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STM Study of Thermal Oxidation Process on Si(111) 7×7 Surfaces

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Thermal (600°C) oxide film growth of Si(111)7x7 surfaces was studied in the submonolayer regime using STM and XPS, and was compared with room temperature oxidation. In STM measurements, the 600°C oxidized areas (which were observed as dark ones in contrast to the unoxidized areas) were found to be more condensed and darker than those of room temperature oxidation. By comparing STM topographs with XPS Si-2p suboxide profiles, we ascribe the darker area to the heavier (closer to SiO_2) oxidized region. These results provide direct evidence of the phase separated or island oxide formation of high-temperature oxidation as previously suggested by Tabe et al. in their work with XPS.

1. INTRODUCTION

Most STM studies of the Si oxidation process have been for room temperature (RT) oxidation.[1-4] For high-temperature reactions, only etching of Si due to volatile SiO formation which occurs at an O_2 pressure (P_{O2}) below a critical value has been studied.[5] However, it is above this critical P_{O2} that the oxide film growth proceeds. Here, for the first time, we apply STM and XPS analysis to investigate the initial stage of thermal (600°C) oxidation under the film growth conditions, in comparison with RT oxidation.

2. EXPERIMENTAL PROCEDURE

For this work, we employed a UHV machine consisting of three chambers—loading, preparation and analysis chambers—that are separated by gate valves. The preparation chamber (base pressure: $2x10^{-10}$ Torr) is equipped with current terminals to apply resistive heating to the sample, a variable leak valve to introduce O_2 gas into the chamber, and a RHEED system. The analysis chamber (base pressure: $5x10^{-10}$ Torr) is equipped with STM and XPS.

Samples used in this study were pieces of P-doped (111) oriented Si wafer with a resistivity of 0.1 Ohm·cm. In the preparation chamber, a 7x7 reconstructed surface was obtained by cleaning at 1250°C for 20sec and was confirmed by RHEED. This was followed by RT and 600°C oxidation at $P_{O2}=1.0x10^{-8}$ and $1.0x10^{-6}$ Torr, respectively. The present P_{O2} of 600°C oxidation is within film growth conditions, as will be confirmed below.

STM and XPS observation of the oxidized surfaces was made at room temperature. For the STM measurements, we used a tungsten tip and images were taken at +1.5V sample bias (unoccupied state) in the constant current mode.

3. EXPERIMENTAL RESULTS

First, the oxide film growth condition was examined by in situ RHEED observation of thermal oxidation in a substrate temperature(Ts) vs. P_{O2} plane. As shown in Fig.1, degradation of 7x7 pattern (open circles) indicative of oxide film growth, occurs above a critical P_{O2}.[6] Since the critical P_{O2} is $6x10^{-8}$ Torr at 600°C, the present condition ($P_{O2}=1x10^{-6}$Torr, Ts=600°C) is well within the film growth region. Figure 1 agrees well with a previous report.[7]

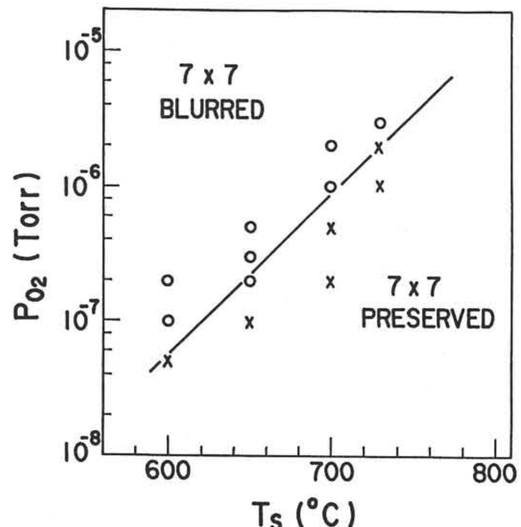


Fig.1 RHEED observation of 7x7 pattern degradation.

Next, the oxygen coverage was measured for the 600°C oxidation as well as for RT oxidation(Fig.2). The oxygen coverage, given in units of ML(=$7.83\times10^{14}cm^{-2}$), was evaluated from the ratio of O-1s to Si-2p peak height of XPS wide-range scan data. Again, our results shown in Fig.2 are consistent with previous data.[8]

