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Rate-Limiting Reaction of Layer-by-Layer Oxidation on Si(001) Surfaces: Dependence on the First Oxide Layer Growth Kinetics

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1. Introduction

Layer-by-layer oxidation on Si surfaces has attracted much attention from a point of view of the oxidation reaction mechanism and is of practical importance to form SiO_2 gate dielectric layers with high electric performances for advanced MOSFETs [1-3]. However, it is difficult to interpret the layer-by-layer oxidation kinetics in an oxide thickness range as thin as ~1 nm using an interfacial Si emission model proposed by Uematsu, Kageshima and Shiraishi [4] as well as a well-known oxidation model by Deal and Grove [5]. One of the reasons for the difficulty is that the growth kinetics of second oxide layer is strongly influenced by that of first oxide layer [3, 6], while the first oxide layer is almost the same in thickness, 0.3-4 nm. Therefore O_2 diffusion is ruled out as a rate-limiting reaction for the second oxide layer growth kinetics. Recently we have found that the behavior of adsorbed oxygen depends on the temperature and therefore can change the point defect generation kinetics due to the volume expansion of oxidation, leading to the different amount of emitted Si atom and vacancy even for the same number of adsorbed oxygen atoms as revealed by band bending [7]. Furthermore the point defect generation depending on the first oxide layer growth kinetics was suggested to be associated with the rate-limiting reaction of the second oxide layer growth kinetics [6, 7].

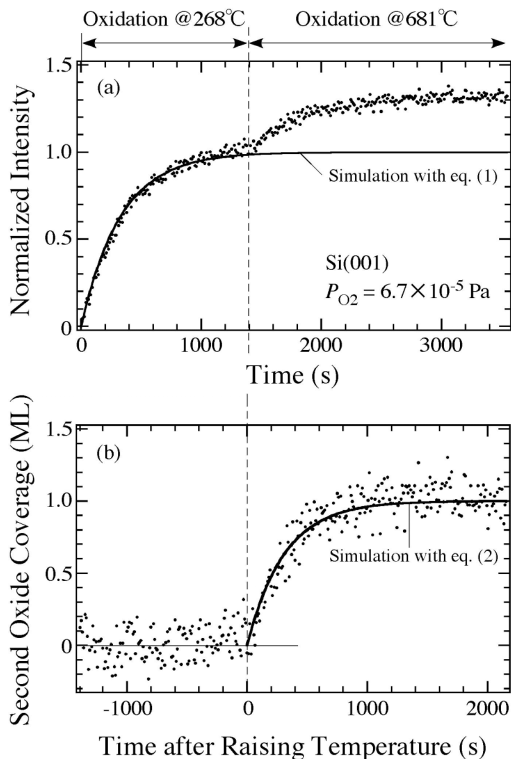

Fig. 1 (a) Time evolution of O KLL Auger electron intensity taken *in situ* during oxidation on a Si(001)2×1 surface at an O_2 pressure of 6.7×10^{-5} Pa. The substrate temperature was elevated from 268 to 681℃ at 1392 s. (b) Time evolution of differences between the data and simulation with eq. (1) in (a). The vertical axis is represented by the normalized second oxide layer coverage.

In this study, the dependence of the second oxide layer growth kinetics on the temperature and first oxide layer growth kinetics on a Si(001)2×1 surface was investigated by RHEED combined with AES to measure in real time the oxide growth rate. Based on the activation energy and preexponential factor of the growth rate of second oxide layer, the Si emission kinetics is discussed to interpret the rate-limiting reaction of the second oxide layer growth.

2. Experimental

The experiments were performed with an apparatus equipped with facilities of reflection high energy electron diffraction combined with Auger electron spectroscopy (RHEED-AES) and O_2 gas introduction with a base pressure of $\sim1\times10^{-8}$ Pa. The REEH-AES measurement was performed using a 10-keV probe electron beam at an incident angle of $\sim1^o$ along the <100> azimuth. The O KLL Auger electron intensity $I_{O\text{-}KLL}$ was obtained by normalizing the O $_{KLII,\,III}L_{II,\,III}$ peak intensity at E_k = ~505 eV by the background intensity at E_k = ~530 eV to eliminate the fluctuations in position and current of the primary electron beam.

B-doped p-type Si(001) surfaces were oxidized by O_2 gas of 99.99% purity at an O_2 pressure 6.7×10^{-5} Pa. The sample was annealed by direct resistive heating with a DC current and the temperature of the sample was measured by an optical and an infrared pyrometer calibrated with a chromel–alumel thermocouple.

3. Results and Discussion

In Fig. 1(a), the second oxide layer was grown at 681℃ following the first oxide layer growth at 268℃, which can be fitted well using eq. (1) based on a Langmuir-type adsorption model [6].

