$^{4+}$ feature to lower binding energy at the HfO$_2$/SiO$_2$ interface has been detected in the Si 1$s$ spectra; however, no corresponding chemical state change has been observed in the Hf 4$f$ spectra acquired over a broad range of electron take-off angles and surface sensitivities. The Si 2$p$ spectra indicate Si–N bond formation beneath the HfO$_2$ layer in the samples exposed to NH$_3$ anneal. The NH$_3$ anneal ambient is shown to produce a metastable Hf–N bond component corresponding to temperature driven dissociation kinetics. These findings are consistent with elemental profiles across the HfO$_2$/Si(100) interface determined by electron energy loss spectroscopy measurements. X-ray diffraction measurements on similarly treated films identify the structural changes resulting from N incorporation into the HfO$_2$ films. © 2007 American Institute of Physics. [DOI: 10.1063/1.2422746]

I. INTRODUCTION

Metal-oxide-semiconductor field effect transistor (MOS-FET) device scaling has driven an industry wide effort to replace the conventional transistor gate dielectric layer, SiO$_2$, with a high permittivity (high-$k$) material since physically thicker high-$k$ films offer lower leakage current characteristics for equivalent SiO$_2$ capacitance.$^1,2$ This initiative has given rise to extensive evaluation of Hf based oxide thin films as one of the most promising candidates for alternative gate dielectrics. However, intrinsic properties of hafnia, HfO$_2$, do not satisfy all the requirements for gate dielectric thin films, particularly crystallization temperature, defect density, and ion diffusivity among others. Therefore, various attempts have been undertaken to modify the hafnia structure to address these issues.

Several groups have reported beneficial results from N incorporation in HfO$_2$ including improved thermal stability of the dielectric material,$^3$ reduction of boron penetration,$^4$ reduction of gate leakage current, increase in dielectric constant, and suppression of the onset of crystallization.$^5$ It has been shown previously that the chemical composition of a thin SiO$_2$ interface between HfO$_2$ and the Si substrate may be modified by exposure to NH$_3$ with significant consequences for carrier mobility and equivalent oxide thickness (EOT) scaling.$^6,7$ In this study, we investigate N incorporation into the HfO$_2$ gate stack by means of pre- and post-high-$k$-deposition thermal treatments in N$_2$ and NH$_3$ ambients to identify physical characteristics of N incorporation corresponding to enhanced performance. Evaluating the change in microstructure and bonding configurations as a function of anneal temperature and ambient will contribute to the evolution of more precise models of NH$_3$ dissociation and the corresponding chemical explanations describing nitrogen-for-oxygen exchange mechanisms. Elucidating the role of N as a diffusion inhibitor and identifying its influence on the local coordination of Hf and associated crystallization kinetics of HfO$_2$ thin films is critical to the understanding and control of fabrication processes integral to device performance optimization.

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A. Nitrogen incorporation

Incorporation of nitrogen into Hf based oxide films is expected to reduce the diffusion rate of all elemental species in the bulk medium, thereby elevating the onset of crystallization temperature, since crystallization is a diffusion-limited phase transition where the rate depends on the Gibbs free-energy difference of the phases.\(^8\) It is also well known that the concentration and position of N near the channel region of transistors must be well controlled to circumvent consequences of reduced electron mobility and N-induced bandgap narrowing.\(^9\) Hafnium oxynitride, HfO\(_x\)N\(_y\), may be formed by nitridation of the oxide or oxidation of the nitride. Adding N reduces the Hf coordination with oxygen by displacing O with N of slightly lower electronegativity. However, when oxidizing the nitride, one concern centers on the formation of NH species where NH\(_0\) is stable while NH\(^-\) is reactive to N\(_2\) itself is not reactive to O with N of slightly lower electronegativity. However, when oxidizing the nitride, one concern centers on the effective transformation of conductive HfN into the dielectric while avoiding formation of electrically nanostructured heterogeneous (ENH) HfO\(_x\)N\(_y\) compositions where conductive nanoscale inclusions are embedded in a dielectric matrix.\(^11\)\(^-\)\(^13\)

