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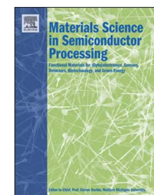

Effects of temperature and pressure in oxynitridation kinetics on Si(100) with N_2O gas

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ABSTRACT

We have investigated oxynitridation of Si(100) surfaces with nitrous oxide (N_2O) gas in a wide range of substrate temperatures (600–1000 °C) and N_2O pressures (10^{-2}–10^{2} Pa). The growth rate and atomic composition of the oxynitride layer have been measured by in situ x-ray photoelectron spectroscopy. The surface morphology of the oxynitride layer has been also observed by scanning electron microscopy. The results show that in higher N_2O pressure (> 1 Pa) regime, the nitridation reaction is suppressed by the oxide layer, which quickly forms on the surface. On the other hand, in lower pressure (< 1 Pa) and higher substrate temperature (> 900 °C) regime, the nitridation reaction strongly occurs because of the active oxidation (etching reaction), which causes the surface roughness. It is found by argon-ion-sputtering measurements that the nitride layer locally exists only near the surface at the reduced N_2O pressure. We discuss qualitatively the oxynitridation kinetics and the effective condition for growing the oxynitride layer.

1. Introduction

Silicon oxynitride film is one of the strong candidates for the gate insulator in highly integrated metal-oxide-semiconductor devices, because it has superior abilities to suppress boron diffusion and improve hot carrier residence [1]. 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) and ammonia (NH_3). However, these gases have high toxicity. Hwang et al. [2] and Fukuda et al. [3] found that oxynitride dielectrics thermally grown with nitrous oxide (N_2O) show very large charge-to-breakdown value and less charge trapping in high-field stressing. Since then, many studies that the dielectrics prepared by N_2O show the excellent electrical properties have been reported [4–9]. Moreover, reaction kinetics of oxynitridation with N_2O has been extensively studied from viewpoints of growth rate [6,10–13], reaction process [7,10–16], nitrogen depth profile [2–6,11,12,14,16–23], atomic and chemical structures [3,23–25], and theoretical reaction model [15,26–29].

Since N_2O has low reactivity, which indicates low toxicity, compared with NO or NH_3, most of the studies on the growth rate have been carried out at the N_2O pressure of 1 atm and the study at the reduced N_2O pressure has been scarcely reported. At the pressures below 10^{-2} Pa, thermal or plasma excitation of N_2O is necessary to grow the oxynitride layer [30,31]. To our knowledge, only one previous study [13] reported the growth rate at the reduced N_2O pressures, although the data were taken at limited temperatures (only 1000–1050 °C). Systematic investigations of the growth rate and atomic composition for the oxynitride layer grown at the reduced pressures is therefore indispensable for comparing with the theoretical models and revealing the reaction kinetics with N_2O. Therefore, in this study, we have performed the oxynitridation of Si(100) substrates with N_2O in a wide range of temperatures (600–1000 °C) and pressures (10^{-2}–10^{2} Pa), where no data have been reported so far, to investigate the best conditions for the reaction and elucidate the oxynitridation kinetics at the reduced N_2O pressures. The growth rate, the atomic composition, and the nitrogen profile of the grown oxynitride layer have been measured by x-ray photoelectron spectroscopy (XPS), and the surface morphology has been observed by scanning electron microscopy (SEM). We found that the growth rate and atomic composition complicatedly depend on the N_2O pressure, and show anomalous behaviors under specific conditions. Based on the results of our study, we discuss qualitatively the oxynitridation kinetics and the effective condition for growing the oxynitride layer.

2. Experimental

Mirror-polished, B-doped Si(100) wafer cut to a size of $10{\times}4{\times}0.5$ mm^3 was used as a silicon substrate. The wafer was rinsed in acetone and propanol with an ultrasonic bath, and then annealed at 1200 °C by direct current resistive heating in the ultrahigh-vacuum

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(UHV) chamber, whose base pressure was ~8×10^{-9} Pa. No contamination was observed by XPS, and reflection high-energy electron diffraction showed clear 2×1 pattern. The oxynitride layers were grown on the clean surface at substrate temperatures between 600 and 1000 °C and at N_2O pressures between 10^{-2} and 10^{2} Pa. The sample temperatures were measured with an optical pyrometer. The N_2O gas with a purity of 99.999% was introduced into the UHV chamber through a variable leak valve. The growth rate and atomic composition were evaluated from intensity ratios of chemical-shift components of Si 2p core-level spectra, and intensities of O 1s and N 1s core-level spectra, respectively. XPS measurements with the monochromatized Al Kα line at 1486.6 eV and a hemispherical electron analyzer with 7-channel detectors (Omicron Multiprobe MXPS-HP), which can operate under the pressure of up to 10^{-1} Pa, were carried out during or after growth. The detection angle of the photoelectron (θ_e) was set at 52° to the surface normal. The full width at half maximum of the x-ray line and the total energy resolution were ~0.35 and ~0.5 eV, respectively. The sampling area was about 1 mm in diameter and the temperature variation in the sampling area was estimated at within 10 °C. The lateral uniformity of the grown films is mostly determined by the temperature uniformity. Therefore, the lateral uniformity in the sampling area was kept in the temperature variation within 10 °C, although it was dependent on the temperature regime. An Ar-ion sputter gun was used to measure the depth profile of the grown oxynitride layer. The current density and energy of Ar-ion beam were ~10 μA/cm^2 and 250 eV, respectively. The sputtering rate was estimated at ~1.5×10^{-2} Å/s by calculating the change of the oxynitride thickness. SEM images of the oxynitride layers were obtained ex situ at room temperature by using an Auger microprobe (JEOL JAMP-9500F).

