Photoemission Study of Ultrathin N incorporated Hf-Silicate on Si(100) Systems

Akio OHTA, Hiroshi NAKAGAWA, Hideki MURAKAMI, Seiichirou HIGASHI,
Seiichi MIYAZAKI, Seiji INUMIYA* and Yasuo NARA*

Graduate School of AdSM, Hiroshima University, Kagamiyama 1-3-1,Higashi-hiroshima 739-8530, Japan
Fax: +81-824-22-7038, E-mail: semicon@hiroshima-u.ac.jp
*Semiconductor Leading Edge Technologies, Inc., 34-1 Miyukigaoka Tukuba, Ibaraki 305-8501, Japan

1. Introduction

The implementation of a gate dielectric with high dielectric constant (high-k) is currently a major technological challenge for the continuous scaling of complementary metal-oxide-semiconductor (CMOS) devices to sub-100nm technologies [1]. Although the use of a physically thicker high-k gate dielectric for the same electrically equivalent SiO_2 thickness (EOT) is an efficient way to achieve a reduction in the gate leakage to some practical limit under a required capacitive coupling between the gate and Si(100), there are formidable challenges regarding interface issues and electrically active defects in most high-k dielectrics [2]. Among various candidates for the high-k gate dielectric, hafnium-based oxides such as Hf-silicates and -aluminates have been intensively studied as the most promising alternatives [3,4] because of their moderate dielectric constant, favorable band alignment to Si(100) showing high potential barrier heights and relatively good thermal stability in comparison with other high-k materials. Recently, nitrogen incorporation into Hf-silicates (or Hf-aluminates) has received much attention because of further improvement of thermal stability against crystallization and phase separation in annealing at temperatures as high as ~1100°C in ambient N_2 [5] and another practical advantage being an increase in the dielectric constant with increasing nitride content [6]. However, there are some concerns with an increase in gate leakage current and/or fix charge density with nitrogen incorporation. Thus, the control of nitrogen incorporation in Hf-silicates is key for good FET performance with keeping a low leakage current. Despite extensive research, the influence of nitridation on the chemical and electrical structures of Hf-silicates is not completely understood. In particular, the impact of nitiridation on the energy band alignment between Hf-silicates and Si(100) as well as the defect state density are still matters of research from viewpoints of a quantitative understanding of the leakage current and its mechanism.

In this work, we focused on HfSiOxNy/Si(100) heterostructures and studied their chemical bonding features as a function of nitrogen content in HfSiOxNy. In addition, from measurements of the bandgaps of HfSiOxNy thin films and analyses of valence band offsets between HfSiOxNy and Si(100), the energy band alignment of the HfSiOxNy/Si(100) system after N_2 annealing at 1050°C has been studied. The energy distribution of electronic defect states in the oxides stack structure was also quantified by total photoelectron yield spectroscopy (PYS).

2. Experimental

The substrates used in this study were 300mm p-Si(100) wafers. After wet-chemical cleaning, 5nm-thick HfSiOx (Hf/(Hf+Si)=~43%) films were deposited by an atomic layer chemical vapor deposition (ALCVD) method. Subsequently, the nitridation of the films was performed by a microwave-excited plasma using a gas mixture of N_2+Ar, and followed by N_2 annealing at 1050°C to densify the oxynitride films. To characterize the chemical and electronic structures of the films, core line spectra such as Hf4f, Si2p N1s and O1s and valence band spectra were measured by utilizing monochromatized AlKα radiation (1486.6eV: S-XPS). To accurately determine the energy bandgaps of the films, energy loss spectra of O1s photoelectrons were measured by hard x-ray photoelectron spectroscopy (H-XPS) excited synchrotron radiation (~6keV) at a beam line of BL47XU in SPring-8 as well as by S-XPS. To evaluate the energy distribution of filled defect states in the HfSiOxNy/Si(100) structures, total photoelectron yield spectroscopy (PYS) was carried out in the photon energy range of 4-6eV. The experimental details for PYS measurements have been described elsewhere[7].