The resultant position of N in Hf based oxide gate dielectric film systems is also a strong function of the nitridation methodology, i.e., N plasma, N-bearing precursor chemistry, N\(_2\)\(^+\) implantation, and anneal ambient (NH\(_3\), NO, N\(_2\)O, N\(_2\)) exposure. During thermal processing, N may exchange for O via displacement of lattice oxygen ions in the evolving grain structures of HfO\(_2\) films and/or incorporate in lattice interstitials as excess N. Plasma nitridation has been shown to incorporate molecular nitrogen, N\(_2\), as interstitials in SiO\(_2\)N\(_x\) films.\(^14\)\(^,\)\(^15\) In the case of plasma nitridation, ionized N\(_2\)\(^+\) species are likely to incorporate into the film. No atomic dissociation of N\(_2\) is expected, which is consistent with the fact that nitrogen is known to be an inert anneal ambient for oxides at 900 °C.\(^16\) In contrast to the N\(_2\) molecule, the atomic N interstitial has no affinity for a second electron and is also stable as a positive ion.

N incorporation resulting from ammonia and its reactions has been the subject of numerous studies during the past two decades, involving various experimental techniques utilized to elucidate the adsorption geometries, vibrational interactions, electronic structures, and reaction energies. Initial reports suggested that NH\(_3\) underwent a complete dissociation on the Si (100) surface at low temperature (−180 °C) and that chemisorbed H would saturate the dangling bonds, while N occupied the surface sites.\(^17\)\(^,\)\(^18\) Recently, however, advanced techniques have fostered a consensus that NH\(_3\) molecules adsorb molecularly as well as dissociatively below room temperature with NH\(_3\) and H as the only dissociative products.\(^19\)\(^,\)\(^20\) NH\(_2\) is stable up to ~325 °C and above this temperature NH\(_2\) either recombines with H to produce NH\(_3\) or dissociates to H and N, followed by H\(_2\) liberation and N incorporation.\(^21\)\(^,\)\(^22\) Specific to the HfO\(_2\)/SiO\(_2\) film system, it has been calculated by Gavartin et al.\(^23\) that during postdeposition anneal (PDA) of HfO\(_2\) at 700 °C, NH\(_3\) dissociation consists of NH\(^-\) and a proton, H\(^+\). Further dissociation of the NH\(_2\) molecule may lead to the formation of NH species where NH\(^0\) is stable while NH\(^-\) is unstable, suggesting that the likely final products of the NH\(_3\) PDA process are NH\(_2\), NH\(^0\), H\(^+\), and H\(^+\).

B. Characterization techniques

HfO\(_2\) gate dielectric thin films (3 nm thick) have been atomic layer deposited (ALD) via tetrakis(ethylmethylamino)-hafnium precursor with ozone [(TEMAHf)+O\(_3\)] on chemically prepared p-type Si (100) substrates and exposed to a 700 °C PDA exposure for 60 s in either NH\(_3\) or N\(_2\) ambient at 3 Torr. By comparing films exposed to the NH\(_3\) PDA process with otherwise identical films exposed to N\(_2\) PDA, the effect of N incorporation (NH\(_3\)) may be decoupled from that of the thermal cycle (N\(_2\) itself is not reactive to HfO\(_2\)). The impact of N treatments on the electrical performance was evaluated based on EOT and mobility values collected on complementary metal-oxide semiconductor (CMOS) transistors fabricated with the gate dielectrics described above. The N dose (atoms/cm\(^2\)) in the bulk films exposed to NH\(_3\) has been quantified by nuclear reaction analysis (NRA). Additional duplicate samples exposed to a subsequent higher temperature rapid thermal anneal (RTA) in N\(_2\) ambient have been characterized by grazing incidence x-ray diffraction (GIXRD) for comparative crystallographic phase identification as a function of ambient and temperature. Synchrotron x-ray photoelectron spectroscopy (XPS) has been utilized to determine N ls core level binding energy variations associated with both Hf–N and Si–N bond formation. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) in combination with electron energy loss spectroscopy (EELS) was used to produce atomic-number sensitive “Z-contrast” images and elemental profiles of silicon, oxygen, nitrogen, and hafnium to illustrate chemical intensity gradients as a function of position across the interfacial regions of the HfO\(_2\)/SiO\(_2\)/Si film systems in cross section.

