

Effects of Dissolved Oxygen in HF Solution on Silicon Surface Morphology

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Surface morphology changes on atomically flat H-terminated Si(111) in various dissolved oxygen concentration (DOC) HF solutions were studied by Fourier transformed IR attenuated total reflection spectroscopy (FT-IR-ATR). The absorption peak arising from monohydrides at the terraces decreases and the absorption peaks arising from monohydrides at the surface steps, dihydrides and trihydrides increase with immersion time in HF solution. Such spectral changes were slower with lower DOC. These results indicate that the silicon surfaces were etched by the HF solution and that the dissolved oxygen (DO) in the HF solution plays an important role in such etching.

1. INTRODUCTION

Wet chemical treatments used in semiconductor device manufacturing are traditionally required to remove particles, organic contaminants, and metallic impurities from wafer surfaces. Securement of the physical and chemical state of surfaces (surface roughness, native oxide removal, etc.) has been required recently.

HF solution, one of the most important solutions in wet chemical treatments, removes silicon oxide and terminates the wafer surface with hydrogen.¹⁾ This surface is microscopically rough.²⁾ Meanwhile, it is well known that the dissolved oxygen concentration (DOC) in pure water influences native the oxide growth rate on a hydrogen terminated silicon surface³⁾, however, other effects of dissolved oxygen (DO) on silicon surfaces are still not understood.

In this study, we studied the change in silicon surface morphology after immersion in HF solutions diluted by DOC controlled pure water on atomically flat H-terminated Si(111) surfaces using Fourier transformed IR attenuated total reflection spectroscopy (FT-IR-ATR).

2. EXPERIMENTAL

IR absorption arising from silicon hydrides was observed using about 100 times internal reflection FT-IR ATR.^{1,2)} In order to study Si-H bond direction on the silicon surfaces, p-polarized and s-polarized IR radiation, where the electric field is perpendicular and parallel to the surface respectively, were used. The experiment was performed on 0.5x20x50mm p-type FZ Si(111)

samples of 100Ωcm resistivity with 45° bevels on each of the short sides, cut from 4-inch wafers. As shown in Fig. 1, samples were firstly treated by the RCA clean⁴⁾ and sacrificial oxide films were formed in O₂ at 1000°C. Next, such oxide films were removed by HF solution and the samples were treated by the RCA clean again. One set of samples, as initial surfaces, was treated in 40% NH₄F solution and was rinsed in pure water with 1ppb DOC in a N₂ ambient (below 25ppm O₂ concentration) and another set of samples, as reference surfaces, was

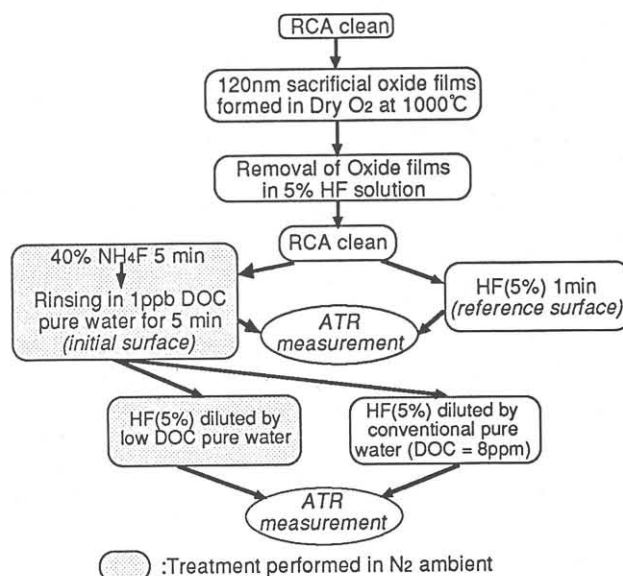


Fig. 1 Schematic diagram of experimental procedure. O₂ concentration of the N₂ ambient was controlled to adapt to the pure water DOC. e.g. 5% O₂ concentration in the N₂ ambient was used for 2ppm DOC pure water.

treated in 5% HF solution. The surfaces of both sets were terminated by hydrogen.^{1,2,5,6} In order to investigate the effects of DO in the HF solution on silicon surfaces, the initial surfaces were immersed in 5% HF solution diluted by low DOC pure water in a N₂ ambient or diluted by conventional pure water (DOC=8ppm) in clean room air at 25°C; both sets were then measured by ATR. In this experiment, conventional 50% concentration HF solutions which contain DO were used. The concentration of dissolved gas in a solution changes with the partial pressure of the gas in contact with the solution according to Henry's law. Therefore, to control the DOC in HF solutions diluted by low DOC pure water, we kept the HF solutions in various O₂ concentration N₂ ambients adjusted to the pure water DOC, and waited until the O₂ concentration in the N₂ ambient stabilized to a fixed value.

