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# Atomic resolution images of H-terminated Si(111) surfaces in aqueous solutions

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The first atomic images of the hydrogen terminated Si(111) surface have been acquired in aqueous sulfuric acid solutions. The observed interatomic distance with threefold symmetry is  $\sim 3.8 \text{ \AA}$ , indicating that the ideal Si(111):H- $1 \times 1$  surface can be prepared by chemical etching in  $\text{NH}_4\text{F}$  solutions. It is demonstrated that *in situ* scanning tunneling microscopy is an extremely important method for revealing chemical processes with atomic resolution in the chemical etching of semiconductors in solutions.

*In situ* electrochemical scanning tunneling microscopy (ESTM) has quickly become an important and promising tool for the surface characterization of electrodes with atomic resolution in electrolyte solutions.<sup>1-4</sup> Although atomically resolved images have been achieved for several systems at metal/liquid interfaces,<sup>1-4</sup> more recently attention has been focused on semiconductor/liquid interfaces,<sup>5-12</sup> because the chemical wet etching of semiconductors, particularly Si, is becoming more important for silicon technology. It has clearly been demonstrated in our previous manuscripts<sup>5-7</sup> that the topography and electronic structure of semiconductor electrodes such as *p*- and *n*-Si can be obtained in aqueous solutions using ESTM. It is well known that Si surfaces terminated by hydrogen (H-Si) are highly resistant to air oxidation at ambient temperature. Such surfaces are passivated toward further chemical attack. It has been confirmed by the infrared spectroscopy that ideally terminated Si(111) surfaces with monohydride can be exposed in  $\text{NH}_4\text{F}$  solutions.<sup>13</sup> Atomic resolution in STM measurements has recently been achieved on these surfaces in ultrahigh-vacuum (UHV) environments.<sup>14-18</sup> An atomic image has also been acquired in air on a Si(111) surface using an atomic force microscope.<sup>19</sup> We have previously reported that H-Si surfaces formed a very strong protective layer towards oxidation even after prolonged exposures to aqueous solution.<sup>7</sup> More recently, a similar observation has been made by Houbertz *et al.*<sup>12</sup> The interesting chemical nature of this surface as well as the industrial importance of silicon etching processes prompted us to attempt to study these surfaces in aqueous solution at the atomic level using *in situ* ESTM.

Here we report the first atomic STM image of the H-Si(111) surface treated with a  $\text{NH}_4\text{F}$  solution in an aqueous sulfuric acid solution ( $\text{H}_2\text{SO}_4$ ). The samples used were *p*-type (boron doped) Si(111) wafers whose resistivities were in the range of 0.1–0.3  $\Omega \text{ cm}$ . After the sample was cleaned by the conventional RCA method, the Si(111) surface was reoxidized in a (1:1:4) solution of  $\text{HCl}:\text{H}_2\text{O}_2:\text{H}_2\text{O}$  at  $\sim 80^\circ\text{C}$  for 10 min as described previously.<sup>18</sup> The sample with a clean oxide layer was loaded onto an electrochemical cell with two polished Pt wires serving as counter- and quasireference electrodes, as de-

scribed elsewhere.<sup>1,20</sup> All electrode potentials are reported with respect to a saturated calomel electrode (SCE). The oxide layer was then etched away in the electrochemical cell using a dilute HF solution (1%) or a (1:50) solution of 50% HF:40%  $\text{NH}_4\text{F}$ . Typical etching times ranged from 2 to 10 min at room temperature. After the removal of the oxide layer, the etching solution was replaced with a 0.05M  $\text{H}_2\text{SO}_4$  solution. The Si(111) surface was always immersed in aqueous solutions during the above pretreatment in order to protect it from contamination. A Pt wire sealed into a glass pipet was used as a tunneling tip in  $\text{H}_2\text{SO}_4$ .<sup>1,7</sup>

Figure 1 shows cyclic voltammetric current-potential curves of the Si(111) surface treated with the  $\text{NH}_4\text{F}$  solution observed in the dark and under illumination in 0.05M  $\text{H}_2\text{SO}_4$ . The cathodic current is fairly small ( $< 0.5 \mu\text{A}/\text{cm}^2$ ) in the dark, but shows a plateau under illumination due to hydrogen evolution.<sup>21</sup> Oxidation current beginning at  $\sim 0.1 \text{ V}$  versus SCE is due to the formation of oxide layers. A peak current is observed at 0.6 V. Note that straight lines in Mott-Schottky plots with a small frequency dispersion are observed in a potential region between  $-0.6$  and  $-1.8 \text{ V}$ , yielding a flat-band potential of  $\sim 0.6 \text{ V}$  versus SCE. Similar value has been found for *p*-Si(100) as reported previously.<sup>7</sup> Based on the electrochemical response shown in Fig. 1, one can conclude that the Si(111) surface should be free from oxidation in 0.05M  $\text{H}_2\text{SO}_4$  as long as the electrode potential is more negative than 0 V versus SCE. We investigated the tunneling current-potential (*I-E*) characteristic of the *p*-Si(111)/ $\text{H}_2\text{SO}_4$  interface prior to acquiring images. When the potential of the tip electrode was more positive than the edge of the valence band ( $\sim 0.6 \text{ V}$  versus SCE), the electron tunneling was found to easily occur from the valence band in Si to the vacant level in the metal tip at the potential more negative than 0 V. Such an *I-E* behavior is fully consistent with the energetics for the semiconductor/liquid interface as discussed previously.<sup>5-8,10</sup> Therefore, STM images could be successively acquired at Si(111) surfaces with the potential poised between 0 and  $-1.8 \text{ V}$  versus SCE.

