Chemical structure of N Atoms in the Transition Region of the SiO(N)/Si Interface
-A New Spectroscopic Method with Hydrogenation Reaction in HF Acid-

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1. Introduction

It is essential to incorporate the N atoms in the ultra-thin gate oxide to control Boron penetration through the oxide layer and to improve reliability during high-speed CMOS device operation [1]. To control the N atoms precisely is important, but little has been known of either the chemical structure at the SiO(N)/Si interface or the depth profile of the N atoms in the SiO(N) layer [2, 3].

It is well known that the Si surface after being removed from the oxide layer completely in HF solution is terminated with the H atoms [4]. This hydrogenated surface can be detected easily in infrared-spectra separately according to the chemical structures and the bound sites [5, 6]. It was concluded that the surface dangling bonds are terminated with the H atoms, but the bulk structure remains after the HF treatment [7, 8]. We applied this idea to the chemical structure of N atoms in the transition region of the SiO(N)/Si interface. During dissociating the film in the HF solution, a few N atoms can be detected as the N-H bond. The N-H stretching frequencies indicate the chemical structure of N atoms. To combine the investigation of wet chemistry and infrared spectroscopy makes it possible to know of the chemical structure and their concentrations of incorporated N atoms in the SiO2 layer and at the SiO2/Si interface.

2. Sample Preparation and Experiment

The Si sample was cut 50 x 15 mm with 45 degree bevels on each of the short sides from a 0.625 mm-thick wafer. Both sides of the prism had been polished to be optical flat. On the surface of this Si prism, the thin SiO(N) film was grown in a NO atmosphere at 1170 K. This film contained 4% N atoms estimated by a standard XPS technique and its thickness was about 2 nm.

The SiO(N) film was slightly etched in 0.1% HF solution and was analyzed its surface by the FT-IR. The hydrogenated structures were detected sensitively by the internal multireflection ATR method. To obtain the depth profile the wet etchings and the FT-IR measurements were repeated.

3. Chemical Structure of N Atoms in the Transition Region of the SiO(N)/Si Interface

Fig. 1 shows the ATR spectra for the O-H and N-H stretching region of SiO(N) and thermal SiO2 surfaces after slightly etched in HF solution. These spectra were same except that the SiO(N) spectrum had a shoulder around 3380 cm\(^{-1}\) due to N-H structure. Fig. 2 shows the peak area of the N-H and Si-H structure as a function of film depth. The depth was determined by the peak height of TO phonon of Si-O stretching mode observed with the etched sample. When the SiO(N) film was slightly etched, the N-H structure was detected (Point A). This N-H peak area was increased at the close to the interface (Point B). When the interface was appeared, the Si-H structure was detected (Point C). Further more, the N-H and O-H structures were finally removed and the surface was covered with Si-H structure (Point D).

The chemical structure is determined by the peak location of spectrum. Fig. 3 shows the change of spectra for the N-H and Si-H stretching regions. Points A - D denote characteristic depths defined in Fig. 2. At the Point A, N-H structure was detected and its frequency was corresponded to the O-Si-NH-Si-O structure (see Fig. 4). The N-H peak area at the Point B was larger than any other points, but the N-H peak locations were almost unchanged to point A. Therefore, the structure of the N atom was those of point A. The N-H peaks gradually shifted to higher frequencies until the interface appeared (Point C). The blue shift of the N-H peak is able to be generally explained by the concentration increment of the O atoms, which is unlikely in our SiO(N) film. It rather suggests the densification of the SiO(N) film, which is consistent with the previous result obtained for SiO2/Si interface [9]. With the etching, the N-H structure in the transition region of the SiO(N)/Si interface shifted to lower frequencies (Point D). This shift indicates that the N-H structure is changed to the Si-Si-NH-Si-Si. The Si-H peak detected at the point C was broader than that at Point D. This result indicates that the area covered with Si-H is very small at the early stage the interface is exposed. With the Si surface area, Si-H peak became sharp.

3. Conclusions

After the SiO(N) film was etched in HF solution, we found that the N atoms were hydrogenated. The change of chemical structure was able to detect by repeating the etching of SiO(N) film and the FT-IR measurement. We successfully detected the N atoms even with the low concentration of 4% and especially demonstrated the change of chemical structure of the N atom in the transition region of the SiO(N)/Si interface.

References

Fig. 1 Infrared spectra of SiO(N) and thermal SiO2 surface in O-H and N-H stretching regions. The SiO(N) spectrum has a clean shoulder around 3380 cm⁻¹ corresponding to N-H stretching.

Fig. 2 Peak area of N-H and Si-H stretching in the transition region of the SiO(N)/Si interface as a function of film depth. The depth was determined by the peak height of TO phonon of Si-O stretching mode observed with the etched sample. Point A:N-H structure in the SiO(N) film. Point B:N-H structure in the film close to the interface. Point C:N-H structure on the interface exposed partially. Point D:N-H structure on oxygen free interface.

Fig. 3 Shift of N-H and Si-H stretching frequencies. The N-H peaks were extracted separately from the original spectra. The points A - D denote characteristic depths defined in Fig. 2.

Fig. 4 Surface structures. At the point A-C, the chemical structure of the N atom was unchanged. When SiO(N) film etched and the interface was exposed, another chemical structure appeared.