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Interfacial Chemistry of p-CVD-grown Ultrathin Si Oxynitride Films

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1. Introduction

Extensive studies have been performed on ultrathin Si oxynitride films because protection against boron penetration and hot carrier resistance can be realized by incorporating nitrogen atoms at the SiO_2/Si interfaces and the poly-Si/SiO_2 interfaces. However, the role and chemical structure of the nitrogen atoms have not been elucidated yet. In order to clarify the role of nitrogen to stabilize the SiO_2/Si interfaces, the depth distribution and chemical structures of nitrogen atoms should be precisely determined with atomic scale resolution. Recently, Ushio *et al.*[1] calculated the N 1s chemical shift based on the LDA-DFT calculation and found that the increase in the second nearest neighbor O atom causes N *1s* shift toward higher energy by 0.3 to 0.8 eV In this study, we have performed high-resolution photoelectron spectroscopy in order to determine the precise chemical bonding structures of ultrathin Si oxynitride films grown on Si by the plasma-enhanced chemical vapor deposition (CVD) method.[2]

2. Experimental

Photoelectron spectroscopy experiments with a Scienta SES100 electron analyzer were performed at the BL-2C of the Photon Factory in KEK. Photon energy was set between 500 eV and 620 eV, where the total energy resolution was measured at the Au Fermi edge to be 180 meV. Plasma-enhanced CVD SiON films were grown on HF-treated Si (100) substrates at 500°C with an SiH_4 gas, an N radical gas and an O_2 gas with different ratios. The oxygen concentration in the SiON films used in this experiment were determined by *in-situ* XPS to be 2 %, 14 % and 42 %.

3. Results and discussion

In Si 2*p* photoelectron spectrum of 2% oxygen, the largest peak is assigned to the Si_3N_4 component with the chemical shift of 2.72 eV from the bulk component of Si $2p_{3/2}$. With increasing the oxygen content in SiON films, the Si_3N_4 peak is decreasing, The analysis of angle-resolved photoelectron peak intensities of Si *2p* chemically shifted components reveals that the SiON film with the oxygen concentration of 2 % has a 0.5 nm thick SiO_2 top layer and an Si_3N_4 layer beneath.

Figure 1 shows N *1s* photoelectron spectra for the SiON film with the oxygen concentration of 2 %. The peak fitting procedure reveals that all of the SiON films with 2%, 14 % and 42 % O concentrations have the N1 component which can be assigned to the dominant $[Si\text{-}Si_{3-x}N_x]_3N$ component located at about 397.6 eV, the N2 component to probably the $[Si\text{-}Si_{3-x}O_x]_3N$ component with 0.7 eV chemical shift, and the quite small N3 component to $[Si_2O]N$. It should be noted that the N2 component becomes larger with increasing the take-off angle, suggesting that the N2 component exists in the more surface region.

In order to determine the in-depth profiles of N2 and N1 components, the intensity ratios of N2/N1 were plotted as a function of the take-off angle. The p-CVD SiON film has a three layer structure consisting of the surface SiO_2 layer (about 0.5 nm thick), the SiON layer with the N2 component (about 0.3 nm thick), and the Si_3N_4 layer with the N1 component.[3] There is a transition region with about 0.2 nm thickness between the N1 and N2 layers. These results indicate that in the case of 2 % O concentration SiON film the Si_3N_4 film is formed with almost no N2 components by plasma-enhanced CVD.

In conclusion, interfacial chemistry in ultrathin SiON films has been analyzed by high-resolution photoelectron spectroscopy based on the second nearest neighbor effect of N *1s* chemical shift.

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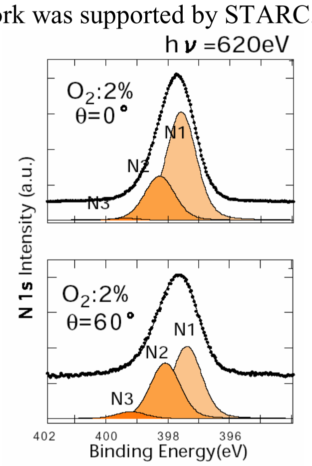

Fig. 1. N 1*s* photoelectron spectra from a p-CVD SiON film.

References

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