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Nitrogen doping and thermal stability in $HfSiO_xN_y$ studied by photoemission and x-ray absorption spectroscopy

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We have investigated nitrogen-doping effects into $HfSiO_x$ films on Si and their thermal stability using synchrotron-radiation photoemission and x-ray absorption spectroscopy. N 1*s* core-level photoemission and N *K*-edge absorption spectra have revealed that chemical-bonding states of N-$Si_{3-x}O_x$ and interstitial N_2-gas-like features are clearly observed in as-grown $HfSiO_xN_y$ film and they decrease upon ultrahigh vacuum (UHV) annealing due to a thermal instability, which can be related to the device performance. Annealing-temperature dependence in Hf 4*f* and Si 2*p* photoemission spectra suggests that the Hf-silicidation temperature is effectively increased by nitrogen doping into the $HfSiO_x$ although the interfacial SiO_2 layer is selectively reduced. No change in valence-band spectra upon UHV annealing suggests that crystallization of the $HfSiO_xN_y$ films is also hindered by nitrogen doping into the $HfSiO_x$.

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HfO_2-based gate dielectrics have a high potential for use in the next-generation of ultra-large-scale integration device applications as alternatives to conventional SiO_2 films which suffer from excess direct tunneling leakage currents resulting from the downscaling of complementary metal-oxide-semiconductor field effect transistors.[1] Compatibility of the gate dielectrics to current device processing is mainly determined by a trade-off between high dielectric constant (high-*k*) and thermal stability. Although a pure HfO_2 amorphous film has the highest dielectric constant in HfO_2-based gate dielectrics, it crystallizes readily by low-temperature annealing around 520 ^{o}C.[2] $HfSiO_x$ emerges as a candidate for improvement of the crystallization temperature due to the Si atom distribution in the film.[3] In order to maintain the thermal stability, a nitrogen passivation is one of the powerful techniques used for high-*k* material fabrication.[4] Visokay *et al* reported that $HfSiO_xN_y$ is one of the most desirable materials for the next-generation device applications due to its ability to retain the amorphous structure through high-temperature thermal annealing processes for activation.[4] However, an excessive nitrogen doping into the films yields some problems in electrical characteristics such as a fluctuation of the threshold voltage[5] and an increase in leakage currents due to the significant decrease in band offsets between $HfSiO_x$ and the Si substrate.[6] Therefore, it is important to understand the chemical bonding states for nitrogen atoms in $HfSiO_xN_y$, which is crucial to characterize the microscopic structures and processes of the nitrogen incorporation. Another problem in the thermal stability of HfO_2-based gate dielectrics is the silicidation,[7] i.e., the changes from insulator to metallic characteristics resulting in the significant increase in leakage currents. Photoemission and x-ray absorption spectroscopy (XAS) are powerful techniques to

investigate these problems from the viewpoint of chemical bonding states. In the previous report, we found that it is possible to detect the silicidation[8] and crystallization[9] separately in HfO_2/Si by photoemission and XAS. In this letter, we discuss chemical bonding states of nitrogen atoms in $HfSiO_xN_y$ fabricated by N_2-plasma nitridation of $HfSiO_x$ and their thermal stability in terms of silicidation and crystallization.

$HfSiO_x$ films were grown on the chemical and ozone oxidized Si(001) substrates in Ar/O_2 atmosphere using atomic-layer-deposition (ALD) techniques. $HfSiO_xN_y$ films were prepared by nitridation treatment of $HfSiO_x$ using N_2-plasma at room temperature. Details about the sample growth procedures were reported in ref. 10. The thicknesses of these films were measured as double-layer structures with the top $HfSiO_x(N_y)$ layer of 1.4 nm and the interfacial SiO_2 layer of 2.6 nm by cross-sectional transmission electron microscope (TEM). We prepared two films of $HfSiO_xN_y$ with y=0 and 0.2 in order to investigate the N_2-plasma nitridation effects.

