

INTERFACIAL STRUCTURE OF OXYNITRIDE LAYER ON SI(100) WITH PLASMA-EXCITED N₂O

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ABSTRACT

Silicon oxynitride films have been grown on Si(100) wafer with plasma-excited nitrous oxide (N₂O) gas, which has a low toxicity in comparison with other oxynitridation agents. Reaction rates are investigated by Auger electron spectroscopy, and compared with those grown with non-excited N₂O gas. Si 2p core-level photoelectron spectroscopic measurements using synchrotron radiation have been also carried out to investigate interfacial structures of the grown oxynitride layers. Temperature dependences of chemical-shift components of the obtained Si 2p spectra show that the interfacial roughness decreases with reaction temperature. Distributions of the suboxide components are discussed in accordance with results of angle-resolved Si 2p spectra.

KEYWORDS: Chemical Shift, Core-Level Photoelectron Spectroscopy, Gate Insulator, MOS FET, N₂O Gas, Plasma Excitation, Silicon Oxynitride

INTRODUCTION

Silicon oxynitride as a gate insulator of a highly integrated metal-oxide-semiconductor device has prominent property in suppressing boron diffusion from the polysilicon gate electrode and improving hot carrier residence [1]-[3]. One of the most popular methods to form the oxynitride film on a silicon surface is to utilize thermal reaction with chemical gases such as nitric oxide (NO) [4]-[5] and ammonia (NH₃) [6]-[7]. However, these gases have a high toxicity. In the previous study [8], we focused on nitrous oxide (N₂O) as a chemical gas for the oxynitridation, because N₂O has a relatively low toxicity. However, N₂O has also a low reactivity in comparison with the other gases mentioned above. In order to enhance the reactivity of N₂O and activate the nitridation reaction, we employed thermally-excited N₂O, which was generated by passing the gas through a ceramic cell heated above 1000 °C before introducing it to the silicon surface. The oxynitride layers were grown on the silicon surface under several growth conditions, and then the growth rates, nitrogen concentrations, and chemical bondings of the grown layers were investigated. As a result, we found that the thermal excitation of N₂O selectively enhances the oxidation reaction, resulting in increasing the growth rate [8]. The enhanced oxidation is probably due to atomic oxygen generated by the thermal excitation of N₂O.

In this study, we employ plasma-excited N₂O gas to enhance the nitride reaction. Reaction rates are investigated by Auger electron spectroscopy (AES), and compared with those grown with non-excited N₂O gas. Si 2p core-level photoelectron spectroscopic measurements using synchrotron radiation (SRPES) have been also carried out to investigate interfacial structures of the grown oxynitride layers. The interfacial roughness is discussed from the temperature dependence of chemical-shift components of Si 2p spectra.

EXPERIMENTAL

Prior to loading into an ultrahigh vacuum chamber (base pressure $\sim 2 \times 10^{-8}$ Pa), a mirror-polished, B-doped Si(100) wafer cut to a size of $20 \times 5 \times 0.5$ mm³ was cleaned by standard RCA method, and then annealed at 1000 °C by direct current resistive heating in the chamber. The cleanliness of the surface was checked by the surface state in valence-band and Si 2p core-level spectra, which showed no surface contamination. The SRPES measurements were carried out with synchrotron radiation derived from Beamline 3B at Photon Factory, the High Energy Accelerator Research Organization. The photon energy was set at 135 eV, where the overall instrumental energy resolution was estimated to be less than 200 meV. N₂O gas with a purity of 99.999% was excited by Penning discharge plasma source before exposing the sample. Oxynitridation was carried out at the substrate temperatures of RT – 800 °C and at the N₂O pressure of 5×10^{-4} Pa.

