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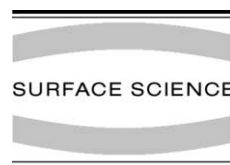**136** PUBLICATIONS **1,977** CITATIONS

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Fluorine etching on the Si(1 1 1)-7 × 7 surfaces using fluorinated fullerene

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Abstract

Fluorine etching on the Si(1 1 1)-7 × 7 surfaces using fluorinated fullerene molecules as a fluorine source has been investigated. At room temperature, adsorbed fluorinated fullerene molecules reacted with the Si(1 1 1)-7 × 7 surface to create a *localized distribution* of fluorine on the surface. Nanoscale etch pits were created by annealing at 300 °C, due to the adsorption of the fluorine localized around the $C_{60}F_x$ molecules. Annealing at 400 °C resulted in the delocalized fluorine distribution on the surface and healing of the etch pits, due to the enhancement of the diffusion of both the fluorine and silicon atoms. Subsequent annealing at 500 °C led to desorption of SiF_2 reactants formed on the surface. The fluorine diffusion process was found to be an elemental process in the etching because the diffusion of adsorbed fluorines is a key for the formation of the SiF_2 species and their subsequent desorption.
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1. Introduction

Nanotechnology has the potential to impact significantly the fabrication process of semiconductor devices. It is a challenging task to utilize the size and shape of the molecules for achieving nanoscale-localized chemical reaction. Recently, there have been many attempts to achieve nanoscale dimensions in device fabrication with a local probe at a nanoscale level by removing atoms [1], by growing self-assembled quantum dots [2], and by constructing nanometer-sized metallic wires [3] on semiconductor surfaces. Certain molecules may play an important role in the nanofabrication

process because their sizes are on the same length scale as the nanostructures. An example of such approach is the use of carbon nanotubes as field-effect transistors [4].

Recently, we found that highly fluorinated fullerene ($C_{60}F_x$, $x = 42$–48) molecules adsorbed on the Si(1 1 1)-7 × 7 surface act as ''nanoscale fluorine bottles'', as they react with surface in the unique way, printing the fluorine atoms in a narrow path by the rolling over the Si surface. Printed fluorine atoms are localized within a radius of ∼6.5 nm from the adsorbed molecules, because there is no migration of the adsorbed fluorine atoms at room temperature [5]. Considering this we anticipate, that nanoscale modification of the surface can be achieved by the etching of the surface with localized fluorine atoms, making thus a

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good use of this localized distribution. From the other hand, fluorine reactions on the Si(1 1 1)-7 × 7 and Si(1 0 0)-2 × 1 surfaces studied by scanning tunneling microscopy (STM) have attracted much interest, as analyzing the atomic-scale surface modifications should yield better understanding of the chemical bonding configurations and structural changes on the surface [6]. However, no one has yet exploited this ability of the STM to investigate the reaction and etching on silicon surfaces using such ''nanoscale fluorine bottles''.

In this paper, surface reactions of $C_{60}F_x$ on the Si(1 1 1)-7 × 7 surface were investigated in order to clarify the etching process as a function of annealing temperature. The evolution of fluorine adsorption sites and creation of etch pits by the annealing were studied by STM.

2. Experimental procedures

All measurements have been carried out in a custom-made FI-STM system [7] combined with a commercial LK2000 high-resolution electron energy loss spectrometer (HREELS). The 7 × 7 reconstruction of the Si(1 1 1) surface was prepared by resistive flashing at 1300 °C for 10 s and subsequent annealing at 800 °C of the sample. This procedure was repeated several times in order to obtain the defect density as low as 0.2%. Depositions of the $C_{60}F_x$ molecules were performed using a Knudsen effusion cell. During deposition sam-

ples were kept at room temperature. The source temperature was set at 110 °C, which corresponded to deposition rate of about 0.02 ML/min. Surface structures of both, as-deposited and annealed samples were investigated by STM.