3. RESULTS and DISCUSSION

Fig. 2 shows the IR absorption spectra arising from silicon-hydrogen (Si-H) bonds obtained for hydrogen terminated Si(111) surfaces. In this figure, spectra (a) were obtained for H-terminated Si(111) surfaces formed in NH₄F solution followed by low DOC pure water rinsing and, as is well reported,^{5,7} the p-polarized spectrum shows only the sharp absorption peak arising from

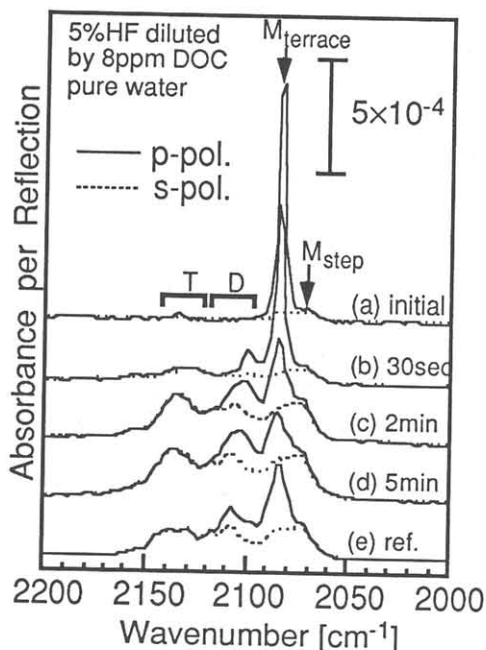


Fig. 2 IR absorption spectra arising from Si-H stretching vibration obtained for H-terminated Si(111) surfaces. (a) atomically flat H-terminated surface(initial surface) (b), (c), and (d) initial surface immersed in HF solution(5%) diluted by conventional pure water (DOC=8ppm) for 30sec, 2min, and 5min respectively in clean room air. (e) treatment in HF solution(5%) diluted by conventional pure water (DOC=8ppm) for 1min in clean room air after RCA clean (reference surface)

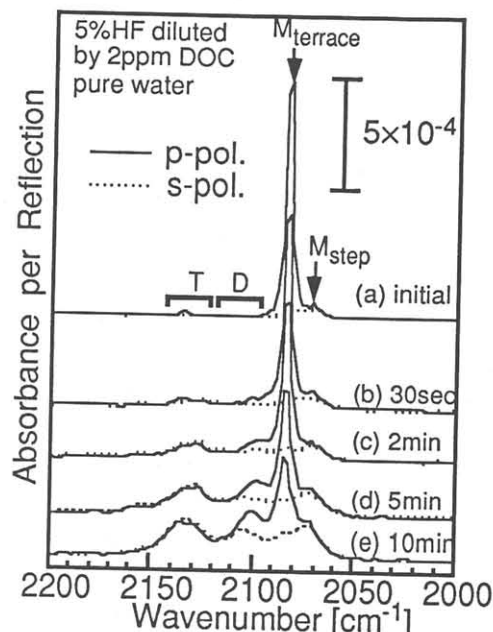


Fig. 3 IR absorption spectra arising from Si-H stretching vibration obtained for H-terminated Si(111) surfaces. (a) initial surface (b), (c), (d), and (e) initial surface immersed in HF solution(5%) diluted by 2ppm DOC pure water for 30sec, 2min, 5min, and 10min respectively in 5% O₂ concentration N₂ ambient.

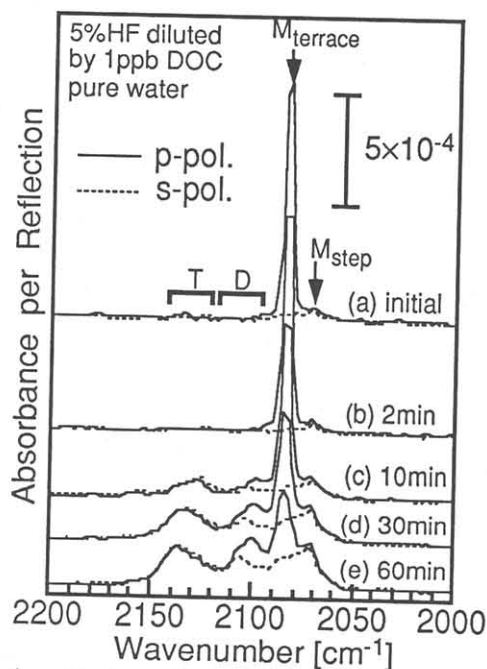


Fig. 4 IR absorption spectra arising from Si-H stretching vibration obtained for H-terminated Si(111) surfaces. (a) initial surface (b), (c), (d), and (e) initial surface immersed in HF solution(5%) diluted by 1ppb DOC pure water for 2min, 10min, 30min, and 60min respectively in 25ppm O₂ concentration N₂ ambient.