3. Results and discussion

Fig. 1 shows typical time evolution of Si 2p, N 1s, and O 1s core-level spectra during oxynitridation at the N_2O pressure of 5×10^{-2} Pa and at the temperature of 950 °C for about 1 h. The main peak (Si^0) at the binding energy of 91.2 eV and the broad peak (Si^{ON}) at around 103 eV in Fig. 1a can be assigned to the signals from the silicon substrate and the oxynitride layer, respectively. Although the broad peak must be composed of several components associated with suboxides and SiO_xN_{2-x} compositions, the obtained spectra do not have enough energy resolution to distinguish them. In this study, however, it is not serious because we employ the Si 2p core-level spectra only for evaluating the growth rate of the oxynitridation reaction. The thickness of the oxynitride layer (D) for each spectrum is given by the measured ratio of Si^{ON} area ($I_{Si^{ON}}$) to Si^0 area (I_{Si^0}) according to the formula:

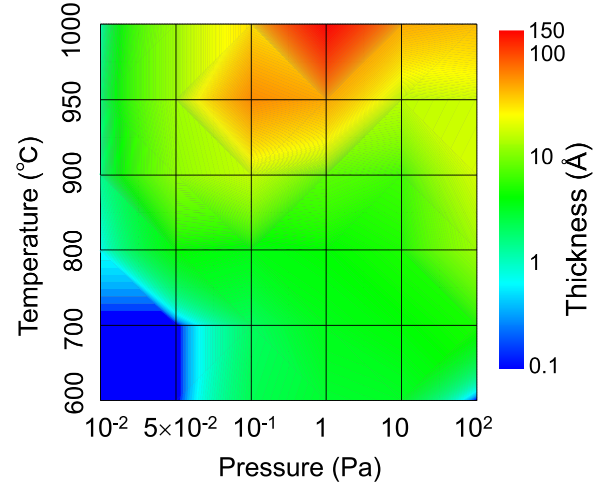

Fig. 2. A 2D map of the thickness of oxynitride layers grown for 1800 s as functions of N_2O pressure and substrate temperature. The experimental data were taken only at the intersection of the mesh lines. The data in each mesh area were deduced from a linear interpolation with the data at the intersections of the mesh. The color bar is in a logarithmic scale. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$D=\lambda\cos\theta_e\ln\left(R\frac{I_{Si^{ON}}}{I_{Si^0}}+1\right) \tag{1}$$

where λ is the electron inelastic mean free path (EIMFP) in the oxynitride layer and R is a dimensionless coefficient depending on a photon energy. At the photon energy of 1486.6 eV, the EIMFP and coefficient for the SiO_2 layer are estimated from previous analysis of experimental data [32] at 3.14 ± 0.31 nm and 1.136 ± 0.040, respectively. When we estimate the error of the obtained oxynitride thickness, we have to consider the parameter errors and the depth-dependence-composition effect. As described above, the error of the EIMFP (about 10%) is much larger than that of R, and R is in the logarithmic function. Therefore, the error of R can be negligible. According to Maillot et al. [33], the EIMFP in Si_3N_4 layer is estimated at 3.0 nm. This value is within the error for the SiO_2 layer. The EIMFP in the oxynitride layer must be the value for between the SiO_2 and Si_3N_4 layers. Therefore, we consider that the depth-dependence-composition effect can be also negligible. We thus adopt the EIMFP and coefficient for the SiO_2 layer as λ and R, and estimate the error of the oxynitride thickness at about 10%. Fig. 2 shows a two dimensional (2D) map of the thickness of the oxynitride layer grown for 1800 s as functions of the N_2O pressure and the substrate temperature. As shown in the figure, roughly speaking, the thickness becomes thicker as the pressure and temperature increase. However, the thickness has a maximum value at the pressure of 1 Pa and at the temperature of 1000 °C, and

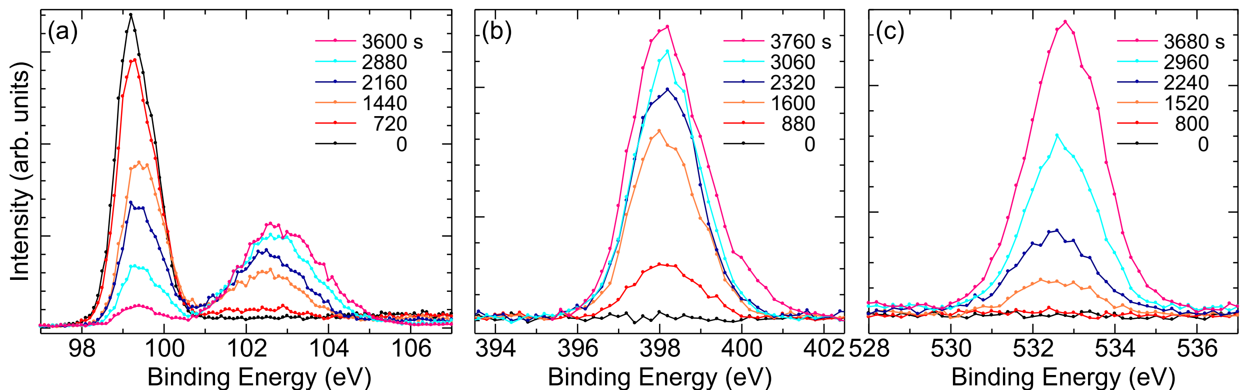

Fig. 1. Typical time evolutions of Si 2p, N 1s, and O 1s core-level spectra during oxynitridation at a N_2O pressure of 5×10^{-2} Pa and at a temperature of 950 °C for about 1 h. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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