II. EXPERIMENT

Table I indicates the three basic NH\(_3\) processes corresponding to the primary three-sample set under evaluation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Interface</th>
<th>Pre-deposition anneal</th>
<th>High-k deposition</th>
<th>Post-deposition anneal</th>
<th>STEM</th>
<th>STEM HfO(_2) thick</th>
<th>[N] (1 × 10(^{15}) cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ISSG 2 nm</td>
<td>None</td>
<td>HfO(_2)</td>
<td>NH(_3)/PDA</td>
<td>1.9–2.0</td>
<td>3.2–3.3</td>
<td>3.57</td>
</tr>
<tr>
<td>B</td>
<td>HF-last</td>
<td>NH(_3)/pre-DA</td>
<td>HfO(_2)</td>
<td>None</td>
<td>1.3–1.4</td>
<td>2.9–3.0</td>
<td>2.14</td>
</tr>
<tr>
<td>C</td>
<td>HF-last</td>
<td>NH(_3)/per-DA</td>
<td>HfO(_2)</td>
<td>NH(_3)/PDA</td>
<td>1.2–1.3</td>
<td>3.2–3.3</td>
<td>5.91</td>
</tr>
</tbody>
</table>
Sample A consists of a Si surface that had an in situ steam generated (ISSG) 2 nm thick thermal SiO$_2$ layer grown on it prior to HfO$_2$ deposition, and samples B and C consist of Si surfaces that were cleaned with an HF-last chemical sequence (H-terminated Si) and then annealed in NH$_3$ at 700 °C for 15 s (predeposition anneal) prior to HfO$_2$ deposition. A 3 nm thick ALD HfO$_2$ film was then deposited on each substrate. After HfO$_2$ deposition, samples A and C received a 700 °C anneal for 60 s in NH$_3$ (postdeposition anneal), while sample B was characterized as deposited. The nitrogen dose indicated for each sample in Table I has been quantified by NRA utilizing a Van de Graaf accelerator sensitive to $^{14}$N from the $^{14}$N($d$,a)$^{12}$C reaction at 1.1 MeV incident deuteron energy with a detection limit of $\sim 5 \times 10^{13}$ atoms/cm$^2$.

In order to evaluate physical parameter variations including material intermixing corresponding to chemical processing, phase contrast high resolution transmission electron microscopy (HRTEM) and Z-contrast HAADF-STEM with EELS elemental chemical profile scans were performed on the three-sample set. STEM, EELS, and energy dispersive x-ray spectroscopy (EDXS) data were recorded at 300 keV using focused electron probes of $\sim 0.3$ nm full width at half maximum (FWHM). A detailed explanation of this measurement technique is described elsewhere. Unlike phase contrast imaging which is primarily sensitive to crystalline order, the Z-contrast images clearly distinguish, by the degree of brightness, high density HfO$_2$ from the low density (dark) SiO$_2$-like interfacial layer (IL) and produce the more accurate layer thickness dimensions, relative to HRTEM, indicated in Table I.

Electrical properties of the dielectric films and interfaces have been characterized by MOSFET measurements. Transistors were fabricated using 3 nm HfO$_2$ gate dielectric with 10 nm TiN/poly-Si gate electrodes formed by chemical vapor deposition (CVD) of tetrakis(diethylamido)titanium (TDEAT) with NH$_3$, followed by 180 nm of phosphorus doped poly-Si. The relationship between gate current density $J_g$ at $V_{fb}^{-1}$ (where $V_{fb}$ is the flatband voltage) and EOT for the gate dielectric stacks with several types of bottom interfacial oxides, with and without NH$_3$ treatment, is illustrated in the plot of Fig. 1(a). For each bottom interfacial oxide studied, incorporating NH$_3$ resulted in slightly lower EOT relative to the same interfacial oxide without NH$_3$. This is consistent with the higher permittivity reported for silicon oxynitride relative to SiO$_2$. The influence of the NH$_3$ treatment on $J_g$ is more difficult to isolate since leakage current is a strong function of EOT.

