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Citation	Journal of The Electrochemical Society, 148(6), C421-C426 https://doi.org/10.1149/1.1370964
Issue Date	2001
Doc URL	https://hdl.handle.net/2115/42506
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Type	journal article
File Information	JES00C421.pdf

Spectroscopic Studies on Electroless Deposition of Copper on a Hydrogen-Terminated Si(111) Surface in Fluoride Solutions

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The cementation or electroless deposition of copper on a hydrogen-terminated (H-)Si(111) surface in concentrated ammonium fluoride (NH$_4$F) and dilute hydrofluoric acid (HF) solutions containing copper ion (Cu^{2+}) was investigated using attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS). When the H-Si(111) sample was immersed in a 40% NH$_4$F solution containing 10 μM Cu^{2+}, the ATR-FTIR showed a decrease in the monohydride (SiH), and XPS revealed the copper deposition and Si oxide formation as well as the existence of a small amount of fluorinated Si species on the H-Si(111) surface. After the surface was rinsed with ultrapure water, the amounts of SiH and Si oxide decreased and increased, respectively, while the fluorinated Si species disappeared. Copper and Si oxide were observed on the Si surface even after being etched in a Cu^{2+}-free NH$_4$F solution, indicating that the Si oxide grew underneath the copper layer. When the H-Si(111) sample was immersed in a 0.5% HF solution containing 10 μM Cu^{2+}, the amounts of SiH decreased while those of the dihydride and trihydride significantly increased, reflecting the increase in the densities of the steps and kinks on the Si(111) surface. The amount of copper deposited on the H-Si(111) surface in the dilute HF solution containing Cu^{2+} was much less than that in the NH$_4$F solution containing the same amount of Cu^{2+}. The oxide was not observed on the H-Si(111) surface after being immersed in the dilute HF solution containing 10 μM Cu^{2+}.
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It is well known that a trace amount of metallic impurities on an Si wafer surface can drastically degrade the electronic performance of semiconductor devices.[1-3] Many studies on Cu impurity have been carried out because Cu is easily deposited on an Si surface in hydrofluoric acid (HF)-based etching solutions.[4-12] Furthermore, Cu is now attracting much attention because of its possible application as a conduction material in the fabrication of the wiring structure on ultralarge-scale integrated circuits (ULSIs).[13,14]

Ohmi *et al.* investigated Cu deposition on an Si(100) surface in various electrolyte solutions in detail.[4-6] They found that the Cu deposition was significantly affected by the solution pH and open-circuit potential and proposed a metal-induced pitting mechanism to explain the Cu deposition in dilute HF solution. Graf *et al.* observed that an additional water rinse could significantly enhance the surface oxidation of the Si wafer after immersion in 5% HF solution containing copper in the parts per million range.[7] Parks *et al.* showed that the amount of Cu deposited on an Si(100) surface from HF-based etching solutions increased as the Cu concentration in the solution increased based on total reflection X-ray fluorescence measurements.[8-10] Kimerling *et al.* demonstrated that the nucleation rate of Cu on a Si surface depended on the reduction rate of Cu^{2+} while the growth rate of Cu nuclei was determined by the rate of the Si anodic dissolution.[11] Recently, Li *et al.* reported that a trace amount of Cu^{2+} in a buffered HF solution caused not only metallic contamination but also an increase in the roughness of the Si(100) surface.[12]

Most of these studies were carried out on Si(100) surfaces because of its importance in the semiconductor industry. Quantitative investigation on an Si(100) surface is difficult since there is no established technique to prepare a well-defined Si(100) surface in air or in electrolyte solutions. However, a method to expose an atomically flat (1 × 1) surface terminated by hydrogen is well established on Si(111) both in air and in electrolyte solutions by etching in a concentrated NH$_4$F solution.[15,16] But deposition studies of metallic impurities on the hydrogen-terminated (H-)Si(111) surface are very limited. Hara and Ohdomari investigated the morphology of a

p-type H-Si(111) surface during the electrochemical deposition of copper in a sulfuric acid solution by *in situ* atomic force microscopy (AFM) and reported that 50 nm wide Cu wires were preferentially formed at the intersections of the step edges at a potential of −0.70 V *vs.* normal hydrogen electrode (NHE).[17] Homma *et al.* investigated the morphology of an n-type H-Si(111) surface during the initial nucleation process of Cu deposition in an NH$_4$F solution containing Cu^{2+} by *ex situ* scanning tunneling microscopy (STM) and found that Cu selectively nucleated along the step edges.[18] However, the AFM and STM measurements provide only morphological information about the Si surface. Information on the chemical species on the Si surface during the copper deposition, which is essential to a quantitative understanding of the mechanism of copper deposition on the Si surface, is not now available.

In this study, attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy and X-ray photoelectron spectroscopy (XPS) were employed to investigate the electroless Cu deposition processes on a well-defined H-Si(111) surface in two typical etching solutions, 40% NH$_4$F solution and 0.5% HF solution containing Cu^{2+}, to obtain detailed information about the chemical nature of the Si surface.

