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Native Oxides Formed During Wet Chemical Treatments

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From the detailed studies on the chemical structures of native oxides formed in a solution of NH_4OH and in a hot solution of HNO_3, Si-Si bonds and Si-H bonds are found to be distributed in the native oxide films. Furthermore, the reflectance in the vacuum ultraviolet implies that the cluster size of SiO_2 in the plane of the native oxide films are smaller than 100 nm.

1. Introduction

The roughness at the interface produced by the photoexcited chlorine radical-enhanced dry etching through native oxides were found to depend on the procedures of wet chemical treatments to form native oxides[1]. This suggests that the mobilities of chlorine radicals through native oxides depend on the wet chemical treatments studied. If the thickness of the gate oxide used in MOSFET is small, the existence of the native oxides was found to affect the structures of thermal oxides[2]. Namely, the native oxide can not be annealed because of short oxidation time and can affect the formation velocity of thermal oxides[3].

The native oxides studied so far were formed in dry oxidation atomosphere[4-9] and during wet chemical treatments[1-3]. According to the X-ray excited Phtoelectron Spectroscopy(XPS) studies[2], the chemical structures of native oxides can be characterized by the distribution of Si^{3+} in the native oxides. In order to find out the structural origin of Si^{3+}, the detailed studies on the chemical structures were performed using high resolution XPS. Furthermore, the reflectance spectra of native oxides were measured near the optical absorption edge of fuzed quartz.

2. Experimental

The procedures to form native oxides and the nondestructive depth profiling of the chemical structures of native oxides by measuring Si 2p photoelectron spectra were the same as those described previously[2]. Here, Mg Kα excited XPS was used in the previous study, while monochromatized Al Kα excited XPS was used in the present study. The effective electron escape depth Λ_e can be expressed by the following equation with Λ_o as an electron escape depth in silicon oxide. $\Lambda_e = \Lambda_o \sin\theta$. Here, Λ_o is 3.4 nm. The measurements were performed for the take off angle of 90°, 56.7°, 41.8°, 32.5°, 24.7° and 19.5°. Furthermore, the measurement of reflectance in the vacuum