3. Result and Discussion

The changes in Si2p, Hf4f and N1s spectra for the sample before N_2 annealing at 1050°C are shown in Fig. 1. Each spectrum was normalized with $Si2p^{0+}3/2$ peak at 99.3eV originating from the Si(100) substrate. The oxynitride component observed in the Si2p spectrum is shifted toward the lower binding energy side with an increase of nitrogen content in the film and there was no significant increase in the total intensity of the chemically shifted Si2p signals. These results imply that Si-N bonding units in the film were generated during nitridation by a microwave-excited plasma as also suggested from N1s signals. Correspondingly, the Hf4f spectrum was markedly changed with increasing nitrogen content, so that new components in the lower binding energy side become significant due to the formation of Hf-N bonding units. In the sample with a nitrogen content as high as 20.5at.%, Hf-Nx (x≥2) bonds were likely to be generated in the film. In addition, for samples with nitrogen contents higher than 12at.%, N1s signals at the higher binding energy side from the N-Si component were observable and attributable to NOx units presumably being trapped in voids in as-deposited films. Figure 2 shows Si2p, Hf4f and N1s spectra for the samples after N_2 annealing at 1050°C. The chemically shifted Si2p signals increased through N_2 annealing although the nitrogen content in the film is decreased,
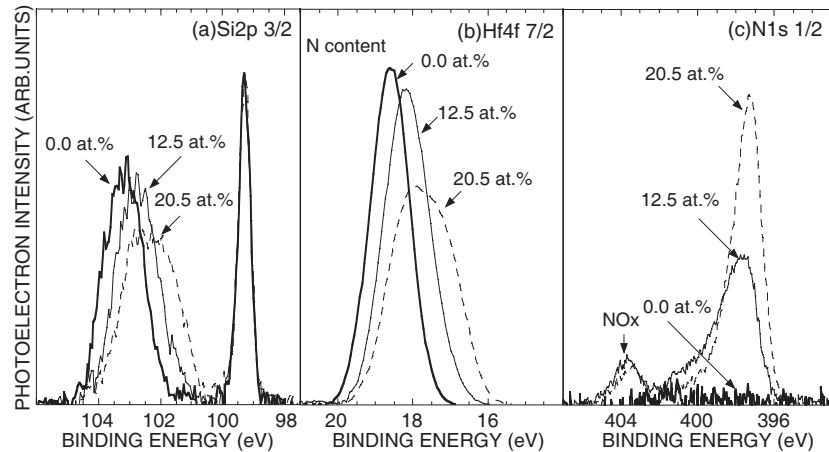
Fig. 1. (a) Si2p3/2, (b) Hf4f7/2 and (c) N1s spectra for ~5nm-thick HfSiOxNy (Hf/(Hf+Si)=~43%,y=0~20.5at.%)/Si(100) before N_2 annealing at 1050°C. The binding energy was calibrated by the Si2p3/2 peak at 99.3eV for the Si(100) substrate and the photoelectron intensity was normalized by the peak intensity of Si2p3/2 signals from the Si(100) substrate.
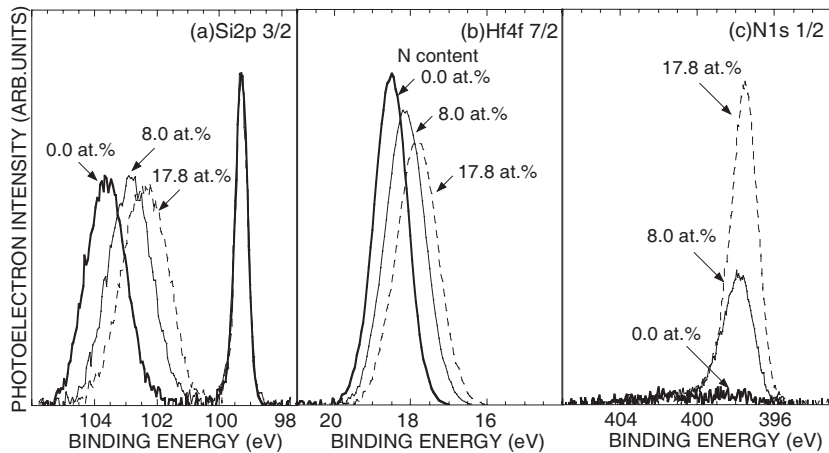

Fig. 2. (a) Si2p3/2, (b) Hf4f7/2 and (c) N1s spectra for ~5nm-thick HfSiOxNy (Hf/(Hf+Si)=~43%,y=0~17.8at.%)/Si(100) after N_2 annealing at 1050°C.

