

In-Situ Observation of Oxygen Exposed Hydrogen Terminated Silicon Surfaces

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In-situ observation of hydrogen (H) terminated silicon (111) surface after exposure in 133 Pa dry O₂ was performed using Fourier transformed IR attenuated total reflection spectroscopy (FT-IR-ATR), X-ray photoelectron spectroscopy (XPS), Penning ionization electron spectroscopy (PIES), and ultraviolet photoelectron spectroscopy (UPS). The IR absorption peak attributed to the terminating Si-H bonds did not change at all after exposure in N₂ at 180 °C, while this absorption peak decreased after exposure in O₂ at 180 °C. Then XPS and ATR measurements could not confirm the formation of Si-O bonds. We considered that such decrease in IR absorption peak reflects the very early oxidation process.

1. INTRODUCTION

In our previous study¹⁾, we have investigated the native oxide growth in pure water on atomically flat hydrogen (H) terminated silicon (Si) (111) surfaces using Fourier transformed infrared attenuated total reflection spectroscopy (FT-IR-ATR) and FT-IR reflection absorption spectroscopy (FT-IR-RAS). We then observed that the sharp IR absorption peak arising from Si-H bonds terminating the surface terraces²⁾ (labeled by M_{terrace} in Fig. 1) decreases with broadening in the early stage native oxide growth process as shown in Fig. 1. This phenomenon arose much earlier than the formation of Si-O bonds, we therefore suggested that such phenomenon reflects the progress of very early native oxide growth.

In this study, we performed *in-situ* observation of

H-terminated Si(111) surface after exposure in 133 Pa dry O₂ at 145~245 °C^{3,4)} using *in-situ* observation techniques of FT-IR-ATR, X-ray photoelectron spectroscopy (XPS), Penning ionization electron spectroscopy⁵⁾ (PIES), and ultraviolet photoelectron spectroscopy (UPS). We will show the change in the IR absorption spectra arising from Si-H stretching vibration after O₂ exposure, and the surface condition will be discussed.

2. EXPERIMENTAL

Samples used in this study were floating zone p-type Si(111) with resistivity of 100 Ωcm. Atomically flat H-terminated Si(111) surfaces prepared in NH₄F solution⁶⁾ were employed as initial surfaces. We used two *in-situ* observation systems, each one equips the sample

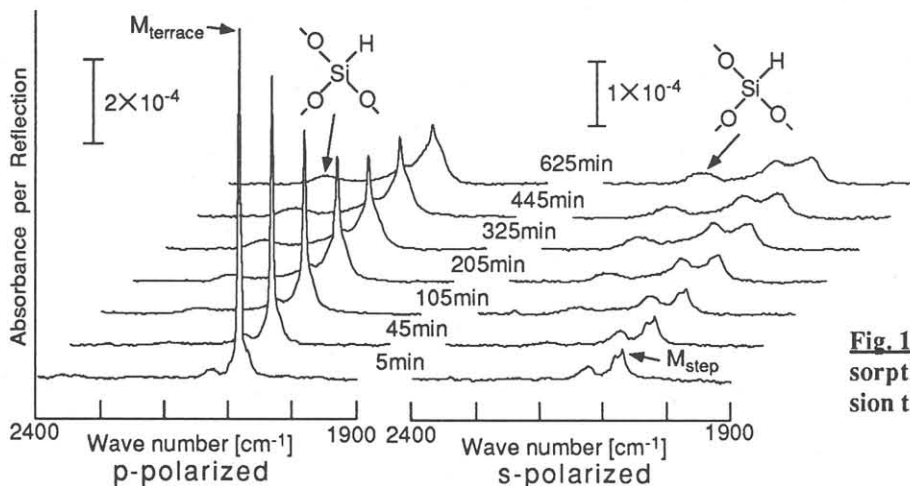


Fig. 1 Change in p- and s-polarized IR absorption spectra as a function of immersion time in pure water in ref. 1.

treatment chamber with temperature control and gas inlet system. One of the equipments furnishes with FT-IR-ATR and XPS, and the another furnishes PIES and UPS. IR light was internally reflected about 100 times in the sample Si prism for ATR measurement. In XPS measurement, MgK α line ($h\nu=1253.6\text{eV}$) was used as X-ray source, and we measured with 15° take-off angle to improve the surface sensitivity. The He I resonance line ($h\nu=21.2\text{eV}$) was used as a UV source in UPS measurement, and the He* metastable atoms (2^3S : 19.8eV) were used in PIES measurement. Oxygen exposure was performed in 133 Pa dry $\text{O}_2^{3,4)}$ at comparatively low temperature not desorbed terminating H atoms.^{7,8)}