monohydrides on the surface terraces (M_{terrace}) at 2083cm^{-1} and there is little absorption in the s-polarized spectrum. This indicates that these surfaces are almost atomically flat, and terminated by hydrogen and were used as initial surfaces. Figs. 2-(b), -(c) and -(d) show the IR absorption spectra obtained for these initial surfaces after immersion in HF solution diluted by conventional pure water for 30sec, 2min and 5min respectively. The sharp absorption peak arising from M_{terrace} decreases and the absorption peaks arising from monohydrides at the surface steps at 2071cm^{-1} (M_{step}),⁵ dihydrides (D) and trihydrides (T) increase with immersion time. In particular, it is found that spectra (c) and (d) are very similar to spectra (e) obtained for the reference surface^{2,6,8} (H-terminated Si(111) surfaces formed in HF solution following RCA clean). Namely, these spectral changes indicate that the initial surface was atomically roughened and H-terminated in the HF solution diluted by conventional pure water. Figs. 3 and 4 show, as in Fig. 2, the spectral change in the case of the initial surfaces immersed in HF solution diluted by 2ppm and 1ppb DOC pure water respectively. As in Fig. 2, the absorption peak arising from M_{terrace} decreases and the absorption peaks arising from M_{step} , D and T increase with immersion time in both figures. Here, we compared Fig. 2-(c), Fig. 3-(c) and Fig. 4-(b) with each other in the case of immersion for 2min in diluted HF solutions. As stated above, the spectra in Fig. 2-(c) are very similar to the reference spectra of Fig. 2-(e). The absorption peak arising from M_{step} , D and T increase slightly in Fig. 3-(c), but the spectral change is small compared with Fig. 2-(c). Furthermore, the spectra in Fig. 4-(b) does not

change considerably from the initial surface spectra of Fig. 4-(a), which indicates that the surfaces are still atomically flat, and terminated by hydrogen. From these results, the atomically flat H-terminated Si(111) surface is roughened in HF solution with increasing immersion time. The surface morphology change rate which depends on the DOC in HF solution decreases with lower DOC. One of the indexes for the degree of change in surface morphology is the change in the absorption peak arising from M_{terrace} . Fig. 5 shows the immersion in HF solution time dependence of the normalized absorption intensity arising from M_{terrace} . This figure clearly indicates that the morphology change is slower with lower DOC. Since the changes in Si surface morphology mean etching of the Si substrate by HF solutions,^{9,10} the DO in the HF solution can be considered to play an important role in such etching.

4. CONCLUSIONS

Surface morphology changes on atomically flat H-terminated Si(111) surfaces in various DOC HF solutions were studied by FT-IR-ATR. It was found that the surface morphology changes with immersion time in HF solutions, this indicates that the silicon substrate is etched in HF solutions. Furthermore, it was also found that such morphology change rate is slower with lower DOC in the HF solution. This indicates that the DO in the HF solution plays an important role in silicon etching.

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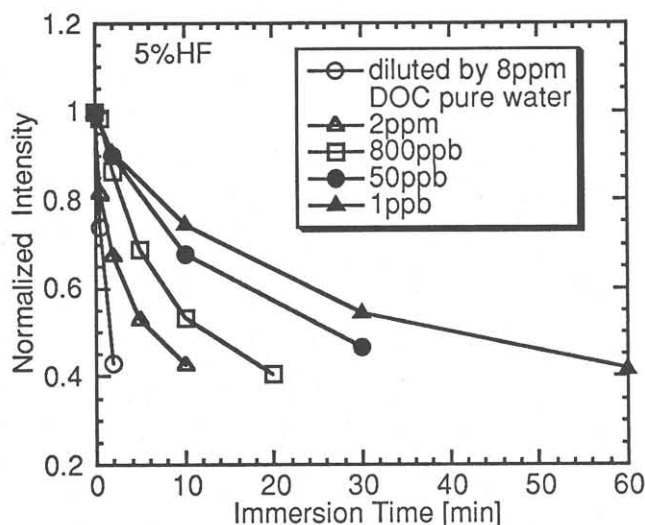


Fig. 5 Normalized absorption intensity of M_{terrace} as a function of immersion time in HF solution. The initial absorption intensity of M_{terrace} is adjusted to 1. In the case of 5% HF solution diluted by 800ppb and 50ppb DOC pure water, treatments were done with 2% and 1250ppm O_2 concentration N_2 ambient respectively.