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Depth Profile of Various Bonding Configration of Nitrogen Atoms in Silicon Oxynitrides formed by Plasma Nitridation

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1. Introduction

Ultrathin silicon oxynitrides are important gate dielectrics in CMOS devices, due to their high reliability and ability to suppress boron penetration [1]. Protection against boron penetration at the SiO_2/polycrystalline silicon interface and hot carrier resistance at the SiO_2/Si interface can be attained by incorporating nitrogen atoms at these two interfaces. However, the excessive incorporation of nitrogen atoms at SiO_2/Si(100) interface increases interface roughness [2], thereby decreasing carrier mobility in the channel region. The nitridation of silicon oxide film in NO ambient has been widely used because nitrogen atoms can be incorporated mostly near the SiO_2/Si interface [3]. The nitridation of silicon oxide in nitrogen plasma (abbreviated in the following as plasma nitridation) has been used recently mainly because nitrogen atoms are considered to be selectively incorporated near the surface of the ultrathin silicon oxide film. This can be only verified non-destructively by applying maximum entropy concept to the analyses of the angle-resolved photoelectron spectra [4, 5] arising from the oxynitride films as shown in the following.

2. Experimental Details

Oxynitride films studied were prepared on p-type Si(100) surfaces by wet oxidation at 950°C followed by two kinds of nitridation. One was plasma nitridation followed by annealing (abbreviated in the following as plasma nitridation), while another was nitridation of silicon oxide in NO ambient [5,6] at 950°C (abbreviated in the following as interface nitridation). According to the time of flight secondary ion mass spectroscopy, an oxynitride film(sample A) formed by interface nitridation contains maximum nitrogen concentration of 5 at.% at the interface, while three oxynitride films(sample B, C and D) formed by plasma nitridation contain maximum nitrogen concentrations of 5, 7, 9 at.% on the surface of the films. Thickness of these films as determined by XPS have equivalent silicon oxide film thickness of 1.10, 1.13, 1.16 and 1.21 nm, respectively. The amount and location of nitrogen atoms in oxynitride films were studied from the measurement of N 1s and Si 2p photoelectron spectra excited by Monochromatic Al Kα radiation at photoelectron take-off angle of 8, 11, 15, 20, 30, 40, 52 and 90 degrees with photoelectron acceptance angle of 3.3° at the entrance of electron energy analyzer using ESCA-300 manufactured by Scienta Instruments AB [7]. Other experimental and analytical details were described elsewhere [6].

3. Experimental Results and Discussion

The deconvolution of N 1s spectra shown in Fig. 1 was performed by considering that an asymmetric part in N 1s spectrum in Fig. 1(a) appears on the high binding energy side and an asymmetric part in N 1s spectrum in Fig. 1(b), (c), (d) appears on the low binding energy side. Accordingly, N 1s spectra can be deconvoluted into N1 at 397.95 eV, N2 at 398.25 eV, N3 at 398.7 eV and N4 is 399.69 eV. N1, N2, N3 and N4 spectrum can be correlated with the configuration N1, N2, N3 and N4 shown in Fig. 2 [8], respectively. The intensity NNn of spectrum Nn in Fig. 1 normalized by the intensity NO of the Si $2p_{3/2}$ spectrum arising from SiO_2 are shown as a function of photoelectron take-off angle in Fig. 3. By applying the maximum entropy concept to the analyses of Fig. 3 and the dependence of intensity NS of the Si $2p_{3/2}$ spectrum arising from silicon substrate normalized by NO on photoelectron take-off angle, the most plausible distribution of Nn in two kinds of oxynitride films were obtained and were shown in Fig. 4. Here, in order to simplify the analyses the densities of the oxynitride films were assumed to be the mixture of silicon oxide and silicon nitride. A value of 3.1 nm was obtained for the electron escape depth in silicon nitride so as to simulate the experimental data. According to Fig. 4, the distribution of nitrogen atoms and their bonding configurations in the oxynitride films formed by the plasma nitridation is quite different from those in the oxynitride films formed by the interface nitridation. Furthermore, the nitrogen atoms localized near the surface having configuration N3 results in dashed line in Fig. 3(c), while the nitrogen atoms localized near the interface having configuration N3 results in dotted line in Fig. 3(c). Therefore, the coexistence of the configuration N3 near the surface and the configuration N3 near the interface result in rather smooth dependence of NN3/NO on the photoelectron take-off angle as shown in Fig. 3(b), (c) and (d).

4. Conclusions

It was found from the angle-resolved photoelectron spectroscopy study that the distribution of nitrogen atoms and their bonding configurations in oxynitride films formed by the plasma nitridation is quite different from those in oxynitride films formed by the interface nitridation.

