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Effects of thermal annealing on charge density and N chemical states in HfSiON films studied by photoemission spectroscopy

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Introduction

High dielectric constant (high-*k*) gate dielectrics are indispensable for decreasing electrical equivalent oxide thickness and low gate leakage current and for overcoming the scaling limit of oxide thickness. Although HfO_2-based materials are suitable candidates for gate dielectrics in terms of their properties, they contain a larger number of trap sites or fixed charges than conventional SiO_2-based dielectric films, resulting in threshold voltage shift, large leakage current, low reliability, etc.[1,2] In photoemission spectroscopy (PES) measurements, the charge density in ultrathin films is evaluated without using electrodes by measuring the band bending in Si substrates; the band bending is estimated from the core-level peak shifts of the substrate components.[3,4] In this report, we have investigated the annealing effects on the N chemical states and charge density in HfSiON/Si samples annealed at various oxygen gas partial pressures by performing time-dependent PES measurements using synchrotron radiation.

Experimental

HfSiO films with thicknesses of 3.0 nm were deposited on cleaned *p*-type Si (001) substrates by metal-organic chemical vapor deposition. N atoms were incorporated into the HfSiO films using Ar/N_2 plasma. After the nitridation of the films, they were annealed at 800 °C for 1 min in a mixture of nitrogen and oxygen gases. The HfSiON sample was annealed at various oxygen gas pressures from 10^{-4} to 1 Torr and also in vacuum. The PES measurements were carried out at the undulator beam line BL-2C of the Photon Factory.

Results and Discussion

Figure 1(a) shows the x-ray irradiation time dependence of the Si 2*p* core-level spectra of the sample annealed in a vacuum. The shifts in the peak positions directly correspond to the band bending in the oxide film and the Si substrate due to the trapped charges in the dielectric films. The peak positions in the spectra shift toward lower binding energy indicating upward band bending in Si and trapping of negative charges in the HfSiON films [1]. The annealing oxygen gas pressure dependence of the peak positions of the Si $2p_{3/2}$ bulk components as a function of the x-ray irradiation time is shown in Fig. 1(b). The binding energy of Si 2*p* bulk components after x-ray irradiation for 40 min increases with the oxygen partial pressure in the annealing atmosphere. This result indicates that the number of negative charges in the HfSiON films decreases by annealing samples in an oxygen atmosphere. However, the peak shifts of the samples annealed at lower oxygen partial pressure (P_{O_2} = 10^{-2} and 10^{-4} Torr) are not decreased as compared with those of the samples annealed in vacuum. Thus, the the number of trapped charges does not change during x-ray irradiation. In contrast, peak shift of the sample annealed at the highest oxygen partial pressure (P_{O_2} = 1 Torr) has clearly decreased as compared with samples annealed at lower oxygen partial pressure, indicating a significant decrease in the number of trapped charges in the HfSiON film after x-ray irradiation. It is considered that annealing at lower oxygen partial pressure mainly leads to changes in the number of inherent charges, and that the number of trapped charges eventually decreases at the highest oxygen partial pressure.

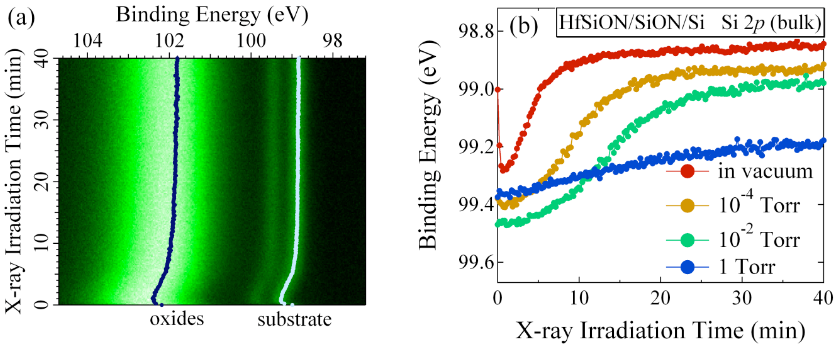

Fig. 1. (a) Image plot of Si 2*p* spectral intensity depending on x-ray irradiation time for HfSiON/SiON/Si sample annealed in vacuum. The Si $2p_{3/2}$ peak positions of the oxide and substrate components obtained by curve fitting are also shown. (b) Binding energy positions of Si $2p_{3/2}$ for substrate components of HfSiON/SiON/Si samples annealed at various oxygen partial pressures as a function of x-ray irradiation time.

References

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