Experimental

The parallelogram ATR prisms (26 × 20 × 0.38 mm, 45° bevel angle) were prepared from n-type Si(111) wafers (Shin-Etsu Semiconductor, 50-500 Ω cm), which were polished on both sides for the ATR-FTIR measurements in a multiple internal reflection geometry. The internal reflection number within the ATR prism was *ca.* 70. The samples for the XPS measurement were obtained from the same Si wafer with a dimension of *ca.* 10 × 10 mm. The 40% NH$_4$F solution (EL grade) was purchased from Morita Chemicals. All the other chemicals were Suprapure reagents from Wako Pure Chemicals and were used without further purification. The solutions and Milli-Q water used for rinsing treatment were purged by purified nitrogen for at least 60 min before each experiment.

An H-Si(111) surface was obtained by etching the Si sample in 40% NH$_4$F solution for 5 min.[16] The electroless deposition of copper was carried out by immersing the H-Si(111) sample in a 40% NH$_4$F solution or a 0.5% HF solution containing 10 μM CuSO$_4$ for various times. After the sample was dried by blowing purified nitrogen, the *ex situ* ATR-FTIR and XPS measurements were performed.

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A detailed description of the ATR-FTIR system has been given elsewhere.[16] Immediately after the preparation process, the sample was mounted on an ATR accessory, and the ATR-FTIR spectra were recorded in a dried air environment in p-polarization with respect to the spectrum of an oxidized Si(111) surface. All spectra were obtained by integrating 128 interferograms with a resolution of 0.5 cm^{-1}.

The XPS measurements were performed with a Rigaku XPS-7000 spectrometer using an AlKα target (1486.6 eV) with an X-ray excitation of 300 W. The binding energies shown in this study were corrected by the C1s peak at 284.8 eV. The electrical contact between the Si sample and XPS sample stage was secured using an In-Ga alloy.

Results and Discussion

Electroless deposition of copper in 40% NH$_4$F solution.—Figure 1 shows the *ex situ* ATR-FTIR spectra in the region of 2300-1900 cm^{-1} of the H-Si(111) surface measured immediately after immersion in a 40% NH$_4$F solution (a) without and (b) with 10 μM Cu^{2+} for (i) 0 min, (ii) 5 min, (iii) 20 min, and (iv) rinsed by Milli-Q water to investigate the surface adsorbed species after treatment (iii).

A very sharp peak was observed at 2084 cm^{-1} on the freshly prepared H-Si(111) surface (i of Fig. 1a). This peak can be assigned to the stretching vibration of the monohydride (SiH). The very narrow bandwidth [full width at half-maximum (fwhm) *ca.* 1 cm^{-1}] reflects the fact that an atomically flat Si(111) surface terminated by hydrogen with an extremely homogeneous state was obtained.[15,16] Almost no change was observed in the spectra even after a 20 min immersion in the Cu^{2+}-free 40% NH$_4$F solution (iii of Fig. 1a). The intensity of the SiH peak of the H-Si(111) sample immersed in the Cu^{2+}-free NH$_4$F solution was not significantly affected by the Milli-Q water rinse (iv of Fig. 1a).

However, the immersion in the NH$_4$F solution containing Cu^{2+} caused a significant change in the spectra, as shown in Fig. 1b. The immersion time dependence of the intensities of the SiH band in the NH$_4$F solutions without and with Cu^{2+} are summarized in Fig. 2. In the NH$_4$F solution containing Cu^{2+}, the intensity of the SiH stretching vibration band decreased with immersion time and became 63% of its original value after the 20 min immersion, although no change was observed in the peak position and peak width of the SiH band. The intensity of the SiH peak of the H-Si(111) sample immersed in the NH$_4$F solution containing Cu^{2+} decreased to *ca.* 70% of its original intensity after the Milli-Q water rinse (iv of Fig. 1b).

No peaks attributed to the dihydride (SiH$_2$, $\sim$2100 cm^{-1}) and trihydride (SiH$_3$, $\sim$2130 cm^{-1}) were observed on the Si(111) surface (Fig. 1a and b), suggesting no increase in the step and kink densities, *i.e.*, no roughening, after a 20 min immersion in the NH$_4$F solution even with Cu^{2+}. This is in contrast to the results reported for the Si(100) surface where a significant roughness increase was observed after the immersion in a buffered HF solution containing Cu^{2+}.[12] The different behaviors observed on the Si(111) and Si(100) surfaces should be caused by the difference in the etching rate between the Si(111) and Si(100) surfaces in the NH$_4$F solution, in which the etching rate for the (111) orientation was much lower than that for the (100) orientation.[19]

At the same time, two new small broad peaks appeared at 2260 and 2000 cm^{-1} after the immersion in the NH$_4$F solution containing Cu^{2+}. The intensities of these two bands slightly increased with immersion time (ii and iii of Fig. 1b). These two peaks completely disappeared after the Si(111) surface was rinsed with Milli-Q water (iv of Fig. 1b).