Figure 2 shows two typical images of the Si(111) sur-

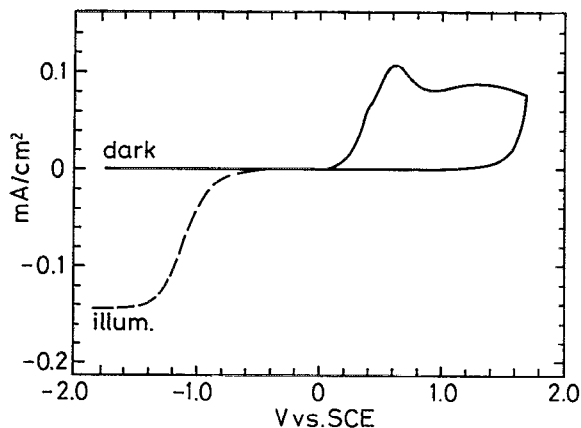


FIG. 1. Current-potential curves of *p*-Si(111) in the dark (solid line) and under illumination (dashed line) in 0.05M H<sub>2</sub>SO<sub>4</sub>. The scan rate of the electrode potential was 50 mV/s.

face at low-resolution prepared by etching with the HF (a) and NH<sub>4</sub>F (b) solutions, respectively. The images obtained from surfaces treated with the HF solution were always atomically rough showing a rolling hill structure. Clear atomic steps were rarely observed on these surfaces. These observations seem to be fairly consistent with other reports in the literature.<sup>15,18</sup> However, the surface treated with the NH<sub>4</sub>F solution consistently showed an atomically flat terrace-step structure, as shown in Fig. 2(b). Atomic steps observed in Fig. 2(b) correspond to the double layer step

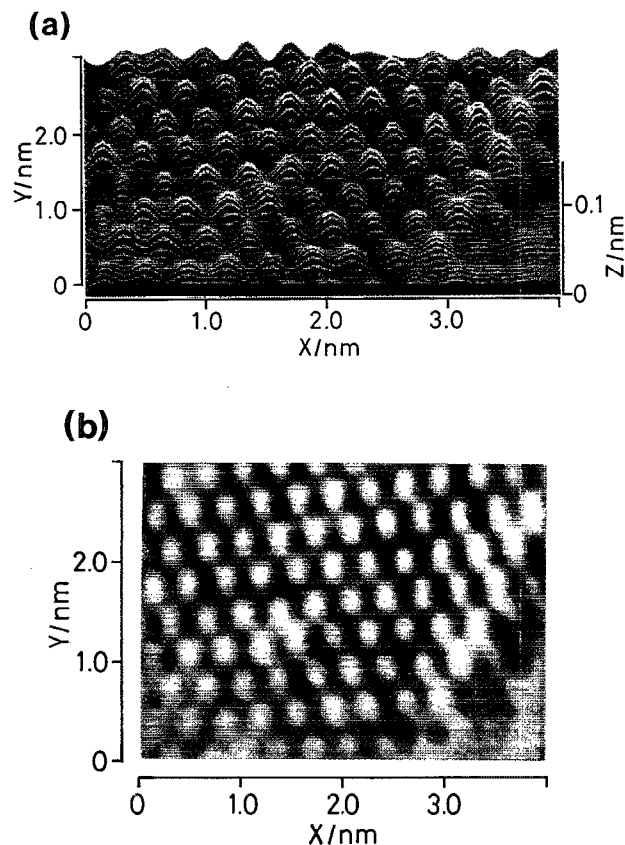


FIG. 3. STM topographic line scans (a) and a topview (b) of a 4×3 nm<sup>2</sup> region of *p*-Si(111) treated in NH<sub>4</sub>F. The electrode potentials were the same as indicated in Fig. 2. The tunneling current was 5 nA. Scan speed was 50 ms/line.

of a height of 3.2 Å. The step lines were usually not straight and lying in a twisting fashion. They were sometimes found to be located in the direction forming an angle of 60° as expected for a surface with threefold symmetry. The above *in situ* observation is consistent with the result obtained by *ex situ* STM in UHV.<sup>16,17</sup>