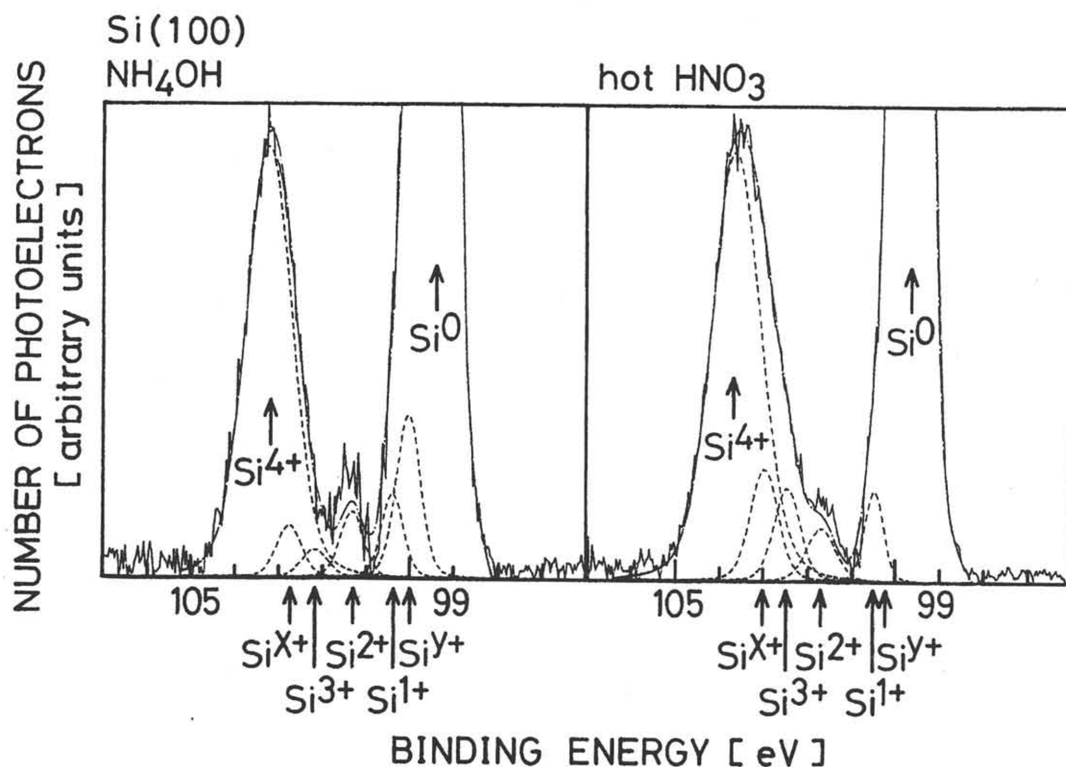

Fig. 1 Si 2p photoelectron spectra and deconvoluted spectra for native oxides formed during wet chemical treatments.

ultraviolet were carried out at BL-1 of 0.38 GeV SOR ring of Institute for Solid State Physics by using a 1 m Seya-Namioka type monochromator in the photon energy range from 2 to 23 eV.

3. Results and Discussions

Fig. 1 shows the Si 2p photoelectron spectra measured for two typical native oxides. These spectra were measured for the take off angle of 90° and the spin-orbit doublet was removed. In this figure the deconvoluted spectra obtained by using the chemical shifts of suboxides Si^{1+}, Si^{2+}, Si^{3+} and Si^{4+} determined for 0.5 nm thick thermal oxides[10] are also shown. In these deconvoluted spectra, the unknown spectra expressed by Si^{x+} and Si^{y+} are also included. According to the analysis based on the local electronegativity developed by Lucovsky[11], Si^{x+} can be correlated with $H\text{-}Si \equiv O_3$ in SiO_2 network. On the other hand the structural origin of Si^{y+} is not clarified yet.

According to the deconvolution considering Si^{1+}, Si^{2+}, Si^{3+}, Si^{4+}, Si^{x+} and Si^{y+}, the spectral intensity ratio (NI/NO) shown in Fig. 2 are obtained as a function of the effective electron escape depth. By comparing these calculated curves with experimental results, the amounts of $Si\text{-}Si \equiv O_3$ and $H\text{-}Si \equiv O_3$ were found to be distributed almost uniformly in the film and are more than a factor of 2 larger in the case of hot solution of HNO_3 than in the case of NH_4OH.

The reflectance of the native oxides measured in the vacuum ultraviolet is shown in Fig. 3. In this figure the calculated reflectances of fused quartz whose thicknesses are the same with native oxides studied here are shown. Here, the optical

