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High-Resolution Photoelectron Spectroscopy of Interfacial Nitrogen in 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 SiO₂/Si interfaces [1]. In the previous photoelectron spectroscopy studies for Si oxynitrides, the broad N 1s spectra (FWHM = 1.5 eV) in X-ray photoelectron spectroscopy (XPS) are usually fitted with wide Gaussian width. Therefore, N 1s peak has been decomposed with only one Si₃N₄ component and other SiO_xN_y components.

In this study, we performed high resolution photoelectron spectroscopy using bright synchrotron radiation (SR) soft x-rays from an undulator in order to determine the chemical bonding structures of ultrathin Si oxynitride films.

2. Experimental

Angle-resolved photoelectron spectroscopy experiments were carried out at the undulator beamline U7 of the Pohang Light Source in Pohang Accelerator Laboratory. Photon energy was set at 500 eV. Samples were Si oxynitride films grown by rapid thermal nitridation (RTN) using NO and N₂O gases on SiO₂ films which were grown on p-Si(100) substrates by RTA using O₂ gas at 800°C. The total thickness was determined by ellipsometry to be 1.8 nm. In situ nitridation experiments were also performed by exposing an clean p-Si(100)2x1 surface to NO gas at 950°C.

The nitrogen concentrations for NO- and N₂O-RTN films were determined to be 5.6x10¹⁴cm⁻² and below detection limit, respectively, by Rutherford Backscattering Spectroscopy (RBS).

2. Results and Discussion

Figure 1 shows angle-resolved photoelectron spectra of N 1s core levels from the NO-RTN sample. In this experiment, we determined the N 1s peak position by

assuming the Si 2p_{3/2} peak position from the Si substrate to be 99.20 eV. In Fig. 1 the N 1s spectra are shown on a scale of relative binding energy with the N1 peak at 397.53 eV as a standard, and the N 1s spectra are decomposed into three components, N1, N2 and N3. The energy shift of N2 from N1 is 0.59 eV, while that of N3 from N1 is 1.13 eV. So far, many XPS data have been reported, concluding that at the SiON/Si interface there exist Si₂-N-O, Si-N-O₂, and/or Si₃-N components. However, judging from the peak position of N1 at 397.53 eV, N1 can be assigned as the Si₃-N component. Based on the first principles calculation of N 1s chemical shifts considering the second nearest neighbor effect, Cerofolini et al. [2] concluded that [Si=Si(O)]₃N having three second neighboring O atoms shows +0.39 eV shift, [Si-Si(O)₂]₃-N having six second neighboring O atoms shows +0.50 eV, and [Si(O)₃]₃N having nine second neighboring O atoms shows +0.66 eV, Chang et al. [3] reported N 1s angle-resolved photoelectron spectroscopy results, showing that mainly the Si₂NO component having 1.77 eV of chemical shift exists in the NO oxynitride film, besides NSi₃, NSiO₂ (3.78 eV) and NO₃ (5.55 eV). However, judging from our chemical shift of 0.59 eV, N2 component can be regarded as NSi₃ shifted by the second neighboring effect. Rignanese et al. [4] reported the first systematic theoretical study of N 1s, showing that N 1s peak from Si₃N₄ in the 2 nm SiO₂ is shifted by about 0.4 eV from that at the interface owing to core-hole screening effect. By combining the second neighboring effect and the screening effect, we conclude that the Si₃-N component exists at the interface, while the [Si(O)₃]₃N component exist in the oxide. The N3 component can be assigned as Si₂NO.

The angle-resolved photoelectron peak intensities of N1 and N2 can be analyzed based on a simple intensity attenuation model with electron escape depths [5]. If we assume that the N2 component exists only at the oxide layer d nm above the interface, we come to the conclusion that the

above the interface. The schematic model is shown in Fig. 2

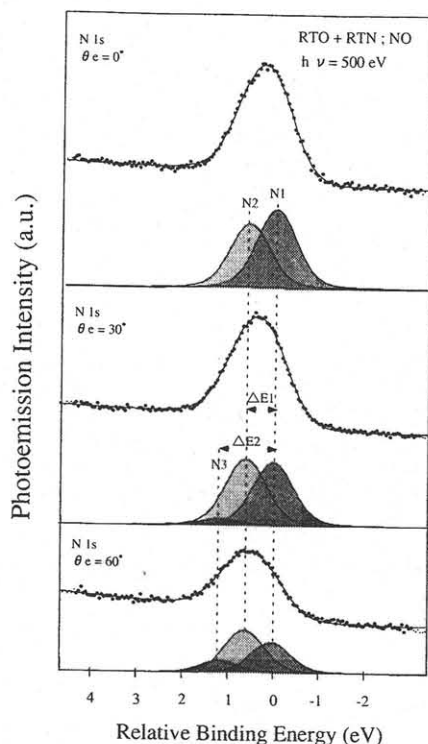


Fig. 1 N 1s photoelectron spectra from the NO-RTN oxynitride film measured with emission angles of 0°, 30° and 60°. Spectra were decomposed with three components N1, N2 and N3.

