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Fluorescence XAFS study of local structures in high-k gate dielectrics HfSiON/SiON/Si annealed at various nitrogen gas partial pressure

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Abstract. Geometric structures for HfSiON/SiON/Si films annealed at various N_2 gas partial pressures were investigated using fluorescence XAFS measurement at Hf L_{III}- and L_I-edge. The XAFS analysis has revealed that the local structures around the Hf atoms strongly depend on the N_2 gas partial pressure. For the sample annealed at the N_2 gas partial pressure of 10 Torr HfN and HfSiON coexist, and for the samples annealed at the N_2 gas partial pressure above 100 Torr Hf atoms form HfSiON only. These results indicate that the formation of HfN for HfSiON/SiON/Si films can be suppressed by annealing at proper partial pressure of N_2 gas.

1. Introduction

High-dielectric constant (high-*k*) materials such as HfO_2 and $HfSi_xO_y$ have attracted considerable attention as alternative gate dielectrics [1]. However, in high-temperature annealing processes for dopant activation there are several problems such as the formation of metallic component, crystallization, and oxygen vacancy [2-4]. It is important to resolve these problems in order to improve the device performance.
In the present work, geometric structures for HfSiON/SiON/Si films annealed at various N_2 gas partial pressures (P_{N2}) were investigated by using fluorescence x-ray absorption fine structure (XAFS) measurement.

2. Experimental

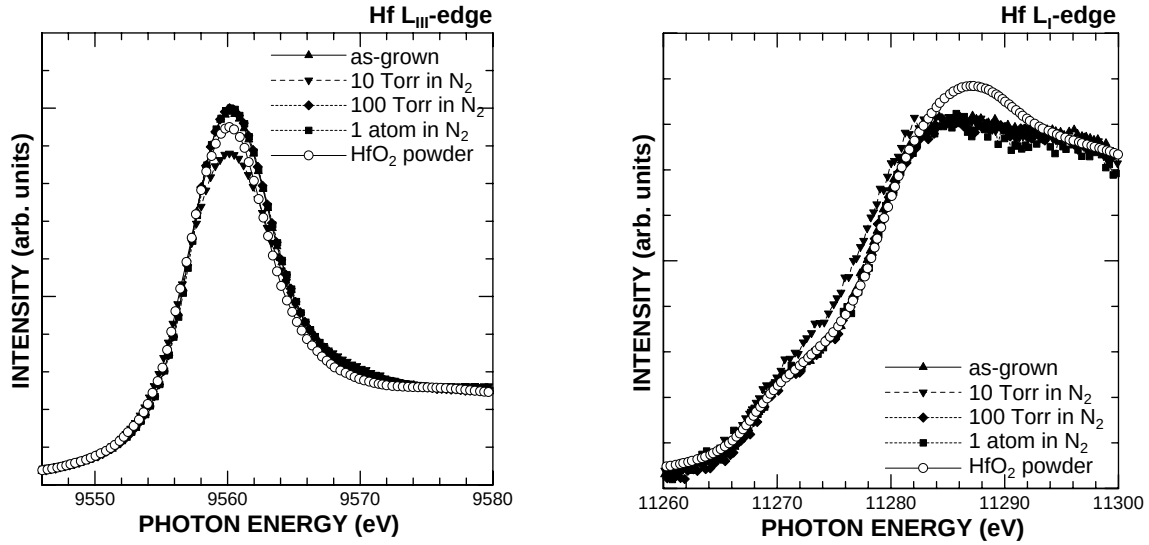
Amorphous HfSiON ([N] = 20%) films with thickness of 2 nm were deposited on clean p-type Si (001) substrates by atomic layer deposition. There was a 0.7-nm-thick SiON interfacial layer between a Si substrate and the HfSiON film. Details of the sample growth procedures were summarized in Reference 5. Each sample was annealed at 1050 °C for 1 min at various pressures of N_2 gas by the direct current flowing method through sample. HfO_2 powder was also measured by transmission mode as reference for HfSiON.

HfSiON is formed by replacing a part of Hf and O atoms by Si and N atoms in HfO_2, respectively. Coordination numbers of first nearest-neighbor O (and N) atoms around Hf atoms in HfO_2 and HfSiON without anion vacancies are the same (7 ~ 8).

The XAFS measurements were performed at the bending-magnet beam line BL14B2 at the SPring-8 with a Si(111) double crystal monochromator using synchrotron radiation from the 8GeV storage ring [7]. The XAFS spectra for the HfSiON films were measured in the fluorescence-detection mode. Intensity of incident X-ray beam was monitored by a nitrogen-filled ionization chamber, while the X-ray fluorescence signal was detected by an array of 19 elements of Ge solid state detectors. All the XAFS measurements were performed at room temperature. The XAFS spectra were analyzed by REX 2000 XAFS analysis package [8].

