Real-time measurements of Si 2p core level during dry oxidation of Si(100)

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The chemically shifted Si 2p core level (Si^{4+}) has been measured in real time during initial thermal oxidation of Si(100) by O_2 gas. The time evolutions of the Si^{4+} intensities showed identical behaviors to those of O 2p intensities reported previously [Y. Enta *et al.*, Appl. Surf. Sci. **100/101**, 449 (1996)], demonstrating that there exist two growth modes for the oxidation: the first-order Langmuir-type adsorption mode and two-dimensional island growth mode at oxidation temperatures below and above 650 °C, respectively. [S0163-1829(98)04211-8]

With further reduction of thickness in the gate oxide of silicon metal-oxide-semiconductor field-effect transistor devices, initial stages of thermal oxidation within a thickness of 1 nm has become one of the most important issues in ultra-large-scale-integration technology. In this respect, a deep understanding on the reaction kinetics of the oxidation process is indispensable for forming high-quality, ultrathin silicon dioxide films with a lower density of defects and flatter oxide/silicon interfaces. Horie, Takakuwa, and Miyamoto[1] have performed real-time measurements of O 2p intensities during the initial thermal oxidation of Si(100) by O_2 gas for temperatures above 700 °C. They demonstrated that the oxidation proceeds with two-dimensional (2D) nucleation of small oxides until the surface is fully covered with the oxides. Recently, by using the same method as Horie, Takakuwa, and Miyamoto, we have measured the time evolutions of O 2p intensities for a wider range of temperatures.[2] We concluded that, at temperatures below 650 °C, the oxidation proceeds randomly without formation of 2D islands by showing that the growth rate follows a first-order Langmuirian behavior, while at temperatures above 650 °C the oxidation was indicated to proceed via 2D nucleation because the growth exhibits some incubation time. The onset of the latter growth mode was accounted for by the oxide decomposition at high temperatures. Our measurements, however, are indirect in the sense that the intensity of the O 2p valence state can include contributions from physisorbed oxygen molecules on the surface. More direct measurements on the amount of the oxide are therefore needed to validate the growth kinetics mentioned above, which encouraged us to extend our study to use chemically shifted Si 2p core-level spectra. The Si 2p core level has been extensively investigated over the past decade and its chemical shifts allow us unambiguous assignments to each of the three intermediate oxides (suboxides) and the stoichiometric oxide.[3–6] In this study, we focused on the stoichiometric-oxide component (Si^{4+}) during dry oxidation of Si(100) and have compared the time evolution of its intensity for various oxidation temperatures.

Experiments were performed with an ultrahigh-vacuum photoelectron spectrometer, which basically consists of a hemispherical electron analyzer and a low-energy electron diffraction optics, using a linearly polarized synchrotron radiation from the beam line BL-3B at the Photon Factory, the High Energy Accelerator Research Organization. The photon energy was set at 135 eV, where the escape depth (~3 Å) of photoelectrons from the Si 2p core level in silicon has a minimum. The overall instrumental energy resolution was estimated to be less than 0.14 eV by obtaining the Gaussian full width at half-maximum (FWHM) for a substrate Si 2p peak from Si(100)2×1 clean surface at room temperature. The Si sample, the sample cleaning procedure, and the oxidation condition are identical to those described in Ref. 2.

The present experiments have been carried out at oxygen pressures below 5×10^{-6} Torr. Under this condition, the oxide growth becomes saturated until the surface is fully covered with oxides, which defines 1 ML. The studies were thus focused on the oxidation up to 1 ML. Figure 1 shows a typical Si 2p core-level spectrum from a saturated, ultrathin oxide overlayer on Si(100). Raw spectrum though it is, the spectrum presents a series of three well-resolved chemically shifted peaks aside from the substrate Si peak. The thickness of the oxide was evaluated to be 0.52 nm using the intensities of the substrate and the shifted peaks, as well as the escape depth of the photoelectrons. The spectrum in Fig. 1 was deconvoluted by a least-squares fitting procedure using Voigt functions. The fitting parameters are listed in Table I. Each peak energy and its Gaussian FWHM are found to be in good agreement with those in the pioneering work by Himpsel *et al.*[6] obtained at 750 °C, although our spectra were obtained with high resolution. The assignments that Si^{1+}, Si^{2+}, and Si^{3+} arise from interfacial silicon atoms bound to one, two, and three oxygen atoms, respectively, are generally accepted. Recently, however, some controversial studies on the assignments of the intermediate oxide were