3. RESULTS and DISCUSSION

Figure 2 shows p-polarized IR absorption spectra arising from Si-H bonds obtained for an initial surface and difference spectra between the initial surface and after exposure in N_2 or O_2 at various temperatures. In the case of initial surface, only the sharp absorption peak of M_{terrace} which is attributed to the Si-H bonds terminating surface terraces was observed.²⁾ From this figure, we found that there is no spectral change after exposure in N_2 at 180°C and that the M_{terrace} peak decreases as the O_2 exposure temperature or time increases. In addition, the absorption arising from Si-H bonds back-bonded with oxygen atom(s)⁹⁾ at $2150\text{--}2250\text{ cm}^{-1}$ was not observed. XPS measurements were also performed on these surfaces, and Si2p photoelectron spectra are shown in Fig. 3. We hardly observe the clear signal due to the intermediate silicon oxide or SiO_2 at binding energy of $101\text{--}104\text{eV}$ in any cases. Figure 4 shows O1s photoelectron spectra measured at the same time. We found that the O1s spec-

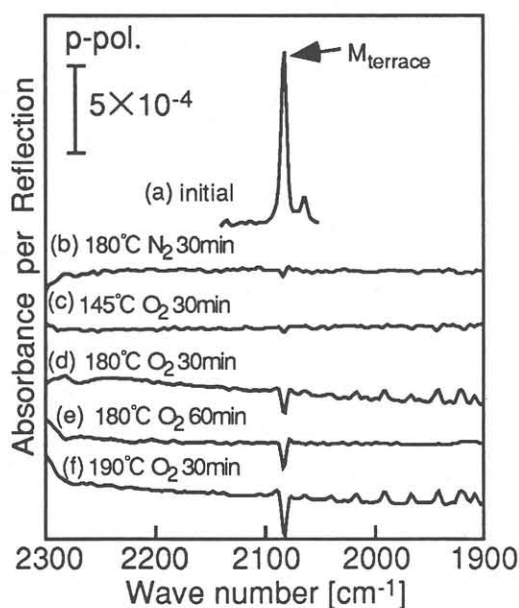


Fig. 2 Change in IR absorption spectra arising from Si-H bonds as a function of exposure time in 133 Pa dry O_2 or N_2 . Spectra (b)-(f) are difference from spectrum obtained for initial surface (a).

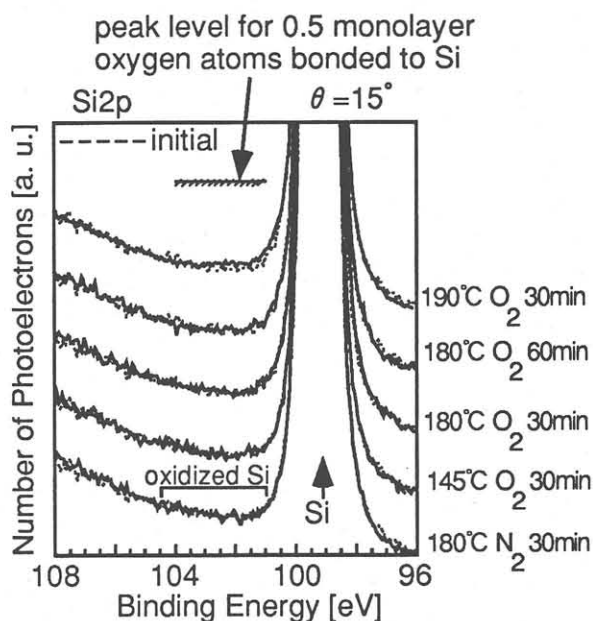


Fig. 3 Change in Si2p photoelectron spectra as a function of exposure time in 133 Pa dry O_2 or N_2 . Dashed line means the spectrum obtained for the initial surface.

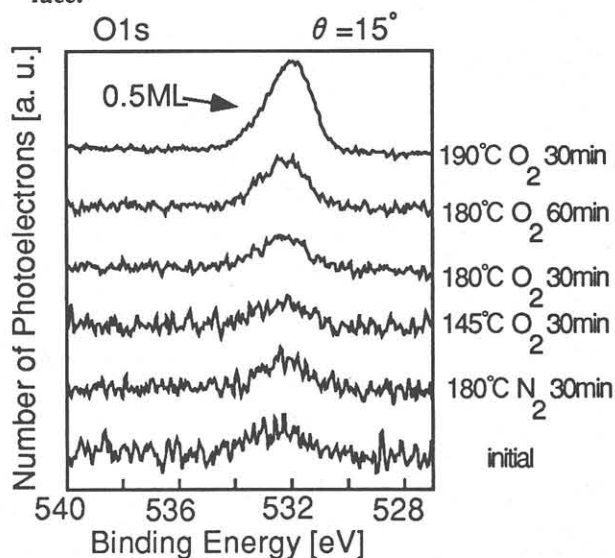


Fig. 4 Change in O1s photoelectron spectra as a function of exposure time in 133 Pa dry O_2 or N_2 . 0.5 monolayer oxygen atoms exist on Si surface after treatment in 190°C O_2 for 30min.