Figure 1(b) shows the plot of EOT versus effective high field electron mobility at 1 MV/cm. Formation of quality thermal SiO$_2$ interface between the Si substrate and high-k dielectric enhances electrical performance, specifically, electron mobility. Although a comprehensive discussion of mobility mechanisms is not the focus of this article, there have been numerous reports that identify various specific components of mobility degradation with HfO$_2$, including phonon scattering, Coulomb scattering, transient charge trapping, and surface roughness. Coulomb scattering has been shown to dominate low field mobility, while phonon scattering and surface roughness dominate mid and high field mobilities, respectively. Kirsch et al. investigated improvements in peak and high field electron mobility corresponding to physical scaling of the HfO$_2$ layer and attributed the results to reduced charge trapping and Coulomb scattering in thinner films. The general trend of mobility degradation with aggressive scaling of the bottom interface thickness is observed in Fig. 1(b), where an HF-last chemically treated Si substrate is compared with a 1.1 nm thick ISSG SiO$_2$ interface, with and without NH$_3$. Mobility degradation associated with the NH$_3$ treated interfacial oxides may correspond to a combination of nonstoichiometric SiO$_2$ and the remote Coulomb scattering (RCS) contribution from the HfO$_2$ film in closer proximity to the substrate.

The chemical state of elements in the transition region between substrate Si and HfO$_2$ strongly influences device performance parameters such as gate leakage current, electron and hole trapping characteristics, and electron mobility across the channel. Therefore, it is critical to distinguish interfacial microroughness originating from nonuniform protrusion of crystalline HfO$_2$ grains into the underlying, low density, amorphous SiO$_2$ layer from chemical intermingling corresponding to Hf silicate (HfSiO$_3$) formation. Since both scenarios are characterized by an (intermediate) electron density between stoichiometric SiO$_2$ and HfO$_2$, the core level binding energies of the samples were measured by high resolution XPS at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory on the National Institute of Standards and Technology (NIST) beamline X24A. A fixed-exit, double-crystal monochromator operating...
with Si (111) crystals provided photons in the energy range of 2.1–5 keV. Variable kinetic energy x-ray photoelectron spectroscopy (VKE-XPS) measurements were performed with a hemispherical electron analyzer housed in a standard ultrahigh vacuum chamber. Core level spectra recorded at varying kinetic energies enabled chemical depth profiling through the SiO$_2$ interfacial layer. Additionally, spectra recorded at different electron take-off angles enabled depth sensitive probing of the exposed outer surface of the HfO$_2$ layer, through the bulk hafnia, to the buried interface.

III. RESULTS AND DISCUSSION

A. Cross-section analysis

The HRTEM micrographs of samples A, B, and C depicted in Fig. 2 illustrate the IL thicknesses of approximately 2.0, 1.3, and 1.3 nm, respectively. The IL is the region formed between the HfO$_2$ film and the Si substrate. The HAADF-STEM Z-contrast images of the same sample pieces appear in the top portions of Fig. 3 for each sample. The intensities in a Z-contrast image are roughly proportional to the atomic number of the atomic species squared, and the images are therefore dominated by Hf ($Z=72$) that appears white. Element profiles are plotted in the lower portion of the figure and were acquired for each sample along a straight line from the Si substrate through the IL and through the uncapped HfO$_2$ layer. They were produced by integrating the background corrected EELS intensity (N $K$, Si $K$, Hf $L$, and O $K$ edges) of each element. The position of each profile is aligned to the width of the corresponding STEM image above. They have not been corrected for differences in scattering cross section or sample thickness variations, and their detection sensitivity, which may be influenced by local composition due to scattering of incident electrons and associated signal interference, is on the order of a few at. %.

The influence of the starting Si substrate chemical treatment is clearly indicated by the position and relative intensity of the N profile of each sample, as described previously. The O, N, and Si intensities overlap in sample A at the beginning of the IL, which is consistent with the spectra of SiO$_x$N$_y$ formation. In contrast, the onset of the N intensity precedes the O intensity profile in the NH$_3$ pre-treated samples B and C and this narrow O-free region is consistent with substrate Si–N bond formation. Medium energy ion scattering (MEIS) was utilized to characterize interfaces representative of samples B and C, and a model consisting of 0.5 nm Si$_3$N$_4$ formed on Si gave a good representation of the data.

The element profiles in Fig. 3 also indicate a Hf-free region near the substrate of each sample (the Si/IL region). This observation is supported by the fact that the EELS is more sensitive to high $Z$ elements in a mixed density medium, and significant elastic scattering from the heavy Hf atoms attenuates the low Z oxygen and nitrogen signals. Ni-
trogen fully penetrates the HfO2 layer and accumulates in the Si/IL region of sample A that was subjected only to nitrogen during the NH3 postdeposition anneal.