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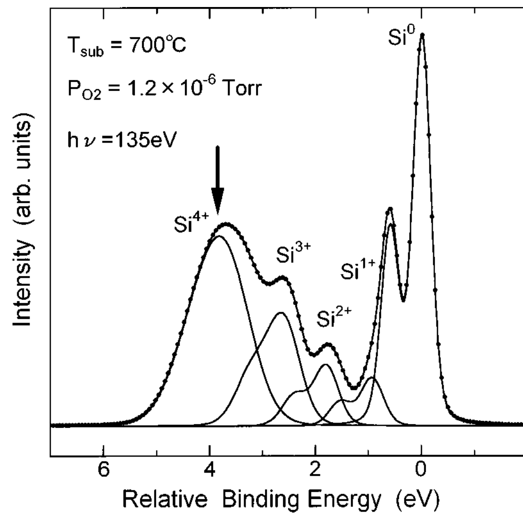

FIG. 1. Typical Si $2p$ core-level spectrum (dots) from ultrathin SiO_2 on Si(100) recorded at 135 eV photon energy. Solid lines denote the curve fitting. The oxide layer was grown with 1.2×10^{-6} Torr O_2 at 700 °C for 12 min.

reported.[7,8] Although we found no remarkable information on the assignments from our spectra, the temperature dependence of the spectra may give a hint for the controversy in the assignments. Detailed measurements at temperatures of 350–720 °C showed no temperature dependence of these quantities, which accounts for the above agreement among the spectra obtained at different oxidation temperatures. As for the relative intensities of the suboxides, however, there appeared an apparent temperature dependence that Si^{1+} and Si^{3+} increase and Si^{2+} decreases with an increase of the temperature even for the same oxide thickness. Indeed, there is a slight difference in the relative intensities between the Himpsel's spectrum at 750 °C and the present one at 700 °C.

For investigating the time evolutions of the oxide coverage, the Si^{4+} peak intensity, indicated by the arrow in Fig. 1, was continuously measured during oxygen exposure. A series of dose dependences of Si^{4+} at various temperatures are shown in Fig. 2. Each intensity evolution has been normalized by its own saturation value, which increased slightly with the temperature. Clearly, the evolutions of the Si^{4+} intensity are classified into two groups: the low-temperature region below ~650 °C and the high-temperature region above ~650 °C. In the low-temperature region, all the Si^{4+} intensities show identical behavior over a wide range of the oxidation temperature. In the high-temperature region, on the other hand, a slight increase of the temperature causes a drastic delay of the onset of the oxidation. Consequently, the dose required for the saturation of the coverage increases by a factor of two for every increase of the temperature by 20 °C.

TABLE I. Fitting parameters and obtained relative intensities of Si $2p$ suboxide peaks in Fig. 1. Lorentzian FWHM for the life time broadening, spin-orbit splitting, and the branching ratio are fixed at 0.085 eV, 0.6 eV, and 0.5, respectively. The instrumental energy resolution has been subtracted from Gaussian FWHM. The difference in the cross section between Si $2p$ suboxide peaks is not taken into account.