The peak at 2000 cm^{-1} can be assigned to the combination mode ($\nu_4 + \nu_6$) of the NH$_4^+$ deformation (ν_4, 1484 cm^{-1}) and NH$_4^+$ torsional oscillation (ν_6, 523 cm^{-1}) of NH$_4$F,[20] which remained on the Si surface after the etching in NH$_4$F solution containing Cu^{2+}. The band at 2260 cm^{-1} cannot be assigned to the surface Si-O species such as O$_3$SiH, O$_2$SiH$_2$, or SiH(OH)$_3$,[21,22] since these spe-
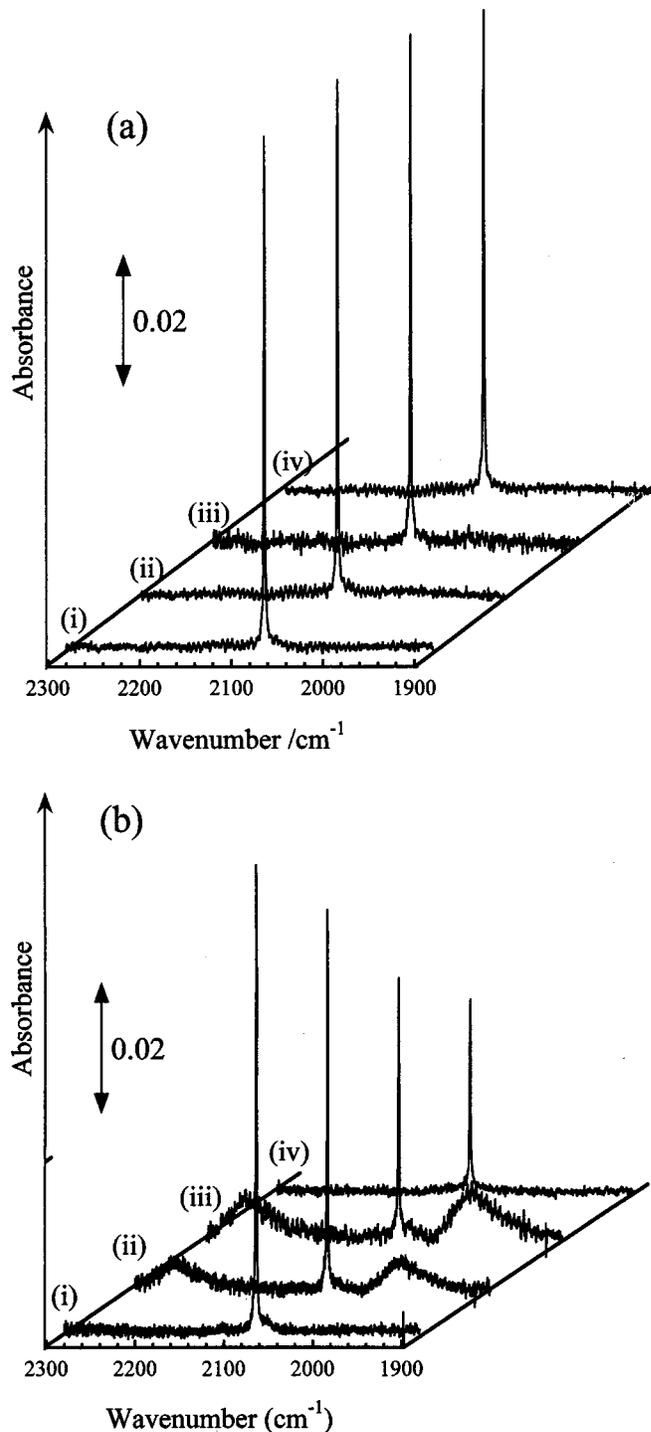

Figure 1. ATR-FTIR spectra of Si(111) surface in the region of 2300-1900 cm^{-1} immediately after the H-Si(111) sample was immersed in (a) 40% NH$_4$F solution and (b) 40% NH$_4$F solution containing 10 μM Cu^{2+} for (i) 0 min, (ii) 5 min, and (iii) 20 min without any rinsing treatment and (iv) rinsed by Milli-Q water after treatment (iii).

cies should remain on the surface after the rinsing treatment. Niwano *et al.* observed a broad band around 2230 cm^{-1} on both the Si(100) and Si(111) surfaces after immersion in a dilute HF solution by *in situ* ATR-FTIR measurement.[23] They found that this peak disappeared after immersion in flowing ultrapure water. Following their arguments, we assign the peak at 2260 cm^{-1} observed in the present study to the fluorinated Si hydride species such as SiH(SiF$_2$)
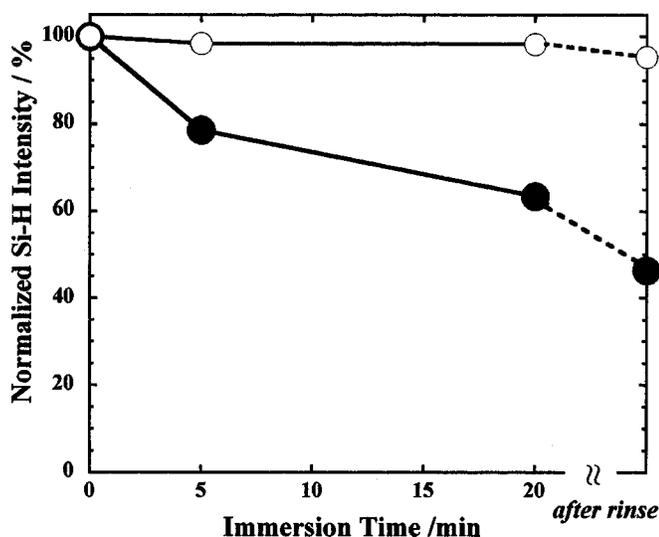
Figure 2. The intensity of the SiH peak as a function of immersion time in 40% NH_4F solutions without (○) and with (●) Cu^{2+}.

