Oxidation of Si during the growth of SiO_x by ion-beam sputter deposition: In situ x-ray photoelectron spectroscopy as a function of oxygen partial pressure and deposition temperature

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Oxidation of silicon during the growth of silicon oxide by ion beam sputter deposition was studied by in situ x-ray photoelectron spectroscopy as a function of oxygen partial pressure at various deposition temperatures below 600 °C. At low temperatures, the variation of incorporated oxygen content is similar to a dissociative adsorption isotherm of O_2 on Si indicating that the surface-confined reaction of the deposited Si atoms with the adsorbed oxygen atoms is the main process. However, it shows a three-step variation with the oxygen partial pressure at high temperatures. The evolution of SiO species confirmed by the XPS indicates that an adsorption-induced surface reaction and a diffusion-induced internal reaction are the main pathways for the Si oxidation.

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Oxidation of silicon has been extensively studied, driven by the rapid progress in the fabrication of Si-based semiconductor devices. In particular, Si-rich silicon oxide (SiO_x, 0 < x < 2) has attracted much research interest due to its possible application as an emission source of visible light. That is because Si nanocrystals embedded in a SiO_2 matrix can emit visible photoluminescence according to the quantum confinement effect, though Si itself is basically an indirect band-gap material. The size and density of Si nanocrystals are the key parameters in determining the energy and intensity of photoluminescence. Therefore, the elucidation of the detailed mechanism of Si oxidation is required to optimize the formation of Si nanocrystals in SiO_2. However, despite much research in the oxidation of Si(100) or (111) surface by thermal oxidation, the studies on Si oxidation during the film growth by physical deposition are quite sparse.

Ion beam sputter deposition (IBSD) under oxygen ambient has been reported to be useful for the growth of the stoichiometric oxide films. This method has an advantage that it provides relatively low temperature process so that it reduces interdiffusion and releases thermal stress. As a result, it produces a uniform oxide film over the thickness, rendering interface-free examination. In addition, looking into the oxidation and growth mechanism, an in situ analysis of the films by x-ray photoelectron spectroscopy (XPS) is a powerful method to avoid the change of the chemical states on the top surface by contamination and further oxidation in the air.

We report detailed oxidation behavior of silicon during the deposition of Si oxide by the IBSD. The variations of the oxygen content and the evolution of SiO_x species observed by the in situ XPS showed that an adsorption-induced surface reaction and a diffusion-induced internal reaction are the main controlling factors for the growth of Si oxides by physical deposition.

The silicon oxide films were grown by the IBSD using a Kaufman-type dc ion gun. The deposition chamber was evacuated to a pressure of 2.0 × 10^{-8} Torr before introducing argon gas into the system. Si target was sputtered by Ar^+ beam with the ion energy of 750 eV and the sputtered Si atoms were deposited with a constant flux onto p-type Si(100) wafers under O_2 gas flow. The Si substrate was heated by direct resistive heating and its temperature was measured with a thermometer calibrated by a thermocouple. After the deposition, the oxygen content of SiO_x film was directly analyzed by in situ XPS. A concentric hemispherical electron energy analyzer was used with pass energy of 10 eV using the Al Ka line at 1486.6 eV as an excitation source. The relative sensitivity factor for the Si 2p and O 1s peaks was calibrated by the comparison with a stoichiometric SiO_2 thin film grown at an oxygen pressure above 2.0 × 10^{-4} Torr.

Figure 1 shows the variation of oxygen content (x) in SiO_x films grown by the IBSD as a function of O_2 partial pressure (P_{O_2}) at various deposition temperatures. As for comparison of the relative dose of the oxygen, the scale of the upper abscissa is referred to the relative arrival rates

![Graph showing oxygen content (x) of the SiO_x films grown as a function of oxygen pressure (P_{O_2}) at RT (■), 200 (○), 400 (▲), 500 (∇), and 600 °C (•).](image-url)
(F_{O_2}) of oxygen molecules per Si atom estimated by the Hertz-Knudsen formula

\[ F_{O_2} = P_{O_2}/\sqrt{2 \pi mkT}, \]

where the \(T\) is the gas temperature.\(^{16}\) The \(F_{O_2}\) value at \(P_{O_2} = 1.0 \times 10^{-5}\) Torr (=1.33 \times 10^{-2}\) Pa) and room temperature is calculated to be \(3.59 \times 10^{19}\) molecules/m\(^2\)s. The number of Si atoms \(F_{Si}\) deposited on the surface per unit area per unit time is derived by the growth rate of \(Si (=0.05\) nm/s) and the density of \(Si (=2.32\) g/cm\(^3\)). The measured deposition rate of \(Si\) is \(2.49 \times 10^{18}\) atoms/m\(^2\)s and the same rate was applied throughout the experiments.