Photoemission and x-ray absorption spectroscopy (XAS) were carried out at beam line 10.1 of Stanford Synchrotron Radiation Laboratory (SSRL) in the Stanford Linear Accelerator Center (SLAC) with photon energies ranging from 200 to 1000 eV. The total energy resolutions were estimated to be 0.5 and 1.2 eV at the photon energies (h) of 210 and 640 eV, respectively, by Gaussian widths of Hf 4*f* photoemission spectra in a metallic Hf silicide. The total-electron-yield method was used for N *K*-edge XAS. Annealing was performed in ultrahigh vacuum by radiative heating from the backside of the samples. The temperature at sample surfaces was monitored by a pyrometer. Annealing was performed for 10 min at each temperature. Curve fittings for core-level

photoemission spectra were carried out by a standard nonlinear least-square-fitting procedure using a Voigt function convoluting Gaussian and Lorentzian functions.[10] Gaussian values are adjustable, while Lorentzian values for N 1*s*, Hf 4*f*, and Si 2*p* of 0.25, 0.05, and 0.08 eV, respectively, are fixed.

N 1*s* photoemission spectra and N *K*-edge absorption spectra of the $HfSiO_xN_y$ films with annealing-temperature dependence are shown in Fig. 1. N 1*s* photoemission spectra in each panel are normalized at the peak-height maxima with curve-fitting results. At the as-grown stage, a sharp peak structure in the N *K*-edge XAS spectrum is observed, which may be derived from an interstitial N_2-gas component within $HfSiO_xN_y$ matrix during N_2-plasma processing.[12,13] In order to clarify the relationship between this N_2-gas-like feature in XAS and photoemission results, N 1*s* photoemission spectra are deconvoluted into four components with binding energies of 1.5, 3.3, and 6.2 eV relative to main peaks appearing around 396-397 eV. The N 1*s* main-peak shifts can be attributed to the differential charging and extra-atomic relaxation effects,[14,15] which are not due to the changes in local chemical bonding states around nitrogen atoms. Considering an angular dependence and annealing-temperature dependence as shown in Figs. 1 (a) and (b), we assigned these components as N-Si_3, N-Si_2O, N-SiO_2,[16] and N_2 gas from the main peak to higher binding-energy side, respectively. The component of the highest binding energy is relatively decreased by changing emission angles from 0 ^{o} to 60 ^{o}, indicating that the N_2-gas component exists in the deep region of the $HfSiO_x$ film. In addition, the NO_x components denoted as N-Si_2O and N-SiO_2 are distributed at the surface region. After annealing at 400 ^{o}C, the N-SiO_2 components completely disappear due to the thermal instability and the N_2-gas component still

remains as a detectable amount. Chang *et al*. previously reported similar behavior in SiO_xN_y films prepared by N_2-plasma nitridation of SiO_2 although their assignment of the highest binding-energy component has ambiguity (not N_2 gas but N-O_3).[17] Since the chemical bond strength of N-O (1.7 eV) is weaker than those of Si-Si (2.0 eV), Si-O (4.8 eV), and Si-N (3.5 eV),[18] the N-O_3 component should be most easily decomposed compared to N-Si_2O and N-SiO_2 components by annealing. Therefore, we suggest that the component of the highest binding energy is derived from not N-O_3 but N_2 gas. In addition, we adopted a full width at half maximum (FWHM) of 1.5 eV for the fitting of N_2-gas component which is smaller than those for other components (1.9-2.0 eV). It is considered that the N 1*s* core-level peak of N_2 gas is sharper than those of amorphous bonding states, as shown in N *K*-edge XAS spectra. Furthermore, the appearance of the highest binding-energy component is related to the degradation of the transistor device performance.[18] Controlling of this component is essential to improve the performance since it promotes to increase the defect density.

Figure 2 shows annealing-temperature dependence of Hf 4*f* photoemission spectra with curve-fitting results in the $HfSiO_xN_y$ film (a) and the $HfSiO_x$ film (b). FWHMs of Hf 4*f* spectra become narrower by annealing at 800 ^oC, which is not due to the crystallization of $HfSiO_xN_y$ but changes in the density of films. By the annealing at 900 ^oC for the $HfSiO_x$ film, the Hf-oxide peak around 18.3 eV disappears and the Hf-silicide peak appears at 14.7 eV, indicating that the silicidation reaction of $HfSiO_x$ is promoted. However, for the $HfSiO_xN_y$ film, the Hf-silicide peak is not detected even by 25-times expanding around 14.7 eV of binding energy. This fact indicates that the Hf-silicide formation is effectively suppressed by the N_2-plasma nitridation into

$HfSiO_x$.