and $SiH_2(SiF)$.[23,24] NH_4F and the fluorinated Si hydride species adsorbed on the Si(111) surface after etching in the NH_4F solution containing Cu^{2+} were not observed after immersion in the Cu^{2+}-free NH_4F solution. Thus, the existence of these species should be related to the changes in the surface properties of the H-Si(111) sample after immersion in the NH_4F solution containing Cu^{2+}. The Si surface became slightly hydrophilic after the immersion in the NH_4F solution containing Cu^{2+}. The NH_4F species seems to be easier to adsorb on the hydrophilic surface sites. However, it is difficult to observe Si-O stretching of Si oxide by an ATR-FTIR measurement because IR is strongly absorbed by Si bulk in the frequency region lower than 1250 cm^{-1}. Further discussions on formation of the fluorinated Si species and surface oxide are given later in conjunction with the XPS measurement results.

Figure 3 shows the XPS spectra in the region of (a) Si ^2p and (b) Cu $^2p_{3/2}$ for the sample that was (i) freshly prepared, (ii) immersed for 5 min in the NH_4F solution containing Cu^{2+}, and (iii) rinsed by Milli-Q water after treatment (ii). The XPS spectra of the freshly prepared sample showed only one peak at 99.4 eV, which is attributed to the elemental Si[25,26] in the Si ^2p region (i of Fig. 3a) and no peak in the Cu $^2p_{3/2}$ region (i of Fig. 3b) as expected, confirming that the H-Si(111) surface was free from oxide and the contamination of copper after the etching process.

The chemical composition of the Si surface drastically changed after the H-Si(111) sample was immersed in the NH_4F solution containing Cu^{2+} (ii of Fig. 3a). In addition to the elemental Si peak at 99.4 eV, a small broad peak was observed at 103.7 eV in the Si ^2p region (ii of Fig. 3a), suggesting that the H-Si(111) surface was partly oxidized. The chemical shift of this peak relative to the elemental Si was approximately 4.3 eV, which is higher than that corresponding to Si dioxide ($\sim$3.8 eV)[25,26] because fluorine, which has the highest electronegativity, can induce a larger chemical shift in Si. This peak may be related to the partly fluorinated Si species on the Si(111) surface. The oxidized Si species corresponds to the peak at 2260 cm^{-1} in the ATR-FTIR spectra after immersion in the NH_4F solution containing Cu^{2+}, which was attributed to the fluorinated Si hydride (hydroxide) species above (ii and iii of Fig. 1b).

A strong peak was observed in the Cu $^2p_{3/2}$ region at 932.8 eV (ii of Fig. 3b), which can be attributed to Cu species formed on the Si surface after immersion in the NH_4F solution containing Cu^{2+}.[25] After the ionization cross section correction, the ratio of oxidized Si species and deposited Cu on the Si(111) surface after the treatment was estimated to be approximately 18:1.
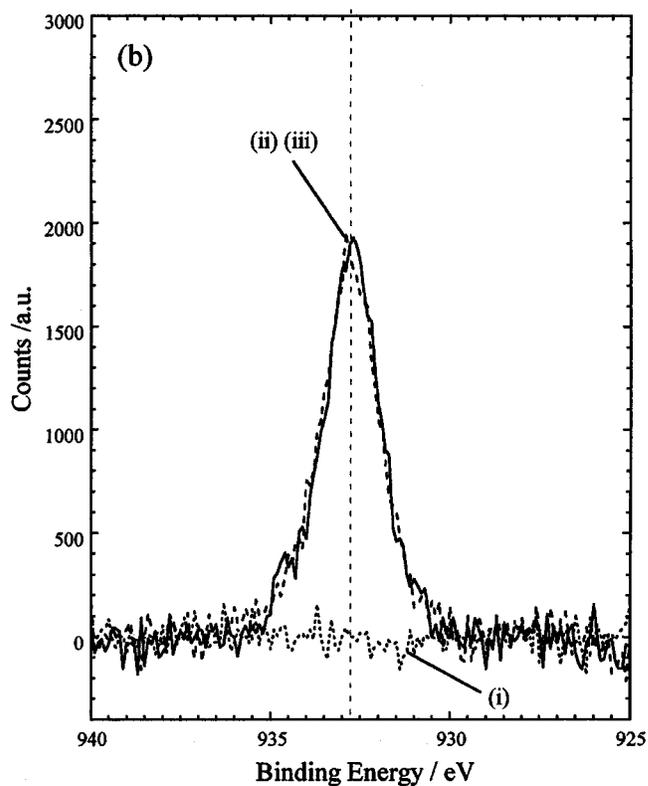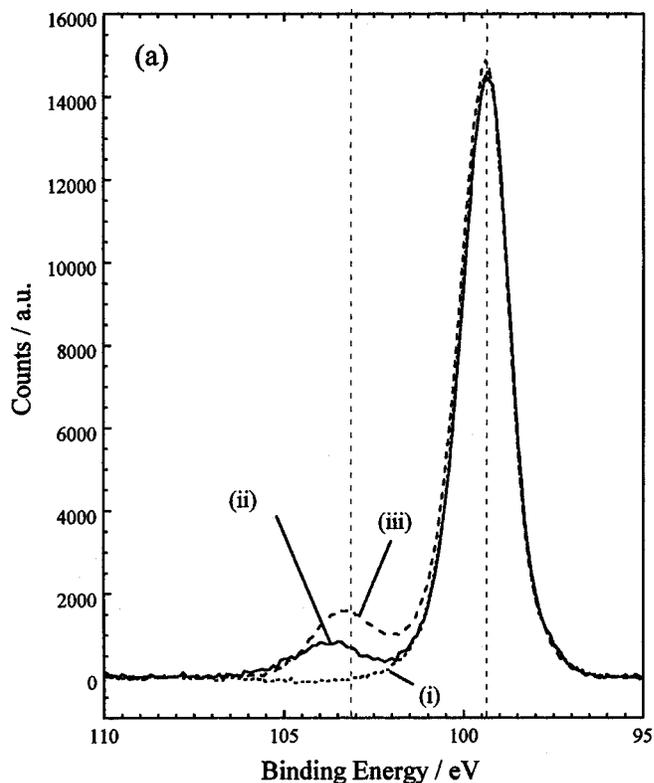