	Energy shift (eV)	Gaussian FWHM (eV)	Intensity ratio (Si^{X+}/Si^0)
Si^0	0	0.32	1
Si^{1+}	0.94	0.43	0.15
Si^{2+}	1.81	0.48	0.21
Si^{3+}	2.61	0.66	0.47
Si^{4+}	3.84	1.04	1.01

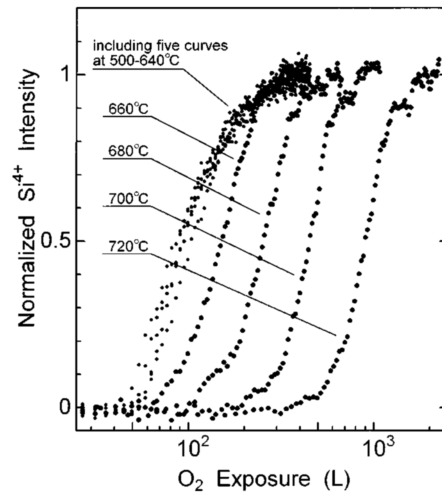

FIG. 2. Si^{4+} peak intensity, indicated by the arrow in Fig. 1, as a function of the O_2 dose in the temperature range 500–720 °C.

Figure 3 shows the time evolutions of the Si^{4+} intensity during oxidation for several oxygen pressures, for a pair of two representative temperatures in each temperature region. A significant difference in the curve shape between the two regions is evident. In the low-temperature region (a), the

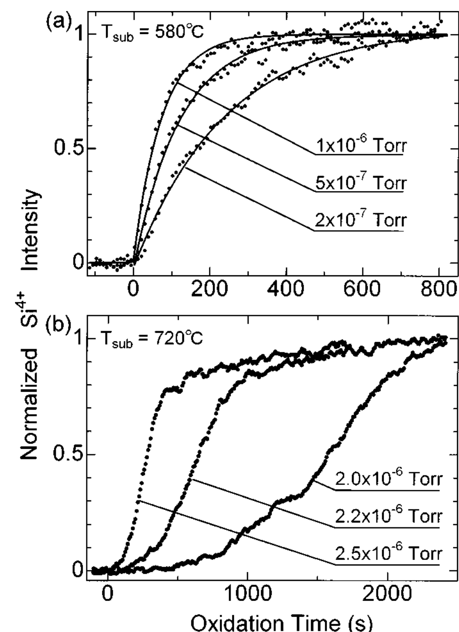

FIG. 3. Time evolutions of the Si^{4+} peak intensity at (a) 580 °C and (b) 720 °C. The solid lines in (a) show the best fits of the data with a Langmuir-type adsorption model described in Eq. (1).

Si^{4+} intensities start to increase immediately after introducing the oxygen gas, and the gradients, which correspond to the growth rate, monotonically decrease until the Si^{4+} intensities saturate. In the high-temperature region (b), on the other hand, the intensities scarcely increase for a certain period after introducing the oxygen gas. Thus, the differential growth rates increase gradually until they show a maximum at around 0.5 ML, and then begin to decrease.

The evolutions of the Si^{4+} intensity shown in Figs. 2 and 3 are almost identical to those of the O $2p$ state shown in Ref. 2, which appears at the binding energy of around 7 eV in the valence-band spectrum. This agreement of the behavior fully demonstrates that the intensity of O $2p$ state is directly proportional to the amount of the oxide on the surface, validating the growth kinetics discussed in Ref. 2. The agreement in turn explains the time evolutions of Si^{4+} intensity in terms of the growth kinetics developed in Ref. 2: the Langmuir-type adsorption in the low-temperature region and the 2D island growth in the high-temperature region. The Langmuir-type adsorption can be formulated in general as

$$\frac{d\theta}{dt} = \alpha P(1-\theta)^n. \quad (1)$$

Here, θ is the grown oxide coverage, α is the sticking probability of the oxygen on silicon surface, P is the oxygen pressure, and n is the reaction order of adsorption. The fitting of the experimental data to Eq. (1), as shown by solid lines in Fig. 3, indicates that the time evolution in the low-temperature region exactly follows $n=1$, that is, a first-order Langmuirian behavior.

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