# Characterization of HF-Treated Si Surfaces by Photoluminescence Spectroscopy and Scanning Tunneling Microscopy

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The properties of Si surfaces treated in HF solution of various concentrations are characterized by photoluminescence (PL) and scanning tunneling microscopy (STM). A number of atomic steps are observed in wide-range STM images of Si (111) surfaces. Close observation of atomic arrangement around a terrace reveals that Si-H and Si-H<sub>3</sub> bonds terminate on the terrace and Si-H and Si-H<sub>2</sub> are observed at [110] step edges. The PL intensity of HF treated Si (111) decreases with exposure time in air as well as in  $O_2$ , while it shows only a slight change in  $N_2$ . The observed decrease in PL intensity would be caused by generation of recombination centers which are induced by oxidation. The PL intensity in oxygen decreases exponentially with plural time constants at the beginning stage, which suggests the presence of multistage oxidation processes via surface defects, atomic steps, kinks or terraces.

## 1. Introduction

HF-treated Si surfaces have been extensively studied by Fourier-transform infrared spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS) and STM techniques. It is revealed that HF-treated surfaces are mainly terminated by hydrogen<sup>1-4)</sup> and fluorine exists as minority species<sup>5,6)</sup>. Si(111) surfaces dipped in HF solution are terminated by Si-H, Si-H<sub>2</sub> and Si-H<sub>3</sub> bonds, which indicates that the surface topography is atomically rough<sup>3,4)</sup>. The micro-roughness reflects the initial interface roughness between Si and SiO<sub>2</sub>. In contrast, the Si(111) surfaces treated by pH modified buffered HF solution are terminated by only Si-H bond<sup>2,7)</sup>, which indicates that the Si surfaces are flattened by anisotropic etching.

R. S. Becker et al. reported on STM observations of the Si(111):H-1x1 surface prepared by dipping into the pH modified buffered HF solution<sup>8</sup>. In contrast, on Si(111) dipped into the dilute HF solution (1%), the well-ordered atomic dots corresponding to the H atoms of Si-H<sub>3</sub> phase have been reported by Morita et al<sup>9</sup>.

The H-terminated Si surface is remarkably resistive against oxidation in air at room temperature and shows good chemical stability<sup>1,10)</sup> through XPS studies. It is discussed that the oxidation of HF-treated Si(111) surface in air proceeds as follows<sup>6,11)</sup>: oxidants such as oxygen and water vapor in air preferentially attack Si-Si back bonds rather than Si-H bonds on the surface. The Si-H bonds on the surface are oxidized only after completion of the back-bond oxidation, resulting in the formation of Si-O and Si-OH bonds on the surface<sup>90</sup>. When HF-treated Si is rinsed in pure water, Si-F bonds are replaced by Si-OH bonds through hydrolysis reaction<sup>1)</sup>. Hence, it is possible that Si-F bonds on the surface is replaced by Si-OH bonds through hydrolysis reaction with water vapor in air. We would suggest the possibility that the Si-O and Si-OH bonds cause defects at the surface such as disordered interface structures as was revealed at Si/native-oxide interfaces<sup>12)</sup>. These defects presumably act as recombination centers which reduce band-to-band radiative recombination.

The quantum efficiency for radiative emission h is expressed by  $\eta = \tau_{nr}/(\tau_{nr} + \tau_r)^{13}$ , where  $\tau_{nr}$  and  $\tau_r$  are non-radiative and radiative lifetimes. Since  $\tau_{nr} < \tau_r$  in the case of Si,  $\eta$  is approximated by  $\eta = \tau_{nr}/\tau_r$ . There are two channels for the non-radiative processes: surface processes ( $\tau_{nr}(surface)$ ) and bulk processes ( $\tau_{nr}(bulk)$ ). If we assume  $\tau_{nr}(bulk) >> \tau_{nr}(surface)$ , the surface processes play dominant role in the nonradiative processes. Hence, quantum efficiency can be expressed as  $\eta \sim \tau_{nr}(surface)/\tau_r$ . Since  $\tau_{nr}(surface) \propto 1/N_s$ , the quantum efficiency directly depends on the surface density of electronic defect density (N<sub>s</sub>) and high-sensitive detection of surface defects would be possible with photoluminescence (PL).

### 2.Experimental

Czochralski grown Si(111) specimen of n-type were dipped into HF solution of various concentrations after the RCA cleaning. Subsequently, they were transfered into an ultrahigh vacuum system ( $\sim 10^8$  Torr) to observe atomically-resolved surface topograpy by STM.

PL spectra were measured using the 488 nm line of an Ar ion laser with special attention placed upon the effects of ambient gases such as air, oxygen and nitrogen on their PL properties.