3. Results and discussion

Figure 1 represents L_{III}- and L_I-edge x-ray absorption near edge structure (XANES) spectra for HfSiON films and HfO_2 powder. In figure 1(a), intensities of white line for the as-grown and annealed HfSiON films at P_{N2} above 100 Torr are higher than that of HfO_2 powder. On the contrary, the white line intensity for the HfSiON film annealed at P_{N2} of 10 Torr is lower than that of HfO_2 power. In figure 2(b), absorption edge of the HfSiON film annealed at P_{N2} of 10 Torr around 11.27keV shift toward lower energy compared to that of the other HfSiON films. The spectral features of the HfSiON films annealed above P_{N2} of 100 Torr resemble that of the as-grown HfSiON film.



(a) (b)

Figure 1. (a) Hf L_{III}- and (b) Hf L_I-edge XANES spectra for HfSiON films and HfO_2 powder.

Figure 2(a) shows the Hf L_{III}-edge $k^3\chi(k)$ extended x-ray absorption fine structure (EXAFS) spectra for the HfSiON films and HfO_2 powder. Compared with the experimental spectra, theoretical EXAFS spectra for HfSiON, HfN, and $HfSi_2$ generated by FEFF8 are also shown in figure 2(b) [8]. It is found that the spectral feature of the HfSiON film annealed at P_{N2} of 10 Torr is quite different with that of the other HfSiON films, and is similar to that of HfN. The spectral features for the as-grown and annealed HfSiON films at P_{N2} above 100 Torr resemble that for HfO_2 powder. Figure 3 shows the Fourier transformed Hf L_{III}-edge EXAFS spectra for HfSiON films and HfO_2 powder. For all the HfSiON film, main peaks were observed at 1.8 Å, which is close to that due to nearest neighboring O and/or N atoms for the HfO_2 powder, HfSiON and HfN. Thus, it is deduced that the main peaks at 1.8 Å are due to Hf-O and/or Hf-N bond. For the HfSiON film annealed at P_{N2} of 10 Torr additional peak was observed at 2.9 Å, which is close to that Hf-Hf bond in the theoretical EXAFS spectra of HfN. Therefore, it is expected that the additional peak at 2.9 Å is

due to Hf-Hf bond in HfN. For the HfSiON films except that annealed at P_{N2} of 10 Torr, peaks due to higher coordination shell above 2Å were not clearly observed in figure 3(a). Thus, it is expected that the annealing above P_{N2} of 100 Torr suppress crystallization of the amorphous HfSiON films.

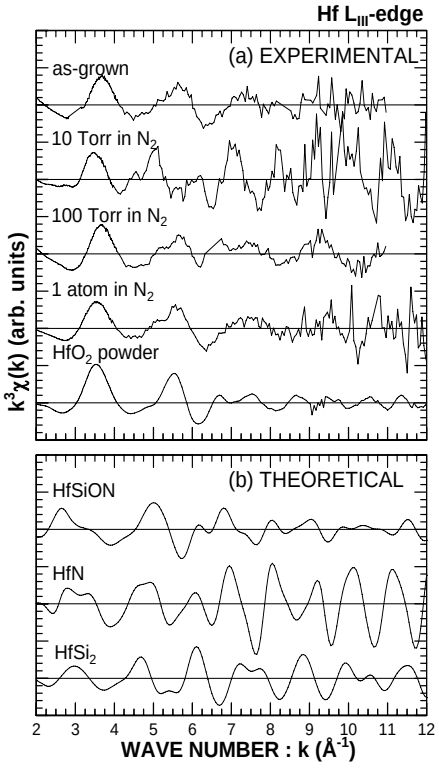


Figure 2. Hf L_{III}-edge EXAFS oscillation functions $k^3\chi(k)$ spectra for (a) HfSiON films and HfO_2 powder, and (b) theoretical EXAFS spectra for HfSiON, HfN, and $HfSi_2$. Theoretical EXAFS spectra were generated by FEFF8. For the theoretical spectra, the Debye-Waller factor was assumed as 0.05 Å for the bond length below 4.0 Å and 0.075 Å for the bond length above 4.0 Å.