B. Depth profiling

Figure 4 demonstrates the Si depth-resolution sensitivity through the thin IL using Si 1s VKE-XPS for sample A recorded over the photon energy range 2100 eV ≤ hν ≤ 3500 eV. The intensity of the Si 1s spectrum at the Si/SiO2 interface recorded at hν=3500 eV photon energy is dominated by the substrate (Si6) signal. Correspondingly, at the low photon energy, hν=2100 eV, few substrate Si–Si bonds (Si6) are detected, and the spectrum consists primarily of oxidized Si at the HfO2/SiO2 interface. Based on the Si4+ peak shift to lower binding energy with decreasing photon energy [Si4+ is the standard Si state synonymous in binding energy (BE) with SiO2], it appears that the Si in the IL is less oxidized closest to the HfO2 layer following NH3 PDA. This is because lower kinetic energy electrons probe less of the IL region while favoring the HfO2 surface. Although this shift may be consistent with Hf silicate formation, it is not thermodynamically favorable for HfO2 to mix with SiO2 during thermal processing. It has been shown that various compositions of Hf silicate films demix and form HfO2 grains embedded in amorphous SiO2 upon exposure to anneal processing sufficient to induce crystallization.35–37

The 3 nm thick HfO2 layer is too thin for effective VKE-XPS depth profiling at these photon energies using the low binding energy Hf 4f core line. Therefore, in order to address the unlikely possibility of Hf silicate formation at the SiO2/HfO2 interface, Hf 4f spectra were recorded at different electron take-off angles for sample A at hν=2200 eV. Figure 5 shows spectra which were recorded at interface-sensitive glancing (5°)-photon incidence/normal-electron take-off angle and surface-sensitive normal (80°)-photon incidence/glancing-electron take-off angle. At normal incidence the path of the ejected photoelectrons through the HfO2 film is increased by approximately a factor of 4 relative to the spectra recorded at glancing incidence. As the escape depth of 2200 eV electrons traveling through HfO2 is estimated to be ~1.6 nm, this increase in path length would effectively eliminate any interfacial signal arising from the IL. Therefore, these data suggest that the chemical composition around the Hf atoms is uniform throughout the film, and there is little if any detectable change in Hf bonding at the IL relative to the outer surface. The data are therefore consistent with no Hf silicate formation at the interface, for Hf silicate would have a significant Hf 4f core level binding energy shift to higher energy relative to the HfO2.38 Additionally, because a corresponding change in the Hf 4f line shape does not accompany the “interface effect” observed in the Si 1s spectra of sample A in Fig. 4, it is clear that Hf has scavenged O and reduced the Si–O coordination near the HfO2/Si interface. This conclusion is consistent with the mechanistic pathways proposed for electrical performance of advanced MOSFET devices described previously.39

The change in chemical bonding of the Si in the IL was also examined by recording high resolution Si 2p spectra at hν=2200 eV for samples A, B, and C. These spectra are shown in Fig. 6 and normalized to the Si6 intensity. Recall that N is observed in the elemental profiles of sample A (Fig. 3) near the bottom interface due to the NH3 PDA process; however, the XPS spectra for this sample shown in Fig. 6 exhibit a Si4+ peak similar to fully oxidized thermal SiO2. Samples B and C, however, which were exposed to NH3 processing pre-HfO2-deposition (and are consistent with Si3N4 at the interface from MEIS data), do not exhibit Si4+, rather, these spectra suggest the corresponding IL may consist of Si–N bonds where N and/or NH has exchanged for O. The resultant SiO2Nx layer remains amorphous as illustrated in the HRTEM image of Fig. 2, and there is little evidence of Si fourfold coordination with O.
C. Hf and N core level spectra