RESULTS AND DISCUSSIONS

Figure 1 shows AES intensity ratios of nitrogen and oxygen to silicon for oxynitride layers grown with plasma-excited N₂O gas as well as non-excited N₂O gas. In case of non-excited N₂O gas, N₂O acts only as oxidant and no nitridation occurs, while in case of plasma-excited N₂O, large enhancement of nitridation reaction can be seen. By mass analysis measurements, we infer that this nitridation enhancement is due to NO radicals generated by plasma excitation of N₂O. In the previous study, we found that the thermal excitation of N₂O selectively enhances the oxidation reaction [8]. Therefore, we expect that both enhancements of oxidation and nitridation reactions can be simultaneously achieved by using a combination of thermal and plasma excitations of N₂O.

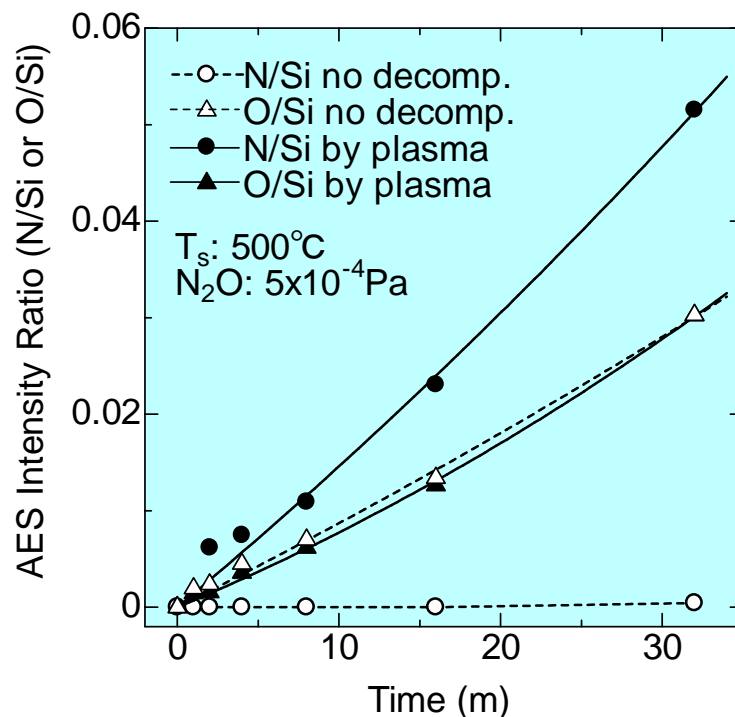


Figure 1: AES Intensity Ratios of Nitrogen and Oxygen to Silicon for Oxynitride Layers Grown with Plasma-Excited N₂O gas (Solid Symbols) as Well as Non-Excited N₂O Gas (Open Symbols)

Figure 2 shows typical Si 2p core-level spectrum of oxynitride layer on Si(100) grown at oxynitride temperature of 500 °C for 16 min. The Si 2p spectra of the oxynitride layers grown under a wide range of the oxynitridation conditions were deconvoluted by a least-square fitting procedure using the spin-orbit split Voigt functions. All of the obtained Si 2p core-level spectra were successfully fitted with five components: substrate silicon (Si⁰) and four chemical-shift components by oxynitride layer (Si¹⁺, Si²⁺, Si³⁺, and Si⁴⁺). The four oxynitride components can correspond to the number of oxygen or nitrogen bonded to a silicon atom, as assigned for silicon dioxide (SiO₂) layer [9]. Since the chemical shift of Si 2p bonding with nitrogen is smaller than that bonding with oxygen, each chemical shift is slightly smaller than that of the oxide layer. These chemical shifts gradually decrease with temperature increasing as shown in Figure 3. This is due to the increment of the nitrogen concentration in the oxynitride layer with temperature increasing as mentioned above. In fact, AES measurements (not shown) support this explanation. Figure 4 shows temperature dependences of intensities of Si¹⁺, Si²⁺, and Si⁴⁺ components. While Si⁴⁺ component is almost constant, Si¹⁺ and Si²⁺ components, which are associated with interfacial roughness of oxynitride/substrate [10], decrease with temperature increasing. This indicates smoother interface at higher temperature, being in agreement with the result of rapid thermal oxynitridation in N₂O [11].

