

H-terminated Si(111) surfaces immersed in HI solutions studied by Si 2p core-level photoelectron spectroscopy

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Introduction

The adsorption of halogen atoms on clean Si(111) surfaces under ultra-high vacuum conditions has been widely investigated by many groups of researchers (F, Cl, Br and I). However, little is known about reactions of Si-H with halide ions in halide solutions except for F⁻. The elucidation of such wet chemical reactions is necessary to develop practical techniques adaptable to mass production. We have reported that the substitution from Si-H to Si-I bonds and formation of rod- or dot-like clusters was competitively occurred on NH₄F-etched, atomically flat H-terminated Si(111) surfaces in the 7.1 M hydrogen iodide solution. Interestingly, those clusters were aligned along the particular directions of threefold symmetry of Si(111)[1].

In the present work, we studied the surface properties of NH₄F-etched, atomically flat H-terminated Si(111) surfaces in hydrogen iodide solutions, for the purpose of clarifying the oxidation numbers of iodine-terminated Si(111) surfaces, their stability in the air or water, and a chemical components of ordered rod- or dot-like clusters formed on the surface.

Experimental

Vicinal Si(111) surfaces, nearly completely terminated with hydrogen (monohydrogen at terraces and monohydrogen and dihydrogen at steps), were obtained by the conventional RCA cleaning method, followed by etching with 5% HF for 5 min and 40% NH₄F for 15 min. The hydrogen (H)-terminated silicon surfaces thus prepared were immersed in 7.1 M HI for certain periods of time in the dark. Surface properties were investigated using high resolution Si-2p core level spectroscopy (Scienta SES-200, $h\nu=130$ eV).

Results and Discussion

Figure 1 shows the Si 2p core-level spectra of H-Si(111) immersed in HI solutions for 12 h at 5 °C and 4 h at 63 °C together with clean H-Si(111). Peaks A and A' are assigned to the Si 2p_{3/2} and 2p_{1/2} of bulk Si respectively. We can see that the small pair of peaks (B and B') is generated only for the samples immersed in HI solutions. The energy shift of these peaks is -0.70 eV which is close to that for Si-I species [2], suggesting that some Si-H bonds are replaced by Si-I bonds on Si(111) surface. From our previous study, the rod-like and dot-like

clusters are also formed on H-Si(111) surface immersed in HI solution at 5 °C for 12 h and at 63 °C for 4h, respectively. We have suspected that those clusters might be composed of iodine and silicon from the previous experimental results. However, the detailed chemical components have not clarified yet. The present results indicate that the Si included in the clusters also have small oxidation number near by Si¹⁺, strongly suggesting that the possible chemical species of the clusters may be polysilane compounds like (SiI)_x. Details are under investigation now.

We also investigated about the stability for H-Si(111) immersed in HI solutions for 12 h and 24 h, followed by being exposed to air (25 °C, humidity 40 %) for 24 h. The results of Si-2p spectra indicated that the Si substrates immersed in HI solution are not oxidized, whereas clean H-Si(111) surface was easily oxidized after 24 h exposure in the air, suggesting that the Si-I bonds or surface clusters formed on Si(111) surface play a role of preventing from surface oxidation in the air.

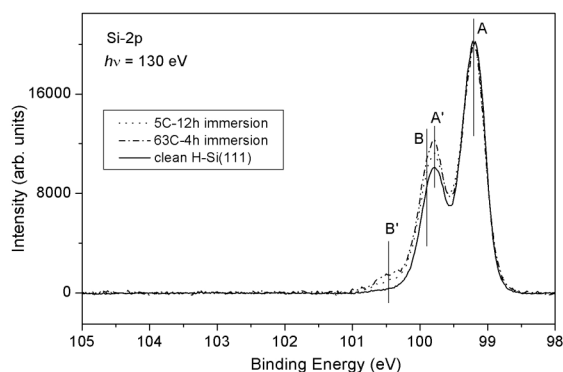


Fig. 1 Si-2p core-level spectra of H-Si(111) immersed in HI solutions for 12h at 5 °C (dotted line) and 4h at 63 °C (half dotted line) together with clean H-Si(111) (solid line).

References

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