and the increment in the chemically-shifted signals was more pronounced for the films with higher nitrogen content. Hf4f spectra show that Hf-Nx bonding units decreased significantly by the N_2 annealing. These results indicate that N atoms are preferentially bonded to Si by N_2 annealing and suggest that a nitridation reaction at the interface between the film and Si substrate is promoted with released nitrogen atoms from Hf-Nx bonds during N_2 annealing. In fact, for the annealed sample with a nitrogen content of 17.8at.%, the formation of a SiON interfacial layer was confirmed from the depth profile analysis by XPS measurements at each step of wet-chemically etching of the HfSiOxNy layer. Note that for HfSiOx with no N incorporation, the Hf4f spectrum becomes narrower by the N_2 annealing, which implies crystallization in the Hf-rich region. In addition, the high binding-energy component, presumably due to NOx units, seen in the N1s spectrum taken before N_2 annealing is hardly observed, suggesting a thermal desorption of trapped NOx units

The energy bandgap (Eg) values for the thin oxide films can be determined from the threshold energy of the energy loss-spectrum of O1s photoelectrons [8-10]. In the case of Hf-based oxides, the superimposing of Hf4s

core-line signals on the energy-loss signals of primary O1s core line signals makes it difficult to determine the onset of the energy loss signal. To overcome this difficulty, we determined Hf4s signals by using H-XPS measurement as shown in Fig. 3. Because the ratio of the photoionized cross section of the Hf4s core line to that of the Hf4f core line increases significantly with increasing excitation energy, the Hf4s signals excited by the synchrotron radiation with a binding energy of around ~538eV become distinguished in comparison to the signals excited by AlKα radiation. As indicated in Fig. 3, we could determine that the energy separation between Hf4s and Hf4f core lines was about 519.7eV. By subtracting the Hf4s component from the measured O1s photoelectron energy loss spectrum, the energy separation between Hf4s and Hf4f was taken into account and the intensity was normalized by Hf4f signal intensity (Fig. 4(a)). By applying the same procedure to the measured spectra, the inherent O1s energy loss spectra were obtained as seen in Fig. 4(b) and then, in each spectrum, the onset of the energy-loss spectrum was defined by linearly extrapolating the segment of maximum negative slope to the background level. As a result, the Eg value of 5nm-thick HfSiOx with no N
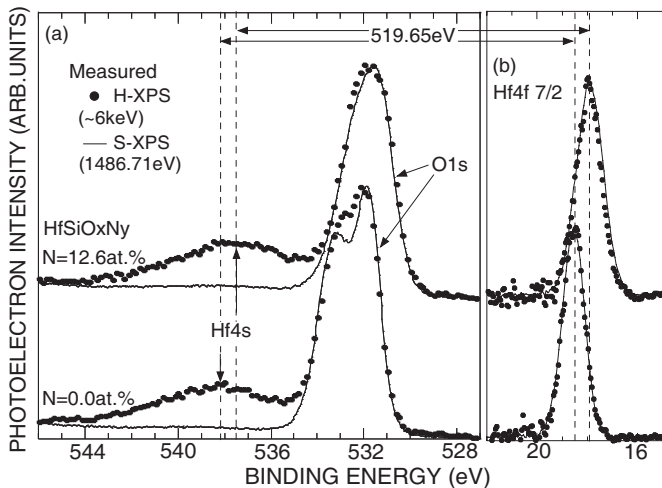
Fig. 3. (a) O1s and Hf4s spectra and (b) Hf4f7/2 spectra for ~5nm-thick HfSiOxNy (Hf/(Hf+Si)=~43%, y=0.0, 12.6 at.%)/Si(100) after N_2 annealing at 1050°C excited by the AlKα (1486.6eV: shown in closed dot) and synchrotron (5951keV : solid line) radiation.
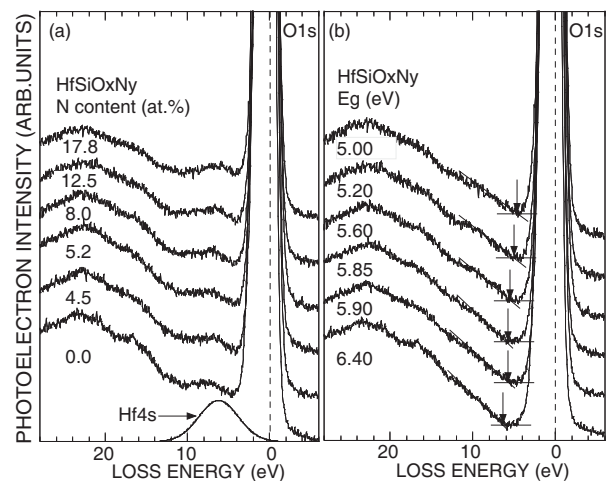

Fig. 4. (a) Measured O1s energy loss spectra for 5nm-thick HfSiOxNy/Si(100) after N_2 annealing at 1050°C and (b) after subtraction of Hf4s contribution from measured spectra as shown in Fig.4 (a). The onset of the energy loss signals for each sample was determined with an accuracy of ±0.05eV.

content after N_2 annealing was determined to be 6.40eV within an accuracy of 0.1eV. For HfSiOxNy, the Eg is gradually decreased with increasing nitrogen content. As the nitrogen content of HfSiOxNy film is increased up to 17.8at.%, the Eg value is reduced by 1.40eV.