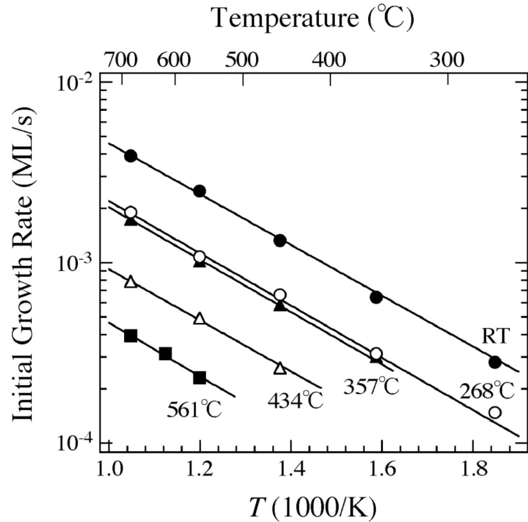

Fig.2 Arrhenius plot of the initial growth rate of the second oxide layer. The first oxide layer growth was performed at temperatures of RT(●), 268℃(○), 357℃(▲), 434℃(△) and 561℃(■).

$I_{1st} = 1 - \exp(-k_1 t)$ (1)

As shown in Fig. 1(b), the difference between the data and the simulation corresponding to the second oxide layer growth is fitted well using eq. (2) as in Ref. [2].

$I_{2nd} = 1 - \exp(-k_2 t)$ (2)

In Figs. 1(a) and 1(b), $I_{O\text{-}KLL}$ and the difference in normalized by the saturation level of first and second oxide layer growth, respectively. The initial growth rate of second oxide layer is given by k_2 using eq. (2).

The dependence of k_2 on the second oxide layer growth temperature is given as a function of the first oxide layer growth temperature in the Arrhenius plot of Fig. 2. It is clearly recognized that k_2 decreases considerably with increasing first oxide layer growth temperature, indicating the strong dependence on the first oxide layer growth as reported previously [6]. For all first oxide layer growth temperatures, k_2 is can be fitted well using straight lines, making it possible to evaluate the activation energy E_a and frequency factor ν of k_2. The solid lines in Fig. 2 are least-squares fittings to the data. The dependence of E_a and ν on the first oxide layer growth temperature is summarized in Fig. 3. E_a is almost constant and the averaged value is 0.27 eV in good agreement with that in Ref. [2], ~0.3 eV. On the other hand, ν decreases by about one order when increasing the first oxide layer growth temperature from RT to 561℃. The dependences of Fig. 3 are clear evidence that the first oxide layer growth kinetics, that is the strain of the first oxide layer, brings a change in the frequency factor of point defect generation with maintaining the energy barrier almost constant at a relatively small value of ~0.27 eV.

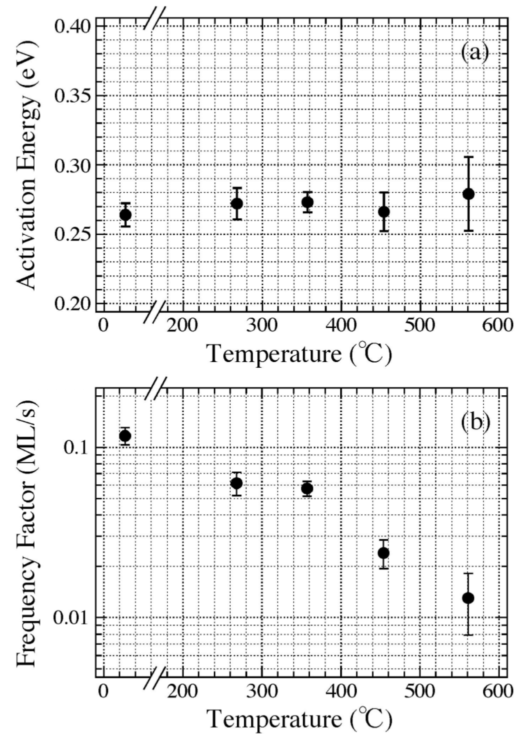

Fig. 3 (a) Activation energy and (b) frequency factor of the initial growth rate of second oxide layer obtained as a function of the first oxide layer growth temperature. The error bars indicate the standard deviations of the least square fitting.

4. Conclusion

To clarify the rate-limiting reaction of layer-by-layer oxidation, the second oxide layer growth kinetics was investigated by RHEED-AES. It was found that the frequency factor of the initial growth rate of second oxide layer decreases by about one order with temperature in a region of RT-600℃, although its activation energy is kept almost constant at ~0.27 eV independent of the first oxide layer growth temperature. Therefore it is concluded that the change in the point defect generation kinetics due to the first oxide layer growth is not a potential energy barrier but a frequency factor for Si mission at the SiO_2/Si interface.

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