At RT, the oxygen content of the film increases gradually at the low \(P_{O_2}\) up to \(1.5 \times 10^{-5}\) Torr and continues increasing slowly up to \(1 \times 10^{-4}\) Torr. Eventually it shows a saturated value for the stoichiometric \(SiO_2\) at pressures above \(2 \times 10^{-3}\) Torr. Such variation keeps more or less similar as the substrate temperature \((T_s)\) increases from RT to 400 °C. The resemblance between the variation of oxygen content and a general adsorption isotherm curve\(^{17}\) shows that an initial adsorption of oxygen controls the main process of Si oxidation at the low temperatures, since the impinging oxygen molecules are chemisorbed by spontaneous dissociation on a Si surface.\(^{10}\)

However, a quite different three-step oxidation mechanism arises at the \(T_s\) above 500 °C. In the case of \(T_s = 600\) °C, the relative oxygen content increases steeply at the low pressures below \(1 \times 10^{-5}\) Torr (first step), and then maintains a constant value up to \(4 \times 10^{-5}\) Torr (second step). But it starts to increase again at \(5 \times 10^{-5}\) Torr and saturates to the stoichiometric state of \(SiO_2\) at the \(P_{O_2}\) above \(1.6 \times 10^{-4}\) Torr (third step). At a fixed oxygen pressure, Fig. 1 shows a significant decrease of oxygen content as the \(T_s\) increases. For example, at the oxygen partial pressure of \(5.5 \times 10^{-5}\) Torr, the \(x\) value decreases from 1.76 to 0.57 when the \(T_s\) increases from RT to 600 °C. In general, the surface-resident time and reactivity of adsorbates are important parameters for determining the chemical oxidation occurring at the surface. The decrease of residence time (or sticking probability) of oxygen molecules at the high \(T_s\) reduces the direct initial oxidation of the surface Si atoms. On the other hand, it causes the enhancement in the reactions associated with suboxides \((SiO_x)\) due to the momentum transfer from the heated surface. Thus, further reactions mediated by the suboxide species should be considered to explain the oxidation behavior at high temperatures as will be described below.

The oxidation process occurring in the film is examined by the relative chemical composition of the silicon oxide. The distribution of chemical states for the final \(SiO_x\) films is analyzed by peak fitting of Si 2p spectra as shown in Fig. 2(a) which exhibits them for the \(SiO_x\) films grown at RT, 400 °C, and 600 °C associated with the oxygen content \((x)\) near 1.25 of Fig. 1. The peak position and intensity of each core level are determined by a standard curve fitting procedure using Voigt functions (convolution of Gaussian and Lorentzian functions) after background subtraction by Shirley method.\(^{10,18}\) A doublet with the constant spin-orbit splitting (0.605 eV) and branching ratio (0.5) is used for each Si 2p peak. Each spectrum is composed of metallic Si (Si\(^0\)), three suboxide species (Si\(^{+}\)−Si\(^{3+}\)), and fully oxidized Si\(^2+\) at the Si 2p\(_3/2\) binding energies of 99.65, 100.60, 101.40, 102.47, and 103.65 eV, respectively. It shows a strong dependence of chemical composition on the \(T_s\). The details of such a trend are illustrated in Fig. 2(b) which shows the evolution of relative peak intensities for the five species (Si\(^{+}\)−Si\(^{4+}\)) in the films. Below 300 °C, all the chemical species exist within a relative amount between about 10% and 30%. Above 400 °C, however, the intensities of Si\(^0\) and Si\(^{4+}\) peaks increase gradually while those of the other suboxide peaks decrease, which leads to a phase separation of the film into Si nanocrystals and \(SiO_2\) matrix.\(^{19,20}\) In particular, the relative ratio of the Si\(^{2+}\) peak intensity decreases significantly and becomes negligible at 600 °C.

In order to validate the involvement of the intermediate \(SiO_x\) phase for the oxidation, the growth rates of Si and \(SiO_2\) films are compared as a function of deposition temperature. In Fig. 3(a), the pure Si film is made by the IBSD method without oxygen atmosphere while the \(SiO_2\) film is under the \(P_{O_2}\) of \(2 \times 10^{-4}\) Torr where the only fully oxidized species is formed in the film. The thickness of each thin film grown for a given time is measured also using the in situ XPS. Both the
growth rates of the Si and SiO$_2$ film decrease at temperatures above 300 °C due to the decrease of the sticking coefficient for Si atoms. However, the stronger decrease of the growth rate of SiO$_2$ compared to that of Si implies that there is a film loss caused by the desorption of SiO species during the growth of SiO$_2$.