3. Results and discussion

Fig. 1 shows STM images of as-deposited $C_{60}F_x$/Si(1 1 1)-7 × 7 surface as well as subsequently annealed at 300 and 400 °C, respectively. On the as-deposited sample (Fig. 1(a)), dark thread-like features and clusters of the adsorbed fluorine atoms are visible around the molecules. Because printed fluorine atoms are localized almost exclusively in the vicinity of the $C_{60}F_x$ molecules, fluorine-free areas with sizes of ∼10 nm^2 can be seen in this image. In the $C_{60}F_x$ molecule, fluorine atoms are covalently bound to a C_{60} core cleaving its π-bonds, which observation is supported by the results of measurements of carbon–fluorine vibration energy using infrared spectroscopy [8]. It is known that the carbon and silicon has similar bonding energy to the fluorine [9]. However, the stress energy coming from the formation of sp^3 hybridization at the fluorinated carbon atoms makes the $C_{60}F_x$ molecule unstable, which will be the driving force for the printing reaction. With annealing of the sample at 300 °C for 10 min (Fig. 1(b)), fluorine-printing process proceeds leading to continuous supply of fluorine
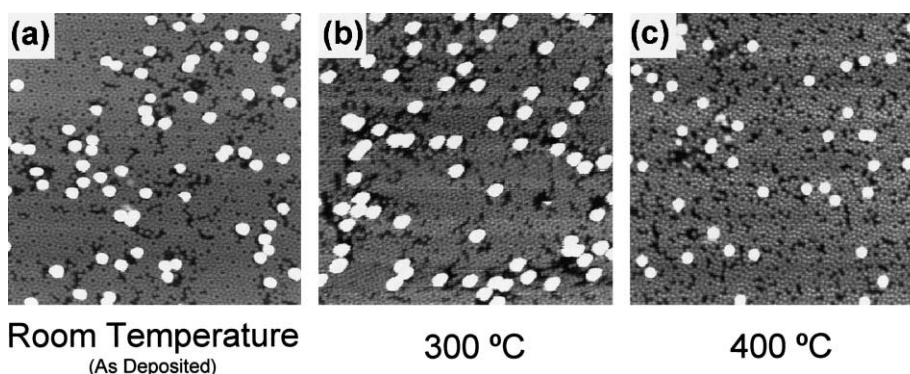

Fig. 1. STM images of the 0.04 ML of $C_{60}F_x$ on the Si(1 1 1)-7 × 7 surface (50 × 50 nm^2; sample bias +2.0 V; tunneling current 20 pA); (a) as-deposited sample, (b) annealed at 300 °C for 10 min, (c) annealed at 400 °C for 10 min.

atoms from the $C_{60}F_x$ molecules and the size of dark area increases. We note that large parts of the 7×7 surface still remain fluorine-free, while the dark-featured sites tend to form clusters at this annealing temperature. This indicates that diffusion of fluorine atoms is limited at 300 °C. When the annealing temperature is set at 400 °C (Fig. 1(c)), large dark features observed at 300 °C around the adsorbed molecules almost disappear and a random distribution of the isolated fluorine adsorption sites is observed. We conclude that most of fluorine atoms on the $C_{60}F_x$ molecules react to the silicon surface at 300 °C because the vibration peak of carbon–fluorine bonds in HREELS, which has been observed in the as-deposited sample [5], disappears after the 300 °C annealing. Thus, the reaction between $C_{60}F_x$ and Si(1 1 1)-7×7 cannot be associated with the re-distribution of fluorine by the 400 °C annealing because this process has been already completed at 300 °C. This indicates the onset of the diffusion of fluorine over the Si(1 1 1)-7×7 surface at 400 °C. It has been reported previously, that in the case of the Si(1 0 0)-2×1 surface, the energy barrier for diffusion of the adsorbed fluorine atom is about 1.8 eV [10]. This value is small enough to allow the migration of the fluorine atoms at 400 °C. However, in the case of the Si(1 1 1)-7×7 surface, the energy barrier for diffusion between different halves of Si(1 1 1)-7×7 is considered to be much higher than in case of Si(1 0 0)-2×1 because the fluorine atoms in the gap between the different halves of 7×7 unit cell have no dangling bonds to interact with, which would compensate the silicon–fluorine bonding energy of about 6 eV [11]. Thus, the fluorine atom is unlikely the actual diffusant for the fluorine redistribution observed here. Another possible process involves the detachment and diffusion of the SiF species. However, it is known that the diffusion of silicon on the Si(1 1 1)-7×7 surface becomes significant at 400 °C and the most of the attachment and detachment of the silicon diffusant takes place at the step in this process [12]. Therefore, once the SiF species are detached from the terrace, they are unlikely to come back to the terrace because the process of defect occupation by the diffusing silicon atoms is not a reversible reaction. Because we have not observed the regrowth

of SiF species or significant accumulation of the fluorine around the step edge, fluorine redistribution process cannot be explained by the SiF diffusion. Consequently, we propose a fluorine exchange reaction between silicon adatoms at the terrace and diffusing silicon as the pathway for the fluorine diffusion. This assumption is reasonable because the temperatures at which the diffusion of silicon and fluorine begins on the Si(1 1 1)-7×7 are similar.