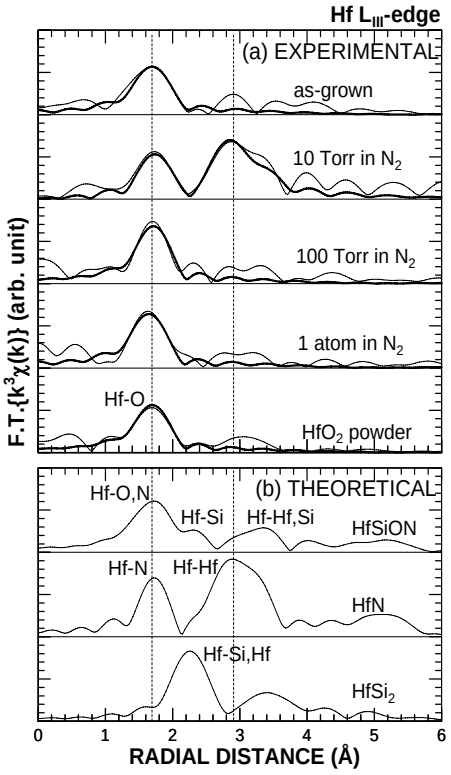


Figure 3. Fourier transform of Hf L_{III}-edge EXAFS oscillation functions $k^3\chi(k)$ spectra for (a) HfSiON films and HfO_2 powder (thin solid lines: experimental data, thick solid lines: curve-fitting data), and (b) theoretical EXAFS spectra for HfSiON, HfN, and $HfSi_2$. The Fourier transformation was performed in the k range of 3.0 – 10.0 Å^{-1}. Theoretical EXAFS spectrum was generated by FEFF8.

In order to investigate the details of the measured EXAFS spectra, parameter fitting was conducted with the theoretically generated spectra. The curve-fitting was carried out with theoretically calculated backscattering amplitude, phase function, and mean free path using FEFF8. Table 1 shows best-fit parameters for HfSiON films and HfO_2 powder. For the as-grown and annealed HfSiON films at P_{N2} above 100 Torr, Hf-O bond was fitted best. Obtained Hf-O bond lengths are 2.11 – 2.15 Å, which are close to that of HfO_2 (2.14 Å) and HfSiON (2.12 – 2.13 Å) [11]. It is difficult to distinguish each atomic species with adjacent atomic number such as N and O atoms by EXAFS analysis. Thus, it is expected that Hf atoms in the as-grown and annealed HfSiON films at P_{N2} above 100 Torr are mainly coordinated by O and N atoms. Obtained coordination numbers of oxygen were smaller than that of HfO_2. For the as-grown and annealed HfSiON films at P_{N2} above 100 Torr, the formation of secondary phases such as $HfSi_2$ and HfN was not observed in figure 3. It is reported that for the HfSiON coordination number decrease as increasing

nitrogen content because of formation of anion vacancy [11]. Therefore, it is suggested that HfSiON with oxygen vacancy was formed for the as-grown and annealed HfSiON films at P_{N2} above 100 Torr. For the HfSiON film annealed at P_{N2} of 10 Torr, it is found that Hf-N and Hf-Hf bond coexist. Obtained Hf-N and Hf-Hf bond lengths are 2.21 and 3.22 Å, respectively. Although the Hf-Hf bond length is close to that (3.19 Å) of HfN, the Hf-N bond length is shorter than that (2.25 Å) of HfN [9]. Thus, it is considered that HfN and HfSiON coexist in the HfSiON film of annealed at P_{N2} of 10 Torr.

Table 1. Best-fit values of parameters for the HfSiON films and HfO_2 powder. r : bond length; N : coordination number, σ : Debye-Waller factor, respectively. The errors on absolute values of Hf-O and Hf-Hf bond lengths are 0.02 Å and 0.05 Å, respectively. The errors on absolute values of the coordination numbers and Debye-Waller factor are the 20-30%.

Samples	Bond type	r (Å)	N	σ (Å)
As-grown	Hf-O	2.12	4.4	0.108
10 Torr	Hf-N	2.21	6.0	0.093
	Hf-Hf	3.22	9.6	0.080
100 Torr	Hf-O	2.15	3.8	0.088
1atom	Hf-O	2.11	3.9	0.099
HfO_2	Hf-O	2.14	7	0.138

The XAFS results revealed that for the HfSiON film annealed at P_{N2} of 10 Torr HfN and HfSiON coexist, and for the HfSiON films annealed at P_{N2} above 100 Torr the Hf atoms formed HfSiON dominantly. These results indicate that the formation of Hf-nitride for the HfSiON/SiON/Si films can be suppressed by annealing at proper partial pressure of N_2 gas (P_{N2} ~ 100 Torr).

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