tral intensity increases as the O_2 exposure temperature or time increase. It should be noticed that the amount of oxygen atoms is approximately 0.5 monolayer after treatment in O_2 at 190°C for 30 min, if all these oxygen atoms contribute to form Si-O bonds, the spectral intensity of Si2p photoelectron spectrum due to the Si bonded with oxygen atom have to be the level showed in Fig. 3. These results are summarized as follows: there is little Si-O bonds near the silicon surface, however, the M_{terrace} peak decreases as the exposure temperature or time increases, and these changes are linked with the increase in amounts of oxygen on the silicon surface. We therefore considered that the decrease in the M_{terrace} peak reflects

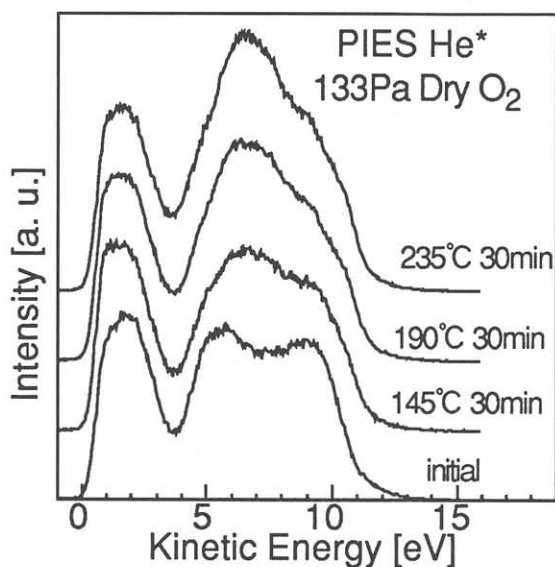


Fig. 5 Change in PIES spectra as a function of exposure time in 133 Pa dry O₂ at various temperature.

progress of very early oxidation on H-terminated silicon surface.

We also performed similar experiment using PIES and UPS at almost same conditions. We then found that the PIES spectra change extremely increasing with temperature in 133 Pa dry O₂ as shown in Fig. 5 and that the UPS spectra change slightly. Since the PIES spectra selectively reflect the information of the outermost surface⁵⁾, change in the surface state due to O₂ exposure must occur at outermost surface. In addition, there is little Si-O bonds at the surface in this case from the results obtained for FT-IR-ATR and XPS measurements, we therefore took notice of O₂ molecule. Figure 6 shows the difference PIES spectra between before and after exposure as shown in Fig. 5. Comparing the Fig. 6 and the PIES spectrum obtained for oxygen gas, we found that the 6.8 eV and 10.8 eV bands in Fig. 6 are due to the π orbital of adsorbed O₂ molecule and that the both bands shifted 3.5 eV to higher kinetic energy. This results are possible to indicate that the adsorbed O₂ molecule accepts the charge. Here, it must appear the band at 5.2 eV due to σ orbital of O₂ molecule, however we could not observe clearly. This reason was inferred that this band overlaps with the band due to the terminating H at the surface and/or the O₂ molecule is placed at the surface as it cannot be observed by PIES. Anyway, since the band due to π orbital of O₂ molecule was observed, we considered O₂ molecule *lies* on the surface.

4. SUMMARY

In-situ observation of H-terminated Si(111) surface after exposure in 133 Pa dry O₂ at 145~245 °C was performed using FT-IR-ATR, XPS, PIES, and UPS. The IR absorption peak attributed to the terminating Si-H bonds did not change at all after exposure in N₂ but this absorption peak decreased after exposure in O₂. Then

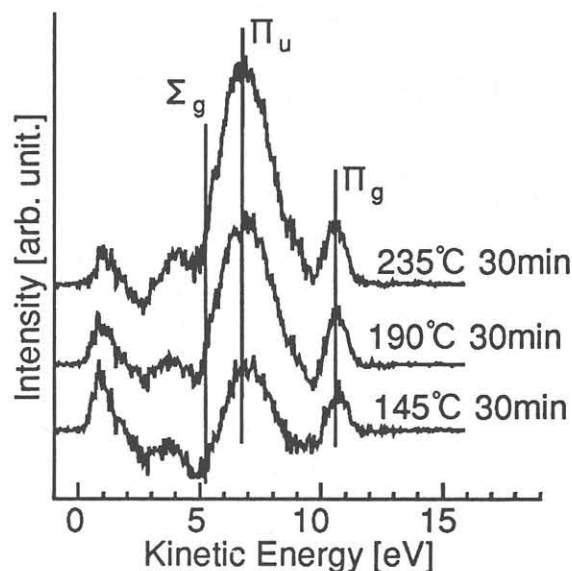


Fig. 6 Difference PIES spectra between before and after exposure as shown in Fig. 5.

XPS and ATR measurements could not confirm the formation of Si-O bonds. We therefore considered that such decrease in IR absorption peak reflects the very early oxidation process. The experimental results obtained by PIES and UPS show that then the O₂ molecule *lies* at the outermost surface.

ACKNOWLEDGEMENTS

We are grateful to H. Kubota, Y. Einaga, R. Kurosaki, M. Nagasaka and J. Kikuchi for their experimental assistance and valuable discussion.

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