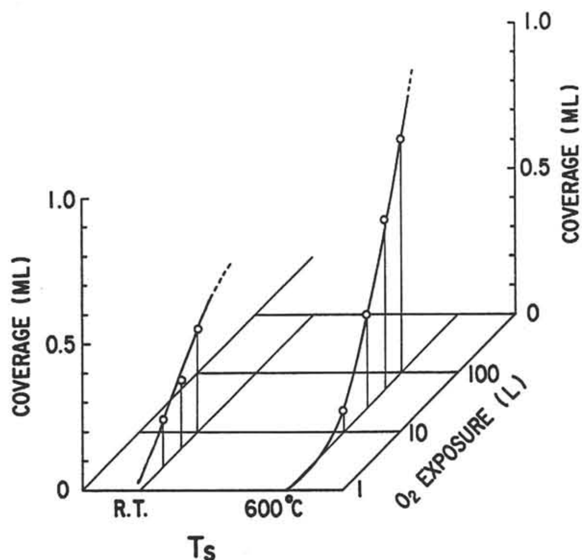
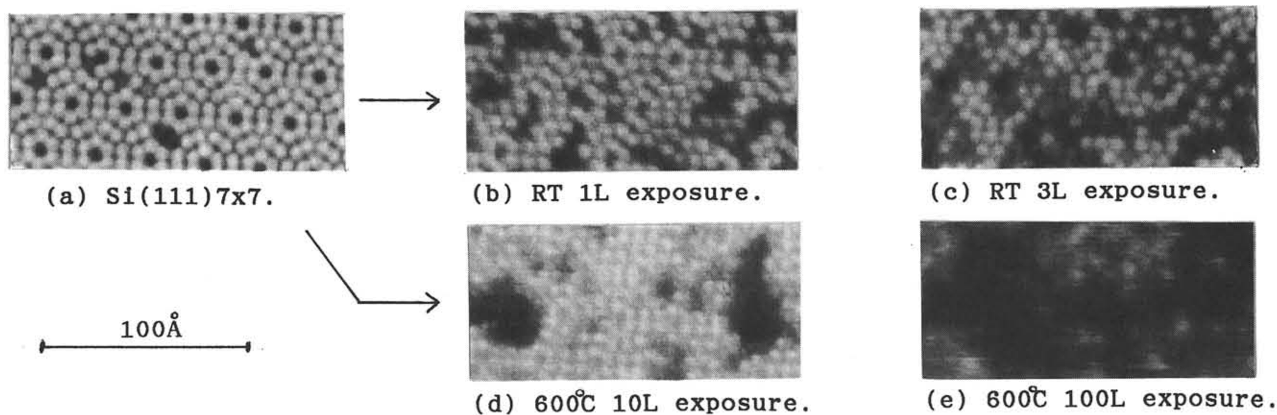


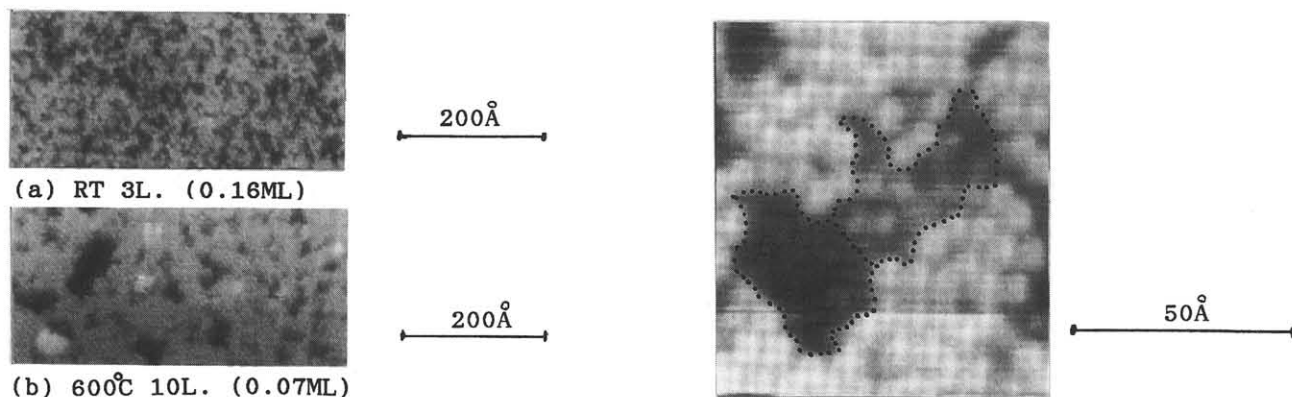
Fig.2 Oxygen coverage by XPS. P_{O2} for exposure are 1×10^{-8} Torr at RT and 1×10^{-6} Torr at 600°C.

STM images of RT and 600°C oxidized surfaces are compared in Fig.3. The dark area increases with O_2 exposure for both RT and 600°C oxidation. It was also found by XPS that the fraction of the dark area is comparable to the oxygen coverage. This substantiates that the dark area represents the oxidized region, as suggested in Refs.1-4. For the 600°C oxidation, the depression generated by etching the surface is another possible candidate to explain the dark area.[5] But, etching rate of Si (not shown) suggests that influence of the etching is minor under the present oxidation condition.[9] Here, in Fig.3, a remarkable difference was found between the RT and 600°C oxidized surfaces. It is apparent that the oxidized region (dark area) of the 600°C oxidation is more condensed than that of the RT oxidation. This difference is accentuated in the wide-range images shown in Fig.4. In the 600°C oxidation, each patch of oxidation is larger and darker (more heavily oxidized) than in the RT oxidation, even though the total amount of oxygen is almost the same. This provides direct evidence that high-temperature oxidation proceeds in a phase-separated fashion (SiO_2 and Si) as suggested by Tabe et al. in their work with XPS.[8]



(a) Si(111)7x7. (b) RT 1L exposure. (c) RT 3L exposure. (d) 600°C 10L exposure. (e) 600°C 100L exposure.