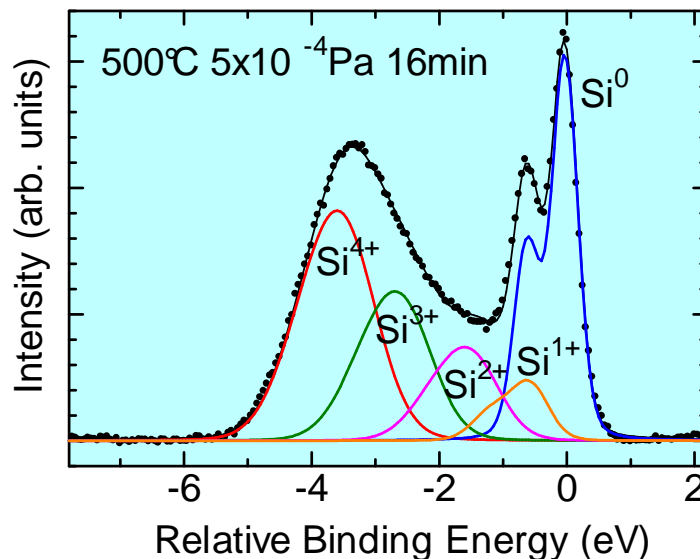


Figure 2: Typical Si 2p Core-Level Photoelectron Spectrum of Oxynitride Layer on Si(100) Grown at an Oxynitride Temperature of 500 °C for 16 min (Dots). The Spectrum is Deconvoluted by a Least-Square Fitting Procedure Using the Spin-Orbit Split Voigt Functions (Solid Lines)

Figure 5 shows angle-resolved photoelectron intensities of Si¹⁺, Si²⁺, and Si³⁺ components. The photoelectrons are detected at angles to the surface normal of 0 – 75°. We have assumed that each component is localized at the interface, and have fitted the experimental data into numerical results simulated by the localized model [12], which are denoted by solid lines in Figure 5. They show good agreements in the Si¹⁺ and Si²⁺ components, while we can not reproduce the Si³⁺ component by the localized model (not shown). Therefore, the Si³⁺ component is considered to exist with a different distribution from the Si¹⁺ or Si²⁺ component.

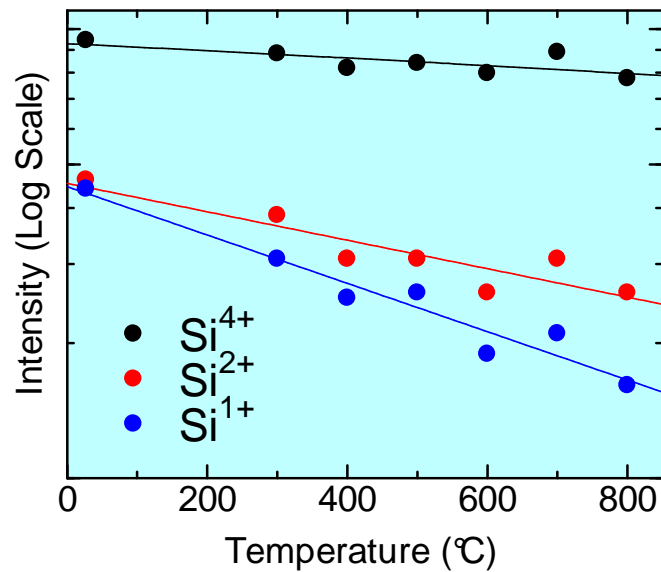


Figure 3: Temperature Dependences of Chemical Shifts of Four Oxynitride Components