Figure 3. XPS spectra of H-Si(111) surface in the region of (a) Si ^2p and (b) Cu $^2p_{3/2}$, for the sample (i) that was freshly prepared (dotted line), (ii) after 5 min immersion treatment in the NH_4F solution containing 10 μM Cu^{2+} (solid line), and (iii) after rinsing treatment by Milli-Q water after (ii) (broken line).

Oxide formation and copper deposition seemed to simultaneously take place on the H-Si(111) surface during immersion in the

NH$_4$F solution containing Cu^{2+}. The oxide formation and copper deposition on the H-Si(111) surface should correspond to the decrease in the SiH band in the ATR-FTIR spectra after immersion in the NH$_4$F solution containing Cu^{2+} as described above (Fig. 1b).

Rinsing the sample with Milli-Q water resulted in a shift of the Si ^{2}p peak from 103.7 to 103.2 eV and an increase in the peak intensity by *ca.* 60% (iii of Fig. 3a). The peak at 103.2 eV can be attributed to SiO$_2$ on the Si surface.[25,26] These results imply that rinsing with Milli-Q water accelerates the surface oxide formation on the Cu-deposited Si wafer surface, as reported previously.[6,7] At the same time, the partially fluorinated Si species formed during the immersion in the NH$_4$F solution containing Cu^{2+} are converted to SiO$_2$ by a Milli-Q water rinse.

No change was observed in the Cu ^{2}p$_{3/2}$ peak after the rinsing treatment (iii of Fig. 3b).

In summary, when the H-Si(111) sample was immersed in an NH$_4$F solution containing Cu^{2+}, a decrease in the Si-H species and the formation of copper and Si oxide with a small amount of fluorinated Si species and NH$_4$F were observed on the Si surface. The two adsorbed species can be removed from the Si surface by a Milli-Q water rinse.

Electroless deposition of copper in 0.5% HF solution.—Figure 4 shows the *ex situ* ATR-FTIR spectra in the region of 2300-1900 cm^{-1} after the H-Si(111) sample was immersed in the 0.5% HF solution (a) without and (b) with 10 μM Cu^{2+} for (i) 0 min, (ii) 5 min, and (iii) 20 min.

After the 5 min immersion in the dilute HF solution without Cu^{2+}, the intensity of the monohydride (SiH) band at 2084 cm^{-1} became weaker, while a number of small broad components attributed to the dihydride (SiH$_2$) and trihydride (SiH$_3$) species were observed in the region between 2100 and 2150 cm^{-1} (ii of Fig. 4a). The intensity of the SiH band decreased, while the intensities of the SiH$_2$ and SiH$_3$ bands increased with immersion time. The total intensity of the bands corresponding to these Si hydride species increased after immersion in dilute HF solution for 20 min (Fig. 4a and 5). The increases in the bands corresponding to SiH$_2$ and SiH$_3$ reflect the fact that the densities of the step and kink increased after immersion in the dilute HF solution. Such changes are not observed after immersion in the NH$_4$F solution (Fig. 1) and should be caused by the isotropic etching of the Si surface in dilute HF solution.[15]

When the H-Si(111) sample was immersed in the dilute HF solution containing Cu^{2+}, the broad peaks due to SiH$_2$ and SiH$_3$ were clearly observed after the 5 min immersion (ii of Fig. 4b). These peaks were very broad, and the total intensity of the peaks due to these Si hydride species became about 2.5 times that of the Si hydride on the H-Si(111) sample immersed in dilute HF without Cu^{2+} for 20 min (iii of Fig. 4b and Fig. 5). This result demonstrates that the etching in the dilute HF containing Cu^{2+} generates more surface defects on the Si(111) surface than that in dilute HF without Cu^{2+} and NH$_4$F solution with or without Cu^{2+}. The increases of surface roughness of the Si(100) surface after immersion in HF solutions containing Cu^{2+} have been reported by other groups.[5,7]