Fig.3 STM images of oxidized surfaces. (tip current: 1.0nA)



(a) RT 3L. (0.16ML)

(b) 600°C 10L. (0.07ML)

Fig.4 Comparison of STM images of RT and 600°C oxidation. (tip current: 0.1nA)

Fig.5 Dark area of 600°C oxidation. (tip current: 1.0nA)

Next, we examined the dark area of the 600°C oxidation in detail. As shown in Fig.5, some of the dark patches are darker than others. We ascribe the darker areas to more heavily oxidized (closer to SiO_2) regions because thicker oxide layers will exhibit higher tunneling resistance.

To compare the degree of darkness of the dark areas of the RT and 600°C oxidations, we show the area fraction (AF) of the dark areas as a function of apparent depth in Fig.6. Note that apparent depth does not mean actual depth, but rather reflects the increase in tunneling resistance due to surface oxidation. As shown in Fig.6, the dark area of the RT oxidation mainly distributes around a "1-Å-depth" (a), whereas the distribution for the 600°C oxidation spreads out towards the darker side(b), and shifts even further for the heavier oxidized sample(c). These results indicate that the oxidized area of the 600°C oxidation comes closer to being fully oxidized Si (SiO_2) than that of the RT oxidation.

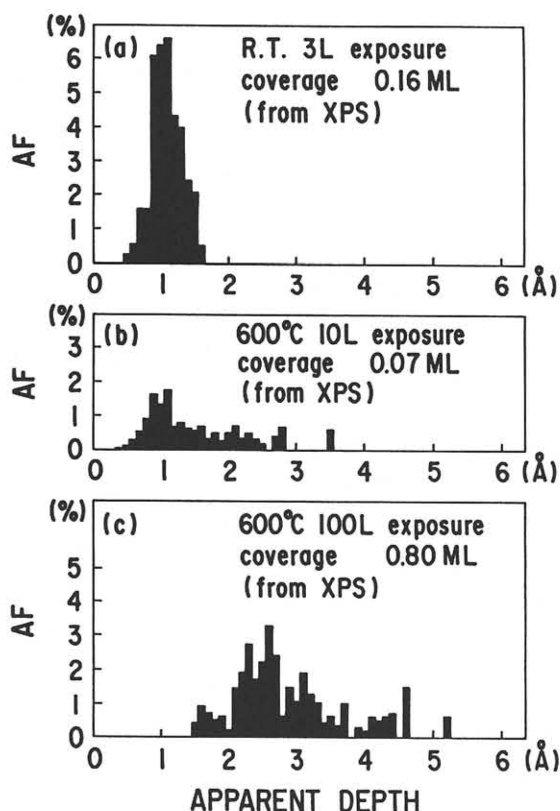


Fig.6 Histogram of AF.

In order to confirm the above results, we also compared the suboxide of Si-2p spectra (i.e. high energy tails) of the RT and 600°C oxidations. As shown in Fig.7, heavily oxidized Si (indicated by the left arrow) predominates for the 600°C oxidation while lightly oxidized Si (the right arrow) predominates for the RT oxidation (a). In addition, the fraction of the heavily oxidized Si increases with oxygen

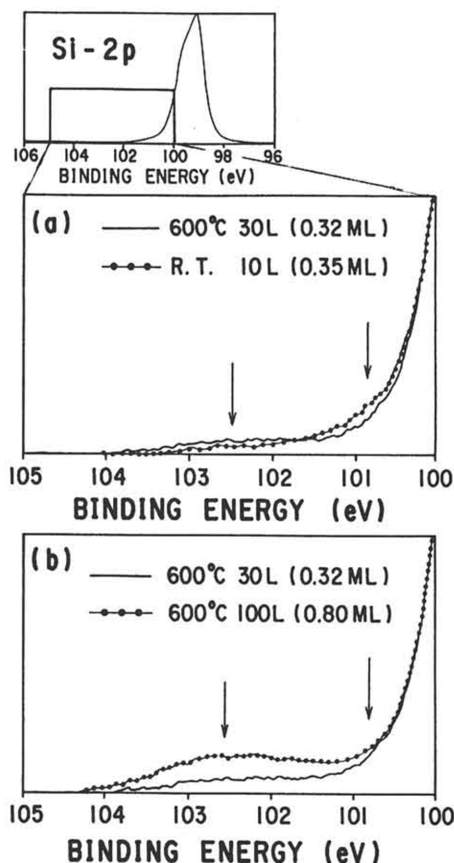


Fig.7 XPS Si-2p spectra.

coverage (b). These results are entirely consistent with the above histogram (Fig.6) and STM images (Figs.3,4).

4. CONCLUSION

We have studied the initial stage of thermal oxidation on Si(111)7x7 surfaces with STM and XPS, and direct evidence of island formation (oxidized areas) was obtained for high-temperature (600°C) oxidation.

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