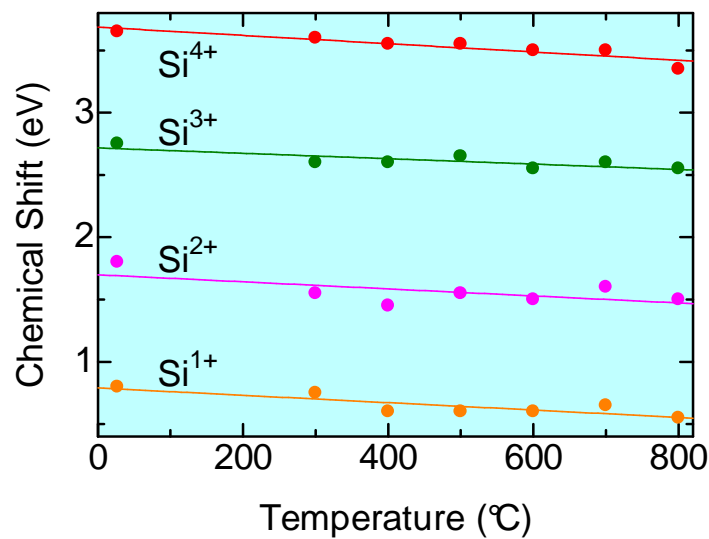


Figure 4: Temperature Dependences of Intensities of Si¹⁺, Si²⁺, and Si⁴⁺ Components. Solid Lines Show Best Fits Obtained by a Least-Square Procedure

CONCLUSIONS

Silicon oxynitride layer on Si(100) grown with plasma-excited N₂O gas has been investigated by AES and SRPES. Reaction rates are compared between plasma-excited and non-excited N₂O gases. In non-excited N₂O gas, N₂O acts only as oxidant, while in plasma-excited N₂O, large enhancement of nitridation reaction occurs by NO radicals generated by plasma excitation. All of the obtained Si 2p core-level spectra for the grown oxynitride layers have been successfully fitted with five components, and the interfacial structures have been discussed from the temperature dependence of chemical-shift components of Si 2p spectra. Si¹⁺ and Si²⁺ components, which are associated with interfacial roughness of oxynitride/substrate, decrease with temperature increasing. This indicates smoother interface at

higher temperature. Distributions of the suboxide components are discussed in accordance with results of angle-resolved Si 2p spectra, which show that the Si¹⁺ and Si²⁺ components are localized at the interface.

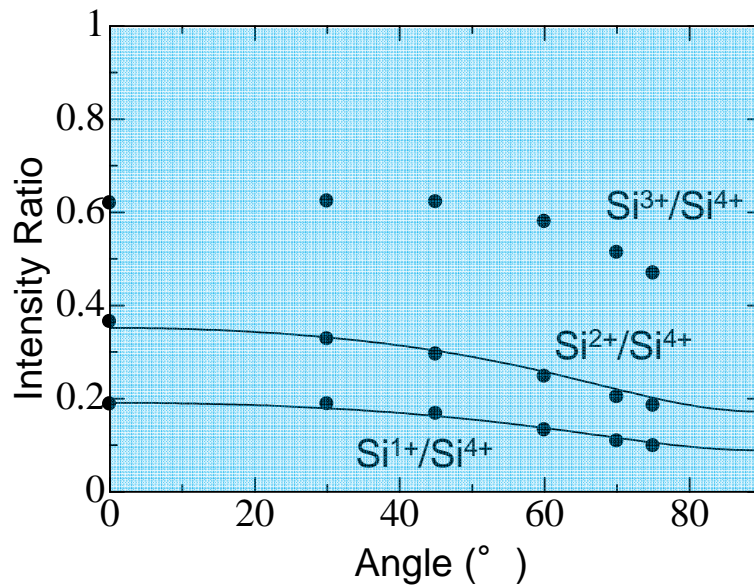


Figure 5: Intensity Ratios of Si¹⁺, Si²⁺, and Si³⁺ to Si⁴⁺ Components. The Spectra Are Taken at Angles to the Surface Normal of 0 – 75°. Solid Lines Show Numerical Results Simulated by the Localized Model

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