Figure 6 shows the XPS spectra of the H-Si(111) surface in the region of (a) Si ^{2}p and Cu ^{2}p$_{3/2}$ for (i) the freshly prepared sample, (ii) after 5 min immersion in the 0.5% HF solution containing 10 μM Cu^{2+}, and (iii) rinsed with Milli-Q water after (ii). The oxidized Si species with a higher chemical shift than that observed in NH$_4$F solution containing Cu^{2+} was not observed, and only one peak at 99.4 eV, which is attributed to the elemental Si, was observed for all the cases (Fig. 6a). Only a very small peak was observed in the Cu ^{2}p$_{3/2}$ region (Fig. 6b) after the immersion in dilute HF solution containing Cu^{2+}. The intensity of the Cu ^{2}p$_{3/2}$ peak was *ca.* one-tenth of that observed in NH$_4$F solution with Cu^{2+}, indicating that much less copper was deposited on the Si surface in dilute HF containing Cu^{2+} than that in NH$_4$F solution containing Cu^{2+}.
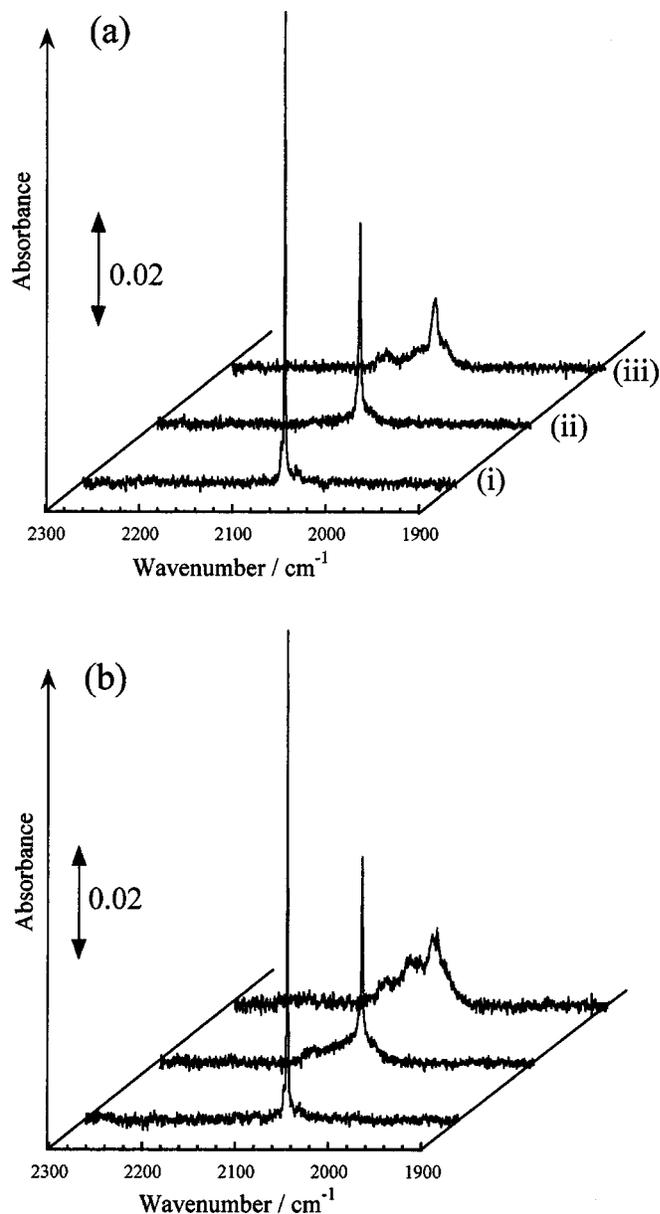

Figure 4. ATR-FTIR spectra in the region of 2300-1900 cm^{-1} immediately after the H-Si(111) sample was immersed in 0.5% HF solution (a) without and (b) with 10 μM Cu^{2+} for (i) 0 min, (ii) 5 min, and (iii) 20 min without any rinsing treatment.

No effect by the rinsing treatment using Milli-Q water was observed on the Si hydrides after immersing in dilute HF solution with or without Cu^{2+}, by both ATR-FTIR and XPS measurements.

Compared to the electroless copper deposition observed on the H-Si(100) surface,[5-7] the copper seemed to be more difficult to deposit on the H-Si(111) surface in dilute HF solution containing Cu^{2+}. This may be related to the stable surface structure of the H-Si(111) substrate. More detailed investigations are necessary.

In summary, when the H-Si(111) surface was immersed in the dilute HF solution containing Cu^{2+}, the amounts of Si oxide and copper formed on the Si surface were much less than those in the NH$_4$F solution containing Cu^{2+}.