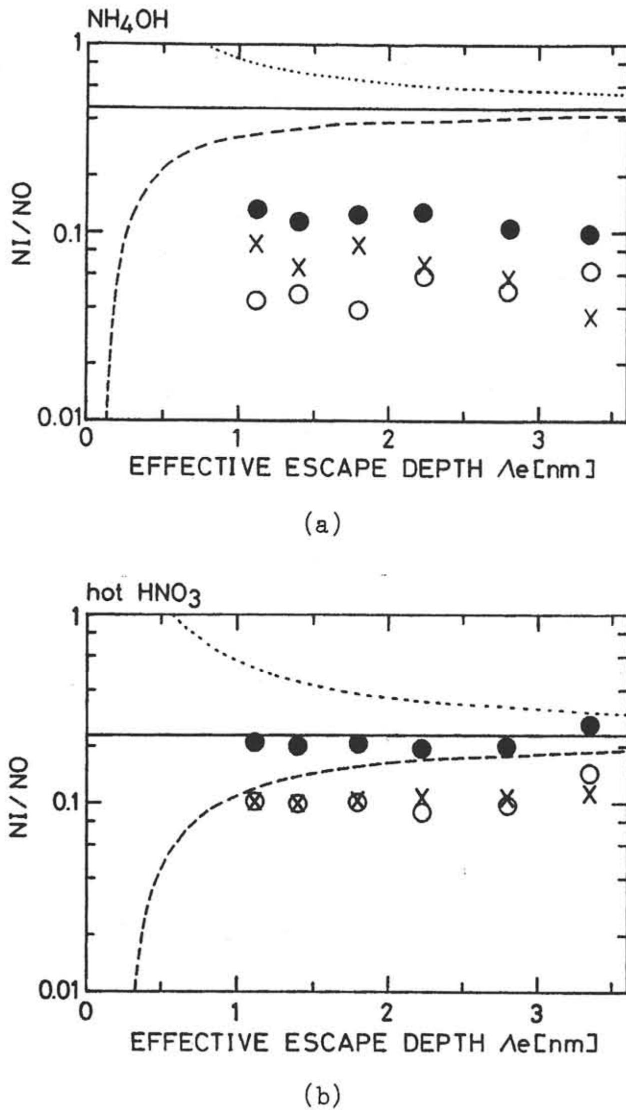

Fig. 2 Dependence of spectral intensity ratio (NI/NO) on effective electron escape depth for native oxide formed in (a) NH_4OH and that in (b) HNO_3. X , O and ● indicates ratio (NI/NO) for Si-Si ≡ O_3, H-Si ≡ O_3 and the sum of both ratios, respectively. Dotted line, solid line and dashed line indicates ratio (NI/NO) for one monolayer suboxide localized on the surface, one monolayer suboxide uniformly distributed in the oxide film and one monolayer suboxide localized near the interface, respectively.

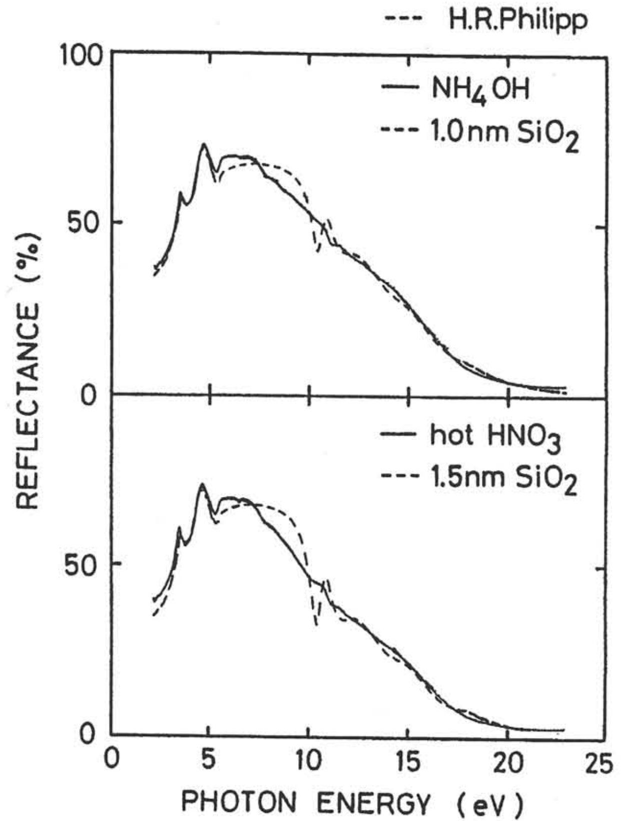

Fig. 3 Reflectance in vacuum ultraviolet for native oxide formed in a solution of NH_4OH and that in a hot solution of HNO_3, respectively.

constants of single crystalline silicon and fused quartz[12] are used to calculate the reflectance. From the comparison of these calculated curves with experimental results, the structures characteristic to SiO_2 were not observed in the native oxide film. On the other hand, according to the Si 2p photoelectron spectra shown in Fig. 1 the main component of the native oxides are Si^{4+}. Therefore, the absence of the structures characteristic to SiO_2 near the photon energy of 10 eV implies that the size of the SiO_2 cluster in the plane of the native oxide film may be smaller than the wavelength of incident light of nearly 100 nm.

4. Conclusion

The chemical structures of native oxides formed during wet chemical treatments were investigated using high resolution XPS. Almost the same amounts of $H\text{-}Si \equiv O_3$ and $Si\text{-}Si \equiv O_3$ are found to exist in the native oxide film studied. The amount of $H\text{-}Si \equiv O_3$ and $Si\text{-}Si \equiv O_3$ in the native oxides formed in hot solution of HNO_3 is more than a factor of 2 larger than that formed in NH_4OH. Furthermore, the reflectance of the native oxide film in the vacuum ultraviolet implies the cluster size of SiO_2 in the plane of the film may be smaller than 100 nm.

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