In order to clarify fluorine behavior in the atomic scale, we studied the distribution of fluorine adsorption sites on the $C_{60}F_x$/Si(1 1 1)-7×7 surface as a function of annealing temperature. Fig. 2 shows STM images of fluorine adsorption sites after the 300 °C annealing. As it is discussed above, clusters of darker sites that look like fluorine adsorption sites are seen around the adsorbed molecules in the empty state image (Fig. 2(a)). However, there is a difference between them and typical fluorine adsorption sites in the filled state STM image (Fig. 2(b)). Analyzing the filled state image, we found that fluorine adsorption sites exhibit interesting features, in which rest atoms becomes visible with weaker contrast of adatom protrusions [5]. In Fig. 2(b), featureless dark areas can be seen instead of such atomic features. We conclude that such bias dependence in the STM images originates at topography rather than form the electronic effect of adsorbed fluorine. Etch pits are created locally at the cluster of fluorine adsorption sites even by this low temperature annealing. Amount of fluorine supplied from a single molecule is large enough for the creation of the local etch pits, as they are also often observed in
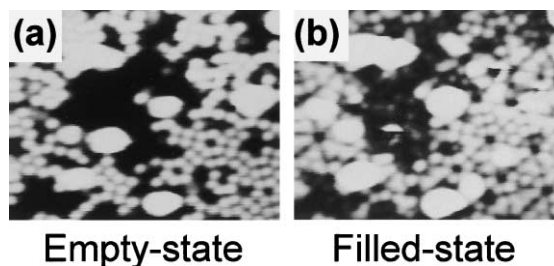

Fig. 2. (a) Empty- and (b) filled-state STM images (15×12 nm^2; sample biases: ± 1.5 V; tunneling current 20 pA) of $C_{60}F_x$/ Si(1 1 1)-7×7 annealed at 300 °C for 10 min.

the vicinity of isolated molecules. Temperature-programmed desorption spectroscopy of the fluorine covered Si(1 0 0) surface revealed that the removal of the SiF_2 takes place at 480–580 °C and that removal at the lower temperature, which needs at least 2 ML coverage of fluorine, should be attributed to the desorption of more highly fluorinated species [13]. Highly fluorinated areas localized in the vicinity of the molecules are created by the supply of fluorine from the molecules due to the lack of migration of fluorine atoms on Si(1 1 1)-7 × 7 surface during annealing, which results in the partial removal of silicon due to desorption of highly fluorinated species at such low annealing temperature.

Fig. 3(a) and (b) shows respectively empty and filled state STM images of surface annealed at 400 °C. Comparing these images we can conclude that the randomly distributed dark sites originate from fluorine adsorption, not defects. Moreover, at this annealing temperature, the etch pits as well as large clusters of fluorine adsorption sites disappear. Also, silicon steps become rougher, indicating that step flow removal of silicon atoms took place. Such step flow etching can be attributed to the healing of etch pits created by annealing at high fluorine concentration areas because isolated fluorine atoms remaining on the surface do not contribute to it.

Fig. 4(a) and (b) shows the empty and filled state STM images of surface annealed at 500 °C. At this temperature, isolated fluorine sites disappear, which observation is supported also by dis-
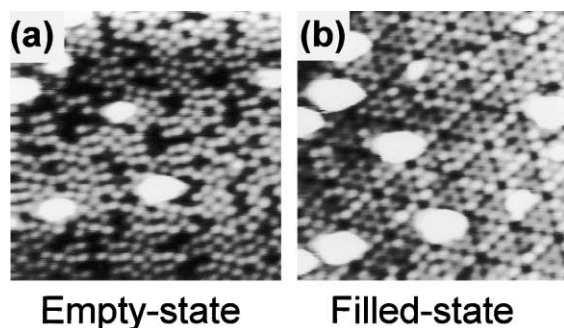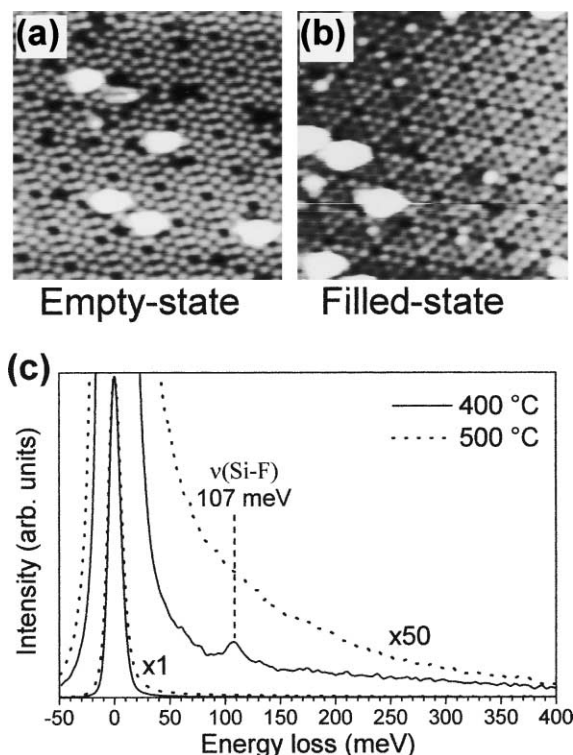