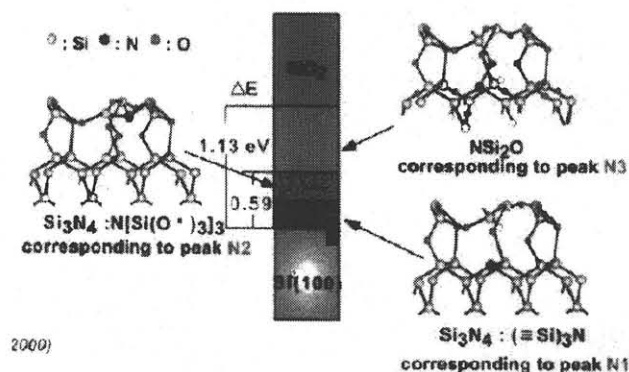


Fig. 2 Schematic model of chemical configuration in the NO-RTN oxynitride film (1.8 nm thick).

Next, in order to understand the formation mechanism of the SiN chemical bonding at the SiO₂/Si interface, we analyzed Si(100) surfaces which were exposed to the NO gas at 950°C in the SR photoelectron spectroscopy chamber. Figure 3 shows N 1s photoelectron spectra from *in situ* NO-nitrided Si surfaces with 1000 and 3000 Langmuir NO doses. Here the N1 component has a binding energy of 397.53 eV, which corresponds to the Si₃-N. N2 shows +0.59 eV chemical shift which is also assigned as the [Si(O)₃]₃N component. The N3 with 1.28 eV shift can be due to Si₂NO.

Si 2p peak analysis revealed that the thicknesses of both oxides were 1.4 nm and 2.4 nm, respectively. Based on the same attenuation model, it is found that for both 1000 L and 3000 L oxynitride films, the N1 components exist at the interface, while the N2 components exist at the oxide layer about 2 nm above the interface.

Thus, it is found that NO-nitridation for SiO₂ films and clean Si(100) surfaces results in the same configuration of nitrogen atoms in the interface region with two kinds of chemical bonding suggesting a “nitrogen double-layer interface model”, where nitrogen atoms play an important role of relaxing the interface strain and probably increasing the atomic density at the interface.

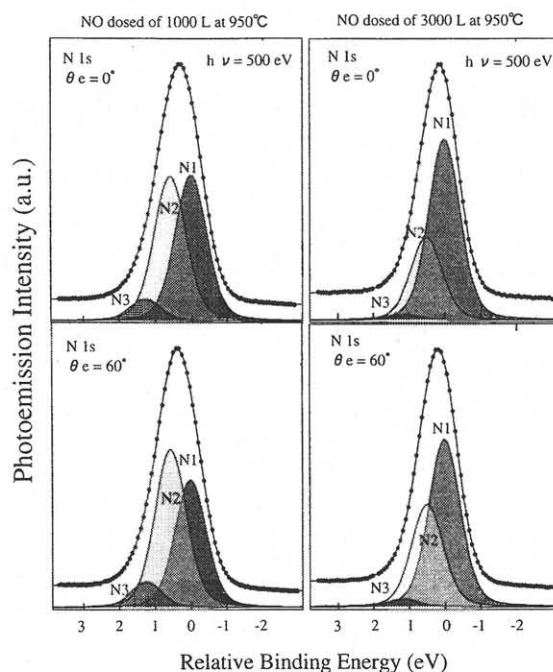


Fig. 3 N 1s photoelectron spectra from *in situ* NO-nitrided Si surfaces with different doses measured with emission angles of 0° and 60°.

4. Conclusions

High-resolution angle-resolved photoelectron spectroscopy analysis of RTN oxynitride films and *in situ* NO-nitrided films revealed that N atoms with mainly two chemical bonding configurations exist in the SiO₂/Si interface region, suggesting the “nitrogen double-layer interface model”.

References

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