To evaluate the valence band (VB) offset between N_2 annealed HfSiOxNy and Si(100), the VB spectra for HfSiOxNy on Si (100) were measured and deconvoluted into two components by subtracting the component originating from the Si(100) substrate. In the spectral deconvolution, the VB spectrum separately measured for wet-chemically prepared H-terminated Si(100) was used. Figure 5 shows the deconvoluted VB spectra of 5nm-thick HfSiOxNy films. From the energy separation of the tops of the deconvoluted VB spectra, the VB offset between HfSiOx with no N content and Si(100) is determined to be 3.85eV±0.05eV. With increasing nitrogen content, the VB offset gradually decreases as quite similarly seen in Eg shrinkage. As nitrogen content is increased up to 17.8at.%, the VB offset is reduced by 1.45eV being almost the same as a decrement of Eg. Based on the the results of Figs. 4 and 5, the conduction band (CB) offsets between HfSiOxNy and Si(100) were estimated and summarized as a function of nitrogen content as shown in Fig. 6. Since a decrease in valence band offset is almost the same as that of Eg, the conduction band offset is almost constant at ~1.5eV. The result is interpreted in terms that the valence band top in oxynitride is derived from non-bonding N2p states instead of non-bonding O2p states, and the conduction band bottom is attributed to Hf5d states independently of nitrogen incorporation.

The energy distribution of electronic defect states is a crucial factor in determining electronic properties especially the leakage current. Therefore, to evaluate electronic defect states in the dielectric stack structure, we measured total photoelectron yields from the samples before and after 1050°C N_2 annealing as a function of photon energy in the range from 3.9 to 5.9eV as shown in Fig. 7. Because there was no photoemission of valence
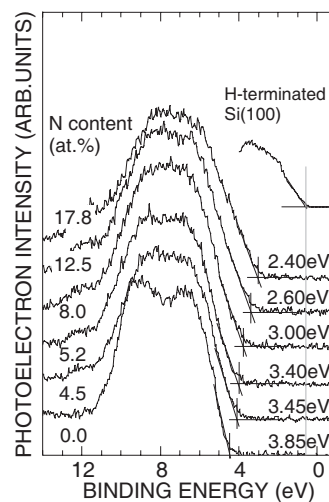

Fig. 5. Deconvoluted valence band spectra for 5nm-thick HfSiOxNy(N=0.0 at.%)/Si(100) after N_2 annealing at 1050°C, where the photoelectron take-off angle was set at 90°. In the spectral deconvolution, the valence band spectrum separately measured for wet-chemically prepared H-terminated Si(100) was used.