Figure 3 shows annealing-temperature dependence of Si 2*p* photoemission spectra with curve fitting in $HfSiO_xN_y$ (a) and $HfSiO_x$ (b). In the Si 2*p* photoemission spectra, peaks located at 99.2 eV are derived from the Si-bulk components and peaks located at 102-103 eV are assigned as the Si-oxide components. By the annealing at 900 ^{o}C for the $HfSiO_x$ film as shown in Fig. 3 (b), the Si-oxide peak completely disappeared, which is well related to the silicidation of $HfSiO_x$. For the $HfSiO_xN_y$ film, the Si-oxide peak is significantly decreased by the annealing at 900 ^{o}C although the Hf-silicide peak in the Hf 4*f* spectra is below detection limit, suggesting that only the interfacial SiO_2 layer is decomposed. The formation of SiO gas by the reaction between SiO_2 and Si substrates during high-temperature annealing above 600 ^{o}C in ultrahigh vacuum, i.e., oxygen free ambient, is well known.[19] Therefore, it is considered that the interfacial SiO_2 layer reduction occurs by the following reaction,

$$SiO_2 + Si \rightarrow 2SiO\uparrow . \quad (1)$$

After the SiO-gas generation at the interface SiO_2/Si, it diffuses into vacuum without the reduction of the $HfSiO_xN_y$ top layer. For ZrO_2/SiO_2/Si and Y_2O_3/SiO_2/Si gate stacks, similar reactions by decomposing interfacial layers selectively were reported.[20,21] By annealing at 900 ^{o}C, the Hf silicidation occurs only for $HfSiO_x$, suggesting that the nitrogen doping into the $HfSiO_x$ film blocks the reduction of SiO_2 at the interface between SiO_2 and Si. Therefore, the increase in silicidation temperature for $HfSiO_xN_y$ can be well explained by higher nitrogen concentration at the interfacial SiO_2 layer than that for the $HfSiO_x$ film and the nitrogen incorporation suppresses the Hf silicidation.

Figure 4 (a) shows annealing-temperature dependence of valence-band spectra in $HfSiO_xN_y$. Peaks appearing around 6 eV are attributed to O 2*p* bands from $HfSiO_xN_y$ or interfacial SiO_2 and valence-band intensities in the binding energy between 0 eV and 3 eV are derived from Si substrate components. Contrary to our previous study for the 5.6-nm HfO_2 film, the double-peak splitting does not appear in O 2*p* bands after annealing at 800 °C and 900 °C,[9] indicating that the $HfSiO_xN_y$ layer in this study is not crystallized by the annealing above 800 °C. Amorphous structures are maintained due to effects of the silicate layer and nitrogen doping. Cross-sectional TEM images for the samples annealed at 900 °C and as-grown, as shown in Figs. 4 (b) and (c), respectively, also reveal that the $HfSiO_xN_y$ layer is not crystallized. After the annealing at 900 °C, the $HfSiO_xN_y$ layer thickness remains unchanged and the interfacial SiO_2 layer locally became thinner than that in the as-grown stage, which is consistent with the Si 2*p* intensity ratios.

In conclusion, we have investigated nitrogen-doping effects into $HfSiO_x$ and their thermal stability by photoemission spectroscopy and XAS with annealing-temperature dependence. Analysis of chemical bonding states in nitrogen atoms revealed that the N-SiO_2 component is unstable as compared to the interstitial N_2-gas component due to a lack of thermal stability. For the silicidation, nitrogen doping into $HfSiO_x$ effectively increases the silicidation temperature although the interfacial SiO_2 layer is selectively reduced. Valence-band spectra photoemission suggest that the $HfSiO_x(N_y)$ films are not crystallized by the annealing below the silicidation temperature.

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Figure captions

FIG. 1: Annealing-temperature dependence in N 1*s* photoemission spectra for the $HfSiO_xN_y$ film taken at emission angles ($_e$) of 0 ° (a) and 60 ° (b). Curve-fitting results are also shown. (c) Annealing-temperature dependence in N *K*-edge absorption spectra for $HfSiO_xN_y$.

FIG. 2: Annealing-temperature dependence in Hf 4*f* photoemission spectra in $HfSiO_xN_y$ (a) and $HfSiO_x$ (b). Curve-fitting results are also shown.

FIG. 3: Annealing-temperature dependence in Si 2*p* photoemission spectra in $HfSiO_xN_y$ (a) and $HfSiO_x$ (b). Curve-fitting results are also shown.

FIG. 4: (a) Annealing-temperature dependence in valence-band photoemission spectra. Cross-sectional TEM images: (b) after the annealing at 900 °C and (c) as-grown sample in $HfSiO_xN_y$.