The Hf 4f core level spectra of the sample set illustrated in Fig. 7 clearly indicate the influence of the NH3 PDA on the local coordination of the Hf atoms. The narrow line shape of the Hf core level spectrum of sample B is identical to that measured (not shown) from an as deposited HfO2 film that serves as a reference standard. In order to construct the line shape parameters to decompose the more complicated spectra of samples A and C, this spectrum was fitted with a single Hf 4f doublet as shown (the dots are the measured data points and the solid line is the fit). The line shape parameters obtained utilizing a Shirley background are spin-orbit splitting of 1.66 eV, 4f7/2 to 4f5/2 branching ratio of 1.31, Lorentzian width of 0.17 eV, and Gaussian width of 1.0 eV. This branching ratio is close to the statistical 2J+1 value of 1.33 for the J=7/2 and 5/2 components, although both the Lorentzian and Gaussian widths are much larger than expected and may be attributed to charge fluctuations in the amorphous HfO2.40 These line shape fitting parameters were then applied41 to the core level spectra of the NH3 PDA samples, A and C, shown in Fig. 7, where the spectra were recorded at the more interface-sensitive glancing-photon incidence/normal-electron take-off angle. Clearly, the effect of N substitution for O around the Hf manifests itself as a distinct Hf core level shift to lower binding energy due to the reduced electronegativity of N relative to O. The arrows in Fig. 7 indicate the appearance of the Hf–N bond component which further broadens the Hf 4f linewidth. This result is consistent with the analysis of similar samples exposed to NH3 PDA by Lee et al.42 in that Hf–N bonding results in a shift to lower binding energy for the Hf 4f doublet. Sample C exhibits additional peak broadening over sample B due to the increased Hf–N bond formation from the NH3 pre-DA. NH3 nitridation of the substrate prior to HfO2 deposition results in N redistribution from the bottom interface to the HfO2 film during the NH3 PDA. Therefore, sample C experiences nitrogen exposure from two (sources) sides during the PDA process, that sample B did not receive, which is revealed by the core level decomposition and is consistent with the measured total N dose. The total N dose (see Table I) for sample C is 5.91 × 10^15 atoms/cm², which is ~1.7 times greater than the N dose of sample A and ~2.8 times greater than the N dose of sample B. The N dose difference between samples B and C is attributed to the NH3 PDA.

The N 1s spectra measured for the three-sample set are illustrated in Fig. 8. Sample A was (only) exposed to the NH3 postdeposition process, and it appears to exhibit Hf–N bonds with no appreciable Si–N bonding, although the elemental profile data (Fig. 3) for this sample do indicate N in the IL. Sample B was (only) exposed to the NH3 predeposition process, and Hf–N bonding is not observed in the N 1s spectrum from this sample. Sample C exhibits a N 1s spectrum that is comprised of both components: the Si–N peak corresponding to the NH3 predeposition anneal process and the Hf–N peak resulting from the NH3 postdeposition anneal process.

D. N exchange for O

Although nitridation of HfO2 increases the barrier for oxygen and boron diffusion,43 introducing N adds electrically active states above the valence band, which lowers the valence band offset and thereby reduces the band gap in...
HfO$_2$. This change in electronic structure is a direct reflection of the lower atomic number and hence less tightly bound valence 2$p$ orbitals of N relative to O. Substitution of N for O in the unit cell leads to a hole in the valence band and favors anion vacancy formation. A direct comparison of the valence band measurement of samples A, B, and C by XPS measured by Charles Evans and Associates using Al K$_\alpha$ source is shown in Fig. 9. Samples A and C reveal an increase in the valence band maximum that trends with the N dose see Table I from the NH$_3$ anneal process: as the N concentration increases, more N 2$p$ states extend toward the conduction band, resulting in the reduction of the band gap. The VBM consists mainly of O 2$p$-like nonbonding orbitals of $\pi$ symmetry, while the conduction band minimum (CBM) is due to Hf 5$d$ nonbonding states. As a result, the band gap of HfO$_x$N$_y$ is set primarily by atomic energies, and adding N reduces the band gap by raising the VBM. It is proposed that NH$_3$ dissociates to NH species which exchange for O during the PDA process, since the electron configuration of NH=O=1$s^22s^2p^4$, and isoelectronic species are expected to exhibit similar chemical and physical characteristics.