electrons in the HfSiOxNy layers in the photon energy region as low as 5.9eV, the photoelectron yield in the energy region corresponding to the Si bandgap reflects filled defect states distributed in oxide layers and at the interfaces. The photoelectron yield for the sample before annealing was decreased with the increase of nitrogen content in the HfSiOxNy films. The result indicates that the defects, which are located in the energy region corresponding to the Si band gap, are reduced by nitrogen incorporation. For the samples after N_2 annealing at 1050°C, the photoelectron yield, namely defect state density, especially near the VB edge was reduced with nitrogen incorporation in the nitrogen content ranging from 4.5 to 12.5at.%. However, in the case of nitrogen contents higher than 17.8at.%, a
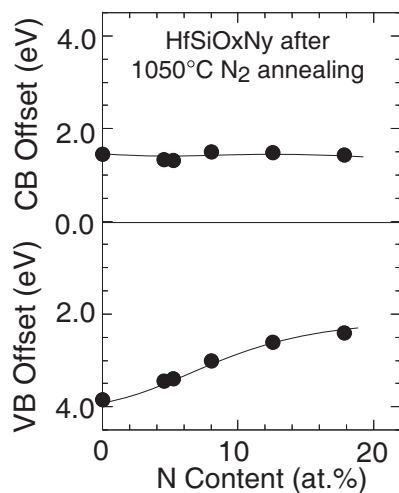
Fig. 6 Changes in the conduction band and valence band offsets between HfSiOxNy and Si(100) after N_2 annealing at 1050°C.
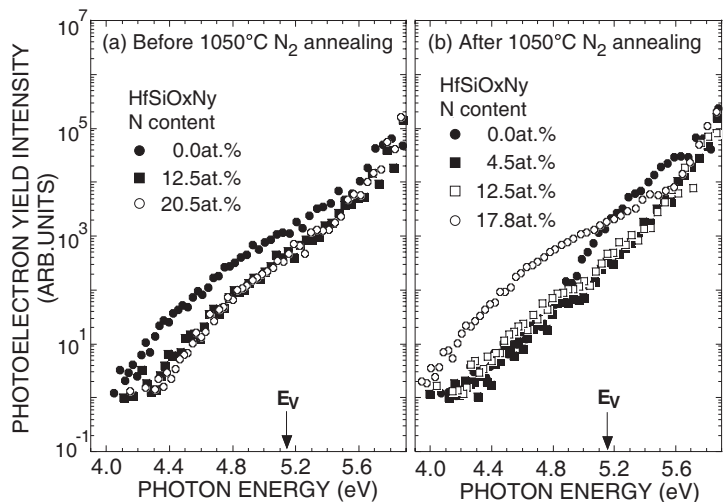

Fig. 7 Total photoelectron yield spectra for HfSiOxNy/Si(100) (a) before and (b) after N_2 annealing at 1050°C. E_v denotes the Si valence band top measured from the vacuum level.

dramatic increase in the photoelectron yield indicates a defect generation in the HfSiOxNy/Si(100) structure by N_2 annealing at 1050°C, which might be related to the interfacial nitridation as discussed in Fig. 2. Further study is needed to gain insight into the origin of defect generation.

4. Conclusion

For the HfSiOxNy(Hf/(Hf+Si)=43%)/Si (100) heterostructure, the influence of nitridation of the dielectric films on chemical and electronic states was evaluated from XPS and PYS measurements. The analysis of Si2p, N1s and Hf4f spectra show that Hf-Nx (x≥2) bonds generated by plasma nitridation are markedly reduced through 1050°C annealing and Si-N bonding units are increased especially at the interface between HfSiOxNy and Si(100). The determination of the energy band alignments between HfSiOxNy and Si(100) has been demonstrated by combining the oxide bandgap values determined from O1s energy loss spectra and the band offsets obtained from valence band spectra. From the PYS analysis, N_2 annealing at 1050°C and nitrogen incorporation less than ~12.5at.% in the HfSiOxNy films are effective in reducing defect state density. In the case of a higher nitrogen content over 17.8at.%, a significant amount of the defects was generated by N_2 annealing at 1050°C.

References
[1] For example: "High Dielectric Constant Materials", Eds H.R. Huff and D.C. Gilmer (2004, Springer).
[2] G.D. Wilk, R.M. Wallace and J.M. Anthony: J. Appl. Phys. 89 (2001) 5243.
[3] G.D. Wilk, R.M. Wallace and J.M. Anthony: J. Appl. Phys. 87 (2000) 484.
[4] M. Yamaoka, A. Ohta and S. Miyazaki: Ext. Abstr. Int. Conf. Solid State Devices & Materials (Tokyo, 2003) p. 810-811.
[5] M.R. Visokay, J.J. Chambers, C.H. Chen, A.L.P. Rotondaro, A. Shanware and L. Colombo: Appl. Phys. Lett. Vol. 80 (2002) 3188.
[6] M. Koyama, A. Kaneko, T. Ino, M. Koike, Y. Kamata, R. Iijima, Y. Kamimuta, A. Takashima, M. Suzuki, C. Hongo, S. Inumiya, M. Takayanagi and A. Nishiyama: IEDM Tech Dig., (2002) p. 847.
[7] S. Miyazaki, T. Maruyama, A. Kohno and M. Hirose, Microelec. Eng., 48 (1999) 63.
[8] S. Miyazaki, N. Narasaki, M. Ogasawara and M. Hirose, Microelec. Eng. 59 (2001) 373.
[9] M. Yamaoka, M. Narasaki, H. Murakami and S. Miyazaki, Proc. of 2nd Electrochemical Soc. Int. Semicond. Tehnol. Conf. (Tokyo, 2002) 229.
[10] S. Miyazaki, J. Vac. Sci. Technol. B19 (2001) 2212.