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Segregation of Nitrogen in SiON layer on Si measured by angle-resolved photoelectron spectroscopy

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1 Introduction

The development of high-k dielectric gate insulators has been extensively performed from the demand of further integration in MOS-FET devices. Silicon oxynitride (SiON) film is one of the strong candidates for the high-k materials. It is necessary for high-quality silicon oxynitride films to control the depth profile of nitrogen.

In the previous study, we investigated SiON layers on Si(100) formed by exposing N_2O gas, which has a low toxicity in comparison with other oxynitridation agents[1]. In this study, we report segregation of nitrogen in the SiON layers measured by angle-resolved photoelectron spectroscopy .

2 Experimental

SiON layers were thermally grown on Si(100) substrate with 99.999% N_2O gas at pressures in the range of 10^{-2} Pa - 100 Pa. The substrate was annealed by resistive heating. The nitrogen distributions were investigated by chemical-shift components in Si 2p core-level spectra. The photon energy was set at 160 eV. The obtained spectra were deconvoluted by a least-square fitting procedure using the spin-orbit split Voigt functions for four components associated with silicon substrate, suboxide, nitride, and oxide.

3 Results and Discussion

Figure1(a) shows Si 2p core-level spectra of a SiON layer (thickness of 3.9 Å) on Si(100) grown at a N_2O pressure of 10^{-2} Pa and at a substrate temperature of 800 °C for 3600 s. Three peaks at binding energies of ~ 1.5eV, 2.5eV, and 4.0eV correspond to suboxide, silicon nitride, and silicon oxide components, respectively. As can be seen in this figure, the silicon oxide component is increased and the silicon nitride component is decreased, as a detection angle of photoelectrons with respect to surface normal increases. This result indicates that nitrogen in the SiON layer is segregated near the interface between the SiON layer and the silicon substrate. The reason can be considered as follows. In the reaction of oxynitridation, N_2O gas dissociates into N_2 and O and thus nitridation and oxidation occur independently on the surface. Under the condition of the low N_2O pressure of 10^{-2} Pa and the high reaction temperature of 800 °C in Fig. 1(a), oxygen atom adsorbed on the surface is not stable and thus quickly desorbs from the surface as a volatile SiO molecule[2]. On the other hand, nitrogen strongly bonds to substrate silicon and stably exists on the surface. Namely, the silicon nitride is formed at the initial stage of the growth and works as a nucleus, where the silicon oxide is subsequently formed. This reaction mechanism can be responsible for the nitrogen segregation near the interface. We have also observed by real-time photoelectron spectroscopy (RPS) that nitridation initially occurs, followed by oxidation.

On the other hand, no segregation of nitrogen can be seen in the SiON layer grown at the pressure of 5×10^{-2} Pa in Fig 1(b). This is because the oxide can be initially formed owing to increasing the N_2O pressure, as well as the nitride. We have also obtained the same result by RPS.

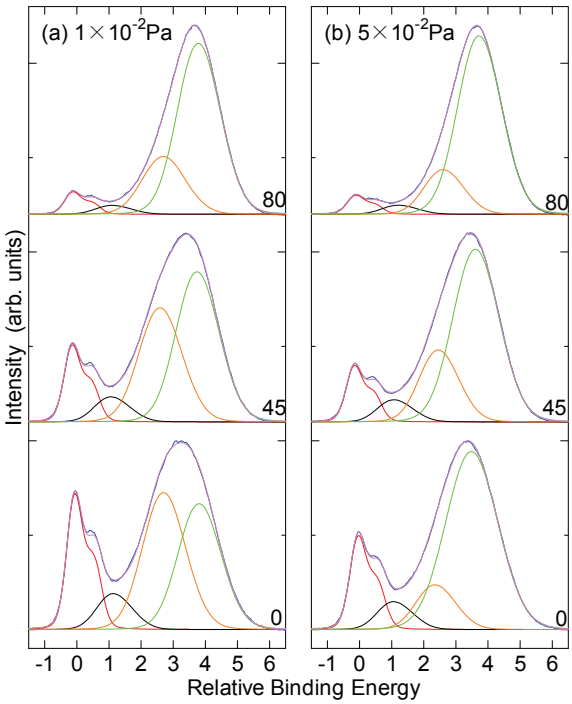

Fig. 1 Si 2p core-level spectra from SiON layers on Si(100) thermally grown at N_2O pressures of (a) 10^{-2} Pa and (b) 5×10^{-2} Pa. The substrate temperature is 800 °C and the growth duration is 3600 s. The detection angle (polar angle) of photoelectrons is changed between 0° and 80°.

References

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