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Depth profiling of chemical states and charge density in HfSiON by photoemission spectroscopy using synchrotron radiation

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Introduction

Among high-*k* materials as alternates to conventional Si-based dielectrics, Hf silicate (HfSiO) has been considered as one of the most promising candidates. In addition, incorporating of N into HfSiO improves the resistance to boron diffusion, inhibits crystallization, prevents the growth of an interface silicate, and increases the dielectric constant. On the contrary, it is reported that N incorporation in HfSiO films introduces defects and causes threshold voltage shift. Therefore, in order to improve performance and reliability for MOS devices with HfSiON gate dielectric films, the evaluation of chemical states and defects of N in dielectrics is necessary.

PES measurements enable us to determine band bending in Si substrate from the energy shift of Si 2*p* core-level for the Si substrate component and consequently evaluate trapped charge in dielectric films. In this study, we have performed time-dependent photoemission spectroscopy using synchrotron radiation for HfSiON/Si with different dielectric film thickness, and investigate the depth profile of N chemical states and charge density in the HfSiON film.

Experimental

The 3.0 nm HfSiO film was deposited on cleaned *p*-type Si (001) substrates by metal-organic chemical vapor deposition and plasma nitridation was performed. The HfSiON/Si sample was dipped into a HF solution in order to gradually reduce the thickness of HfSiON films. Photoemission spectroscopy was carried out at an undulator beam line BL-2C of the Photon Factory in High-Energy Accelerator Research Organization (KEK). The currents from samples to ground (sample currents) are measured by a pico-ampere meter during time-dependent measurements of PES spectra.

Results and Discussion

N 1*s* spectra depending on the HfSiON film thickness were deconvoluted by three components. Depth profiles of atomic concentrations and N chemical states in the HfSiON film were determined from differences between atomic concentrations estimated by intensities of core-level photoemission spectra for samples with different HfSiON film thickness. The obtained profiles show that N atoms are mainly bonded to Si atoms at the interface between the HfSiON film and interfacial layer as well as to Hf atoms near the surface where N atoms have a peak concentration.

For evaluation of charge density in the HfSiON layer, we have measured Si 2*p* core-level photoemission spectra as a function of x-ray irradiation time and have determined the amount of band bending in Si (E_{bb}). The depth profile of charge density in the HfSiON film was determined from the dependence of E_{bb} on HfSiON film thickness. The obtained profiles indicate that the trapping charges are mainly distributed near the surface and there are few charges at the interface between the HfSiON films and the interfacial layer.

Furthermore, charge density is also evaluated by sample current (I_s) as a function of x-ray irradiation time in order to confirm the depth profile determined by PES spectra. The charge density has estimated from integration of transient current during x-ray irradiation and consequently depth profile was determined. The charge density depth profiles determined by two different methods exhibit the same tendency though the amounts of charge density are different as shown in Fig. 1. This indicates that trapping charges are definitely distributed near the surface of the HfSiON film. Comparing with atomic concentrations of N, we found that carrier density has similar depth profile. Moreover, N is mainly bonded to Hf near the surface where these profiles have peaks. These results suggest that Hf-N bonds in the HfSiON film are responsible for the electron trapping.

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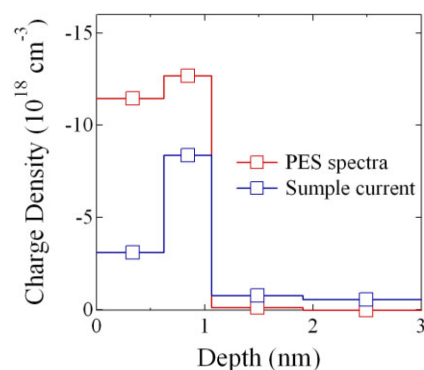

Fig. 1 Depth profile of carrier density in the HfSiON film estimated by PES spectra and sample current.

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