At the low temperature regime, one can easily imagine that once the oxygen atoms are chemisorbed on the Si surface, they can neither diffuse further nor make SiO desorption. This means that the oxygen content (x) of SiO$_2$ is directly related to the uptake amount of oxygen and the oxidation can be described by the Langmuir adsorption isotherm equation for a dissociative adsorption process\(^{21}\)

\[
\theta(O) = \frac{K \cdot P_{O_2}}{1 + K \cdot P_{O_2}} \quad (2)
\]

in which the oxygen coverage $\theta(O)$ is approximately proportional to $P_{O_2}$ under a certain condition corresponding to the equilibrium constant $K$. This curve is fitted well to the variation of the oxygen content at RT in the Fig. 1. For the oxidation at the high temperatures, the adsorbed oxygen atoms can diffuse into the bulk of the film and find extra reaction sites to form the fully oxidized SiO$_2$ by a reaction such as SiO$_{chem}$ + O$_{gas}$ $\rightarrow$ SiO$_2$. On the other hand, suboxide species can be ejected to vacuum due to the reaction such as SiO$_{chem}$ $\rightarrow$ SiO$_{gaseous}$ or Si$_{chem}$ + SiO$_{2(g)}$ $\rightarrow$ SiO$_{chem}$ as inferred in the Fig. 3(a). The production of such a volatile suboxide is well known for the high temperature oxidation (>600 °C) elsewhere as far as a Si-substrate itself is oxidized,\(^{22}\) but it is not so critical for low temperature oxidation. The major difference between the previous cases and ours would be that the IBSD method delivers single Si atoms as a reaction partner which makes more volatile species than a Si atom bound to the substrate does.

The oxidation by the diffusion-induced internal reaction on a pure Si layer can be estimated as in Fig. 3(b) which exhibits the thickness of the SiO$_2$ surface layer grown by oxygen exposure at $P_{O_2} = 3 \times 10^{-5}$ Torr for 50 sec without Si supply. The oxide layer is very thin at low temperatures below 300 °C, which is due to the surface-confined reaction by adsorbed oxygen atoms with the top Si atoms. However, the thickness begins to increase abruptly at 300 °C and maximizes at temperatures above 500 °C. This result indicates that internal diffusion of oxygen atoms making the fully oxidized SiO$_2$ is a significant pathway for the high temperature oxidation surpassing the surface-confined reaction.

From the above results, the variation of oxygen content at 600 °C can be explained schematically as in Fig. 4. The chemisorbed oxygen atoms react with the deposited Si atoms at the surface or they can diffuse further into the film. In the high-temperature oxidation of Si, the formation of SiO$_2$ on the top surface would be suppressed due to desorption of SiO at low oxygen pressures. The only oxidized species left in the film come from the diffusion-induced internal reaction (B in Fig. 4). Thus, the oxygen content follows roughly the adsorption isotherm curve [Eq. (2)] but with a very low sticking coefficient. When the oxygen partial pressure is high enough, however, the oxygen content of Si oxide increases as the SiO has more chance to react with another oxygen atom to form the stable SiO$_2$ before the desorption of the SiO occurs. Once the oxygen chemisorption takes place (A in Fig. 4), the diffusion of the oxygen leads to form the stable SiO$_2$. This results in the increase of oxygen content directly proportional to the oxygen gas flux [i.e., partial pressure in Eq. (1)]\(^{23}\) Therefore the variation of oxygen content at the first and second step in Fig. 1 can be originated from the diffusion-induced internal reaction (B) while the monotonic increase at the third step can be attributed to the adsorption-induced surface reaction (A). Although the two reactions are involved in chemical oxidation and produce the same reac-

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**FIG. 3.** (a) Variation of growth rate of Si and SiO$_2$ thin films as a function of deposition temperature (see text). (b) Thickness of SiO$_2$ layer formed by thermal oxidation of a pure Si layer at $P_{O_2} = 3 \times 10^{-5}$ Torr for 50 s.

**FIG. 4.** Schematic diagram for the oxidation of Si at 600 °C by the combination of an adsorption-induced surface reaction (A) and a diffusion-induced internal oxidation (B).
tion products, their contributions to the surface composition are very different because the intermediate reaction product SiO produced by surface reaction is desorbed instantaneously, and that by internal reaction survives to react with another oxygen atom to form a stable SiO₂ at high deposition temperatures.

In conclusion, Si oxidation during the growth of Si oxide films by IBSD has been studied by in situ XPS at various substrate temperatures and oxygen partial pressures. The oxidation trend is similar to an adsorption isotherm showing that the surface-confined chemical reaction is the primary process of Si oxidation at low temperatures. However, the oxidation at high deposition temperatures shows an unusual dependence of the oxygen content on oxygen pressure. The evolution of SiO species is confirmed by chemical state analysis using XPS and by the growth rate difference between the Si and SiO₂ as a function of substrate temperature. The existence of the intermediate SiO species and the variation of oxidation states at high temperatures indicate that an adsorption-induced surface reaction and a diffusion-induced internal reaction are the operative and competing oxidation pathways.

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