Discussion on the different behaviors of electroless copper deposition in 40% NH$_4$F and 0.5% HF solutions containing Cu^{2+}.—Two oxidation reactions on the Si surface can be considered under the present conditions
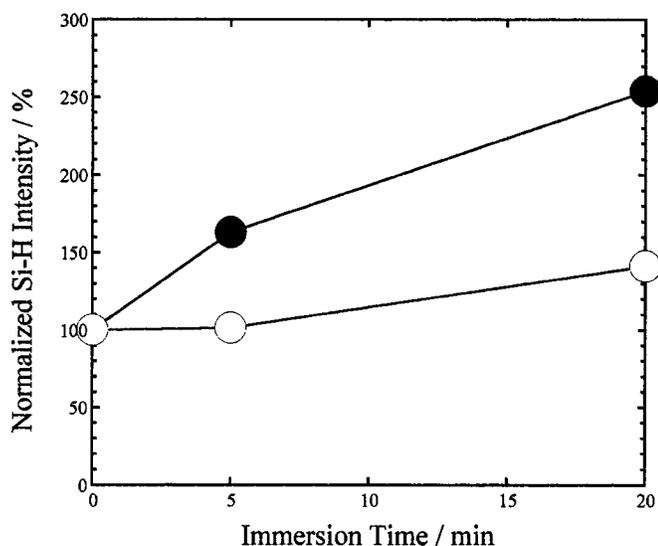
Figure 5. The intensity of the Si hydride peak as a function of immersion time in Cu^{2+}-free (○) and Cu^{2+}-containing (●) dilute HF solutions.

$$Si + 2H_2O \rightarrow SiO_2 + 4H^+ + 4e^- \qquad [1]$$

$$Si + 6F^- \rightarrow SiF_6^{2-} + 4e^- \qquad [2]$$

The equilibrium potentials of Reaction 1 in 40% NH_4F (pH 8) and 0.5% HF (pH 2) are -1.38 and -1.03 V (*vs.* NHE),[27] respectively, while that of Reaction 2 is independent of the pH and was reported as -1.20 V (*vs.* NHE).[27] These potentials are much more negative than those of hydrogen evolution (-0.48 V in 40% NH_4F and -0.12 V in 0.5% HF) and copper deposition (0.19 V in both solutions when the concentration of Cu^{2+} is 10 μM)

$$2H^+ + 2e^- \rightleftharpoons H_2 \qquad [3]$$

$$Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad [4]$$

Thus, thermodynamically it is expected that Si is oxidized and H^+ and Cu^{2+} are reduced when the H-Si(111) surface is immersed in these solutions. Since the equilibrium potential of the H^+/H_2 couple in 40% NH_4F is more negative than that in 0.5% HF by 0.35 V, while the equilibrium potential of Cu^{2+}/Cu couple is the same in both solutions (0.19 V), the current efficiency of the copper deposition on the Si surface is expected to be higher in the 40% NH_4F solution than that in the 0.5% HF solution for the same open-circuit potential. This should be one of the reasons why more copper deposition was observed in 40% NH_4F than in 0.5% HF containing the same amount of Cu^{2+}.

　The dissolution rate of Si at the open-circuit potential seemed to significantly affect the behaviors of the copper deposition in both solutions. Allongue *et al.* reported that the etching rate of the H-Si(111) surface increased with the pH of the NH_4F solution, and the etching rate at pH 8 was *ca.* four times greater than that at pH 2.[28] The etching rate of Si at the open-circuit potential increases with the increase in the pH, a higher deposition rate of copper is expected with the increasing pH, and therefore, more copper is expected to be deposited on the Si surface in 40% NH_4F than in 0.5% HF containing Cu^{2+}.

　However, this explanation is based only on a thermodynamic consideration. Many reactions on the Si surface should be kinetically controlled. As described above, the ratio between the amounts of oxidized Si species and deposited Cu on the Si(111) surface in the NH_4F solution containing Cu^{2+} was approximately 18:1. This ratio is very large if one assumes that two Cu^{2+} ions are reduced when
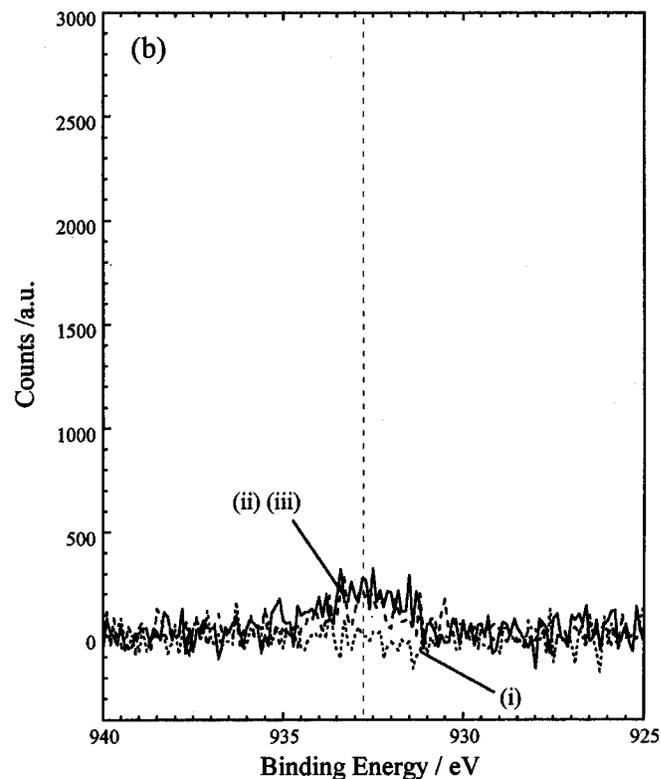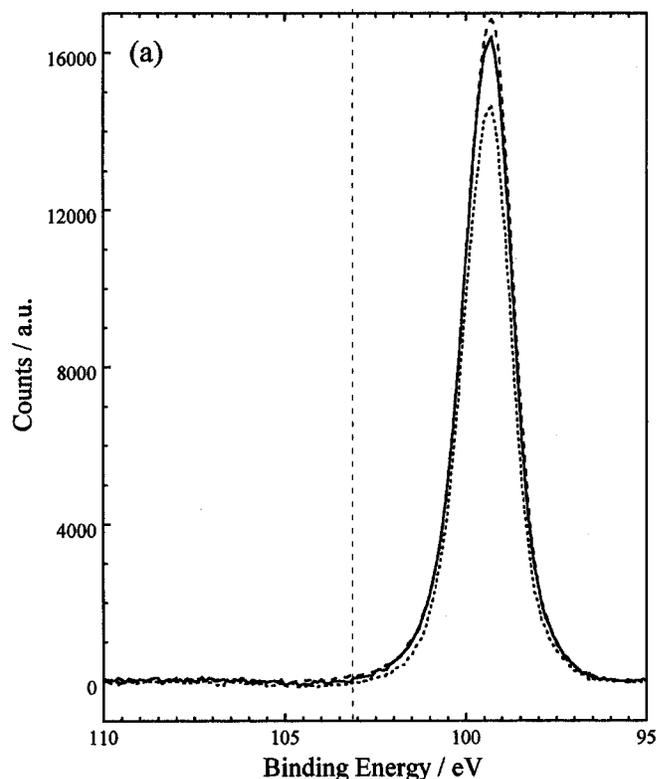