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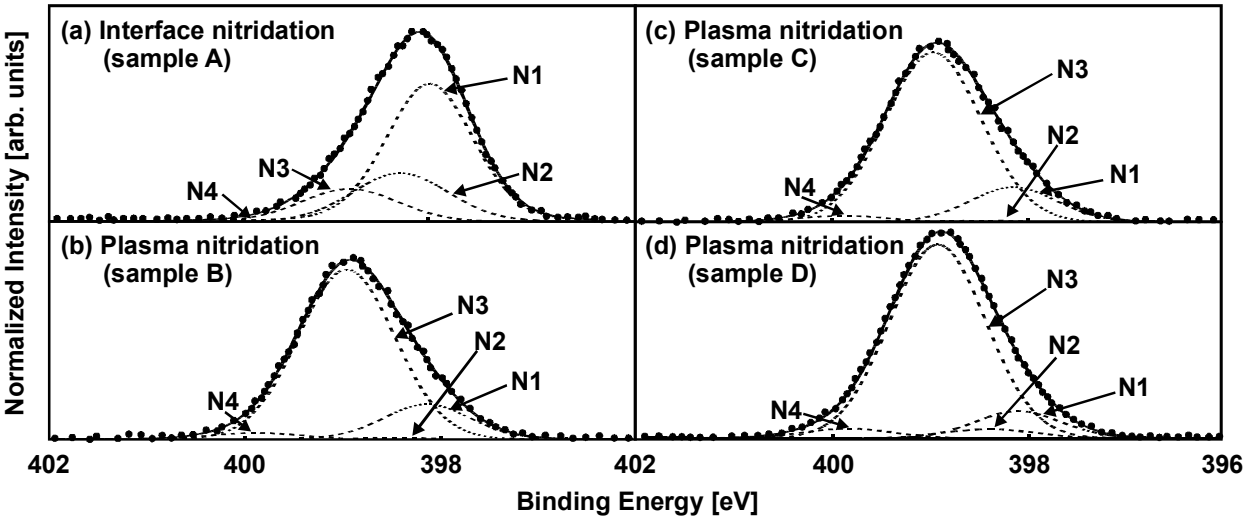
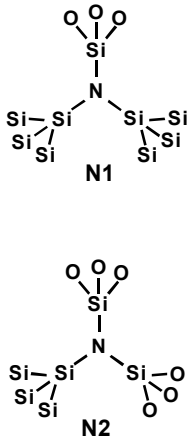


Fig. 1 N 1s spectra measured at photoelectron take-off angle of 90° for four kinds of oxynitride films.



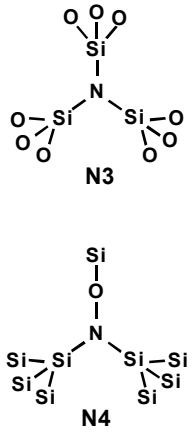


Fig. 2 Bonding configurations of nitrogen atoms.

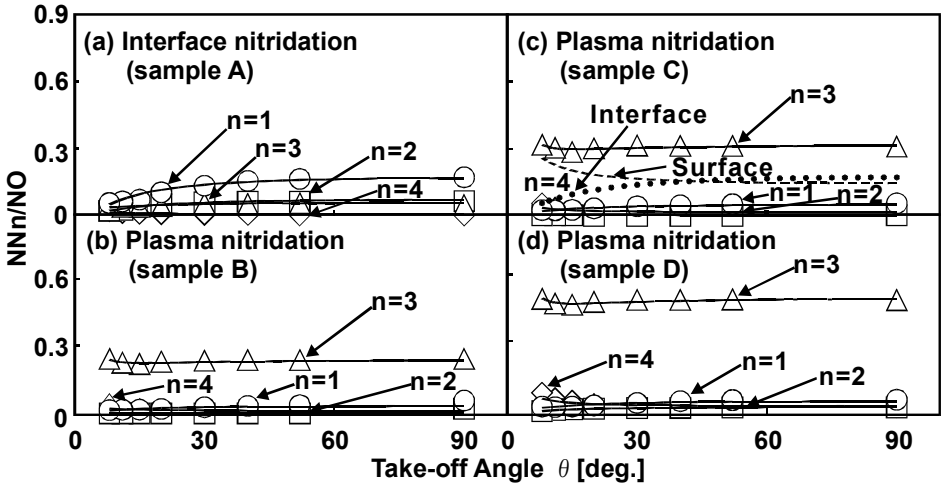


Fig. 3 Dependence of NNn/NO on photoelectron take-off angle measured for four kinds of oxynitride films.

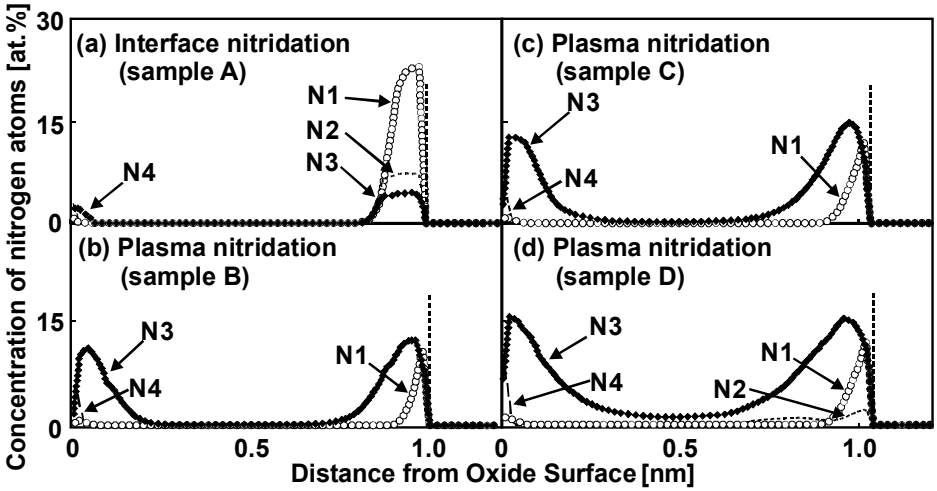


Fig. 4 Distribution of bonding configurations Nn in four kinds of oxynitride films.