E. Crystalline structure analysis

Thin as deposited hafnia films have been reported to exhibit a phase change following exposure to anneal temperature \(\geq 500 \, ^\circ\mathrm{C}\). The films are typically amorphous or nanocrystalline when deposited at 330 °C and become polycrystalline, largely in the monoclinic phase with a smaller fraction of tetragonal and/or orthorhombic phase detected in films annealed up to the 700 °C PDA temperature. This phase transition is clearly illustrated in the GIXRD \(2\theta\) patterns of Fig. 10 which were obtained for a single 4 nm HfO$_2$ sample measured at 100 °C increments in N$_2$ ambient. The arrow in Fig. 10 points to the feature at \(2\theta = 30.4^\circ\) which appears most prominently at 400 °C and diminishes completely above 800 °C where the diffraction spectrum matches monoclinic HfO$_2$ (m-HfO$_2$). This transitional peak corresponds to either the orthorhombic or tetragonal phase of HfO$_2$; it may also signify the coexistence of both phases. Specific identification is hampered by the near coincidence of features from both phases at that position as identified in the International Centre for Diffraction Data powder diffraction card files.

In order to investigate the chemical effect of N incorporation on the crystallization kinetics of HfO$_2$, an additional set of samples, consisting of 4 nm thick HfO$_2$ deposited on 1 nm SiO$_2$/Si(100), has been annealed in N$_2$ and NH$_3$ ambients for x-ray diffraction comparison. The GIXRD patterns corresponding to N$_2$ and NH$_3$ PDA processing at 700 °C are illustrated in Figs. 11(a) and 11(b), respectively; they are plotted on a scale different from Fig. 10. The sample measured in Fig. 11(a) is representative of the thermal response of HfO$_2$ (no NH$_3$ reaction) and therefore provides a reference for identifying differences due to N incorporation during NH$_3$ PDA. The sample measured in Fig. 11(b) is identical to sample A (discussed previously), with the exception of having a 1 nm SiO$_2$ interface layer. The prominence of the peak at \(2\theta\)
As indicated in the GIXRD patterns of Figs. 12(a) and 12(b), following TiN etch, XRD patterns of this film also correspond to m-HfO₂. The significant [N] detected in the IL of the capped sample following RTA, coupled with the resultant m-HfO₂ phase, support the proposal that the RTA cycle dissociates the NH molecule, which liberates hydrogen and results in atomic N exchange for O in m-HfO₂.

IV. CONCLUSION

Thin HfO₂ blanket films have been deposited on chemically prepared (p-type) Si (100) substrates to produce HfO₂/SiO₂/Si samples which have been alternately exposed to anneal cycles in NH₃ and N₂ ambients for direct comparison. HAADF-STEM Z-contrast images with element profiles showing changes in the integrated intensities from EELS and EDXS data recorded for a series of points across the gate stack of 3 nm HfO₂ films have been correlated with synchrotron XPS Si 2p and N 1s spectra to identify substrate Si–N bond formation associated with HF-last+NH₃ substrate treatments. The NH₃ anneal ambient has been shown to produce Hf–N bond formation and influence the crystallographic microstructure of thin HfO₂ films. The Si 1s spectra obtained with VKE-XPS, however, reveal a shift to higher binding energy of the Siɪ⁺ peak at the HfO₂/SiO₂ interface with increasing photon energy, while the Hf 4f core level spectra, obtained over a wide range of incident angles, exhibited no observable change in binding energy or line shape. It is difficult to distinguish chemical intermixing corresponding to Hf silicate formation from microroughness of the crystalline-amorphous interface, since both conditions are characterized as a transition region of intermediate electron density between stoichiometric amorphous SiO₂ and crystalline HfO₂. However, using the combination of the Si 1s spectra recorded via VKE-XPS depth profiling and the Hf 4f...
spectra recorded at different electron take-off angles (at $h\nu = 2200$ eV) shows that the N content and chemistry in the HfO$_2$ film are uniform throughout the thickness of the film and that the underlying SiO$_2$ becomes O deficient in contact with HfO$_2$.

For HfO$_2$/SiO$_2$ thin film systems exposed to the NH$_3$ PDA process, the Hf–N bonding component detected in the GIXRD 2θ patterns is consistent with m-HfO$_2$. Since the at. % N remains essentially unchanged in the capped and uncapped NH$_3$ PDA films following RTA in N$_2$ ambient, it is expected that the N outdiffusion or O$_2$ in-diffusion appreciably influences the measured response. Rather, the RTA process gives rise to further dissociation of the NH molecule, which is accompanied by the liberation of hydrogen resulting in atomic N exchange for O in the m-HfO$_2$ cell structure.

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