Figure 3 shows our first observation of the atomic structure on the Si(111) etched with the NH<sub>4</sub>F solution. We have employed only a high-pass filter (> 1 Hz) for the data acquisition. The corrugation height is ~0.2 Å as can be seen in the line scans shown in Fig. 3(a). Note that a similar corrugation height has recently been observed in UHV.<sup>16,17</sup> A smaller value (0.03 Å) has also been previously reported.<sup>14</sup> It is clearly seen in a topview [Fig. 3(b)] that atomic structure exists with nearly threefold symmetry. The interatomic distance is ~3.8 Å. This indicates straightforwardly that the Si(111) surface is terminated by the monohydride. We found some areas with no clear atomic structure on a terrace where the Si(111)-(1×1) was the predominant structure. These areas can be seen in the lower right-hand corner of Fig. 3. This observation may indicate the existence of the trihydride (-SiH<sub>3</sub>) as a minor component on the same terrace. The trihydride has been observed in UHV on a Si(111) treated with a dilute HF solution.<sup>18</sup> Although the Si(111)-(1×1) was main while the tip position was changed for hundreds of angstroms in any direction, interesting defect sites were ob-

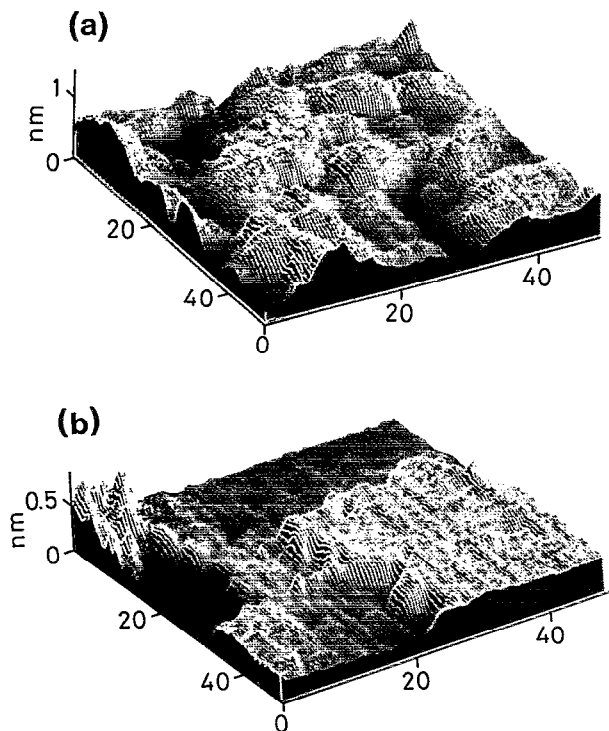


FIG. 2. STM topographic line scan images of a 50×50 nm<sup>2</sup> region of *p*-Si(111) treated in HF (a) and NH<sub>4</sub>F (b) obtained in 0.05M H<sub>2</sub>SO<sub>4</sub>. The electrode potentials of Si and the tip were set at -0.2 and 0.8 V versus SCE, respectively. The tunneling current was 3 nA. Scan speed was 200 ms/line.

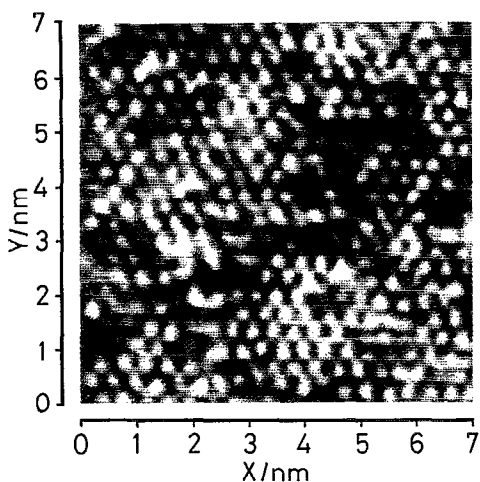


FIG. 4. A topview of a  $7 \times 7 \text{ nm}^2$  region of  $p\text{-Si}(111)$ . The electrode potentials, the tunneling current, and scan speed were the same as indicated in Fig. 3.

served on the flat terraces. Figure 4 shows an example of STM images acquired in a larger area of  $7 \times 7 \text{ nm}^2$ . It is obvious that the flat terraces are not defect free. Small pits and single atomic defects can be seen in Fig. 4. Larger pits have been observed on Si(111) surfaces in UHV.<sup>16</sup>

The atomic structure existed for at least 3 h as long as the electrode potential of Si(111) was negative of 0 V versus SCE. The images indicate that the surface is free from oxides and contaminates under these conditions. However, the atomic image permanently disappeared when the surface was electrochemically oxidized by applying more positive potentials than 0 V versus SCE, as shown in Fig. 1. We have also examined the Si(111) surface treated with the HF solution in  $\text{H}_2\text{SO}_4$  at high resolution. However, no well-resolved atomic image has been obtained from this surface due to the atomically rough structure as shown in Fig. 2(a). Trihydride ( $-\text{SiH}_3$ )<sup>18</sup> could not be resolved in the present work. Finally, it seems to be more desirable to

obtain atomic images in solutions containing HF and  $\text{NH}_4\text{F}$  in order to reveal wet etching processes of Si at the atomic level. We have found it possible to acquire images with atomic resolution in a HF solution using a Teflon coated Pt tip. A more detailed study is now under investigation.

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