Figure 6. XPS spectra of H-Si(111) surface in region of (a) Si ^{2}p and (b) Cu ^{2}p$_{3/2}$ for the (i) freshly prepared sample, (ii) after 5 min immersion in the 0.5% HF solution containing 10 μM Cu^{2+}, and (iii) rinsed by Milli-Q water after treatment (ii).

one Si atom is oxidized (4e$^-$ reaction). Furthermore, the ratio should be even larger if one considers that the Si species are dis-

solved during the etching process (such as SiF_6^{2-}, Reaction 2). Thus, the fact that much less copper was deposited on the Si surface than the amount of oxidized/dissolved Si indicates that the hydrogen evolution reaction is the dominant cathodic reaction at open-circuit potential in the NH_4F solution. Li *et al.* reported that the current efficiency for the copper deposition on the Si(100) surface in a buffered HF solution containing 100 ppb Cu^{2+} was less than 1%.[12] This is in qualitative agreement with the present results. The origin of the high current efficiency of the hydrogen evolution reaction is considered to be the catalytic enhancement of the hydrogen evolution reaction on the copper deposited on the Si surface, due to the lower overpotential of hydrogen evolution on copper than on Si.[10,12] Even when a small amount of copper is deposited on the Si surface, the reaction rate of the hydrogen evolution is significantly accelerated.

SiO_2 can be dissolved by HF and NH_4F solutions. Figures 3 and 5 show that oxide remained on the Si(111) surface after immersion in the NH_4F solution containing Cu^{2+}, while no oxide was formed after immersion in the dilute HF solution containing Cu^{2+}. After an additional 5 min etching in a Cu^{2+}-free NH_4F solution for the Cu-deposited Si(111) sample after the rinsing treatment (iv of Fig. 1b), and ATR-FTIR measurement showed that the intensity of the SiH increased to 80% of its original intensity, but no effect was observed with further immersion. This result demonstrates that part of the SiO_2 is stable on the Cu-deposited Si(111) surface and suggests that SiO_2 grows underneath the copper nuclei, which protects the oxide from etching by NH_4F. A much lower etching rate of the SiO_2 film and higher etching rate of the Si(111) surface in the concentrated NH_4F solution than those in the dilute HF solution[28-30] should contribute to the higher stability of the SiO_2 film in the NH_4F solution containing Cu^{2+}.

Conclusion

When the H-Si(111) sample was immersed in the NH_4F solution containing 10 μM Cu^{2+}, a decrease in the SiH and deposition of the copper and the Si oxide with a small amount of fluorinated Si species were observed on the H-Si(111) surface. After the sample was rinsed with Milli-Q water, the amount of SiH and Si oxide decreased and increased, respectively, while the fluorinated Si species disappeared. Cu and Si oxide still existed on the Si surface even after etching the sample in Cu^{2+}-free NH_4F solution, indicating that part of the Si oxide grew underneath the Cu layer and was stable against NH_4F etching. A wide atomically flat Si(111) domain still existed on the Si surface after the copper deposition.

When the H-Si(111) sample was immersed in the 0.5% HF solution containing 10 μM Cu^{2+}, the amount of SiH species decreased, while those of the SiH_2 and SiH_3 species largely increased, reflecting that more steps and kinks were formed on the Si(111) surface. The amount of copper deposited was much less than in the NH_4F solution containing the same amount of Cu^{2+}, and no oxide was observed on the H-Si(111) surface. The origin for the difference is discussed by considering the competition between the copper deposition and hydrogen evolution, and the pH-dependent anodic etching rate of Si and Si oxide. The lower current efficiency of the

copper deposition on the Si surface is attributed to the catalytic enhancement of the hydrogen evolution reaction on copper deposited on the Si surface.

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