Fig.1 STM images of Si(111) surface dipped in 47% HF solution. (a) The size of the image is 170 x 170 Å. The tunneling current is 1.0 nA and the tip bias is +0.5 V. (b) The size of the image is 50 x 50 Å. The tunneling current is 0.7 nA and the tip bias is +1.0 V.

### **3.Results and Discussion**

Fig.1 shows STM images of a Si(111) surface dipped in 47% HF solution. A number of atomic steps are observed in a wide-range STM image (Fig.1(a)). The step edges oriented along the <110> direction. Close observation of atomic arrangement around a terrace reveals that Si-H and Si-H<sub>3</sub> bonds terminate on the terrace and Si-H and Si-H<sub>2</sub> are observed at [110] step edges, where the Si-H bonds are observed at the step edge on the left hand side and Si-H<sub>2</sub> bonds are observed at the step edge on the right hand side (Fig.1(b)). This observation can be explained by a simple structual model illustrated in Fig.2. Si-H and Si-H<sub>3</sub> phases exist on the terrace. The steps in the  $[1\overline{1}0]$ direction with the step orientation toward the  $[11\overline{2}]$ direction form {111} microfacets at the step edge, which are terminated by Si-H bonds. In contrast, steps in the [110] direction with the step orientation toward the  $[\overline{112}]$  direction form  $\{100\}$  microfasets, which are terminated by Si-H<sub>2</sub> bonds. These results are consistent with the FTIR mesurements which shows the presence of Si-H, Si-H<sub>2</sub> and Si-H<sub>3</sub>, thereby the presence of many atomic steps on HF-treated Si (111) surfaces has been suggested<sup>4)</sup>

The PL spectrum of HF-treated Si shows a phononassisted band-to-band emission peak at ~1.09 eV at room temperature. The intensity of the ~1.09 eV emission of a Si(111) wafer dipped into 1 ~ 47% HF solution decreases with the exposure time to oxygen, while it shows only a slight change in nitrogen. It is suggested that temporal decrease in PL intensity is caused by generation of recombination centers induced by oxidation, while N<sub>2</sub> is inactive to HF-treated Si surfaces. Similally, the PL intensity decreases with exposure time to air. The decrease of PL intensity in air would be caused by the presence of O<sub>2</sub> and/or H<sub>2</sub>O which presumably induce surface defects.



Fig.2 'Ball and stick' model of the H-terminated Si(111) surface.



Fig.3 PL intensity of Si dipped in 4.5% HF solution as a fanction of oxygen exposure time.

The PL intensity of a Si(111) wafer dipped in 4.5% HF solutionin decreases exponentially with three time constants in oxygen as shown in Fig.3. The PL intensity shows abrupt decrease with time constant  $\tau_1$  immediately after exposure to oxygen followed by slower decrease with  $\tau_2$  from  $5 \sim 10$  min after exposure to oxygen. The PL intensity decreases very slowly with time constant  $\tau_3$  beyond 30 min. Typically,  $\tau_1$ =3 min,  $\tau_2$ =25 min and  $\tau_3$ =200 min. The three-step decrease in PL intensity is similarly observed in air. The observed variation in PL intensity suggests the presence of multistage oxidation processes.

Oxidation of a 4.5% HF-trearted Si (111) surface in air was observed at 50 min after HF treatement through XPS mesurements<sup>7</sup>. It is reported that layer-by-layer oxidation occurs in air, and it is proposed that the oxidation reaction proceed parallel to the surface from atomic steps<sup>5)</sup>. Since the time constant  $\tau_3$  is observed beyond 30 min after exposure to oxygen, the exponential decrease in PL intensity with  $\tau_3$ presumably reflects the oxidation process which was observed by XPS. Therefore, it is likely that the initial decreases with  $\tau_1$  and  $\tau_2$  correspond to the beginning of oxidation processes which cannot be detected by XPS measurement. These facts indicate that the oxidation is initiated at the beginning of exposure to oxygen and air, and the initial stage of oxidation proceeds in a multistage fashion via surface defects, atomic steps or kinks.

### **4.**Conclusion

HF-treated Si(111) surfaces have been characterized by STM and PL. The STM observation of atomic arrangement around a terrace reveals that Si-H and Si-H<sub>3</sub> bonds terminate on the terrace and Si-H and Si-H<sub>2</sub> are observed at [110] step edges. The PL intensity of band-to-band emission at room temperature in air or oxygen decreases with three time constants, which suggests the presence of multistage oxidation processes via surface defects, atomic steps, kinks or terraces. HF treated Si in PL intensity shows only a slight change in N<sub>2</sub>, while it decreases with exposure time in air as well as in O<sub>2</sub>, which obviously reflects oxidation processes.

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