Fig. 4. (a) Empty- and (b) filled-state STM images (15 × 15 nm²; sample biases: ± 1.5 V; tunneling current 20 pA) of $C_{60}F_x$/Si(1 1 1)-7 × 7 annealed at 500 °C for 10 min. (c) HREEL spectra of 0.05 ML of $C_{60}F_x$ on the Si(1 1 1)-7 × 7 surface annealed at 400 °C (—) and 500 °C (· · ·).

appearance of ν(Si–F) peak in HREELS (Fig. 4(c)). Broadening of the primary peak and the higher background in the spectrum also indicates the recovery of the surface states on the Si(1 1 1)-7 × 7 surface at 500 °C. Since the Si–F bond strength is high enough to withstand the annealing temperature of 500 °C, desorption of isolated fluorine sites should also involve removal of Si atoms. The temperature of desorption of SiF_2 species from Si(1 0 0)-2 × 1 have been reported to be in the range of 480–580 °C [13], which is in agreement with our observations. The diffusion of fluorine atoms at 400 °C is important here because the formation of the SiF_2 species from the isolated SiF cannot be achieved without the diffusion of fluorine.

The removal of fluorine species at 500 °C results in a significant change in the shape of the Si steps
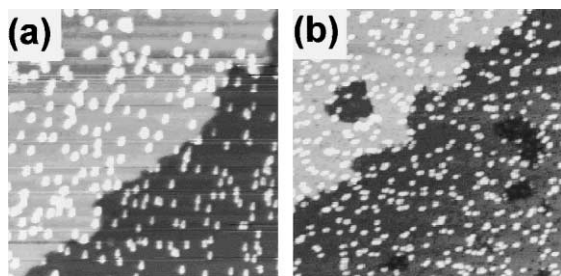

Fig. 3. (a) Empty- and (b) filled-state STM images (15 × 15 nm²; sample biases: ±1.5 V; tunneling current 20 pA) of $C_{60}F_x$/Si(1 1 1)-7 × 7 annealed at 400 °C for 10 min.

Fig. 5. STM images (90×90 nm^2; sample bias: $+2.0$ V; tunneling current 20 pA) of $C_{60}F_x$/Si(1 1 1)-7×7 annealed at 500 °C for 10 min, with the initial $C_{60}F_x$ coverages of (a) 0.04 ML and (b) 0.12 ML.

(Fig. 5(a)). This fact also indicates that the removal of Si atoms takes place with the disappearance of fluorine species. Furthermore, the steps and edges of the pits are pinned to the residual C_{60} cores. It has been reported that the C_{60} forms covalent bonds to the Si(1 1 1)-7×7 upon annealing and the diffusion of C_{60} starts at about 700 °C [14]. Therefore, in our experiment, the residual C_{60} cores are immobile at 500 °C. The pinning effect observed here suggests that the immobile C_{60} cores interfere with the removal of Si atoms from the step-edge. Moreover, when the initial coverage of $C_{60}F_x$ was increased to 0.12 ML (Fig. 5(b)), formation of the etch pits were also observed in addition to the change of step-shape. The diffusion length dictates the spacing between etch pits and steps in this high-temperature annealing. Small defects created by the removal of SiF$_2$ will be healed by the diffusion of Si from the step, instead of aggregating to form larger etch pits, if their distances from the step are smaller than the Si diffusion length. Therefore, the formation of the etchpit indicates that the diffusion length of Si becomes shorter with the increase of the density of residual C_{60} cores that deter the free motion of diffusing Si atoms.

4. Conclusions

Etching on the Si(1 1 1)-7×7 surface using $C_{60}F_x$ fluorine source has been investigated by both STM and HREELS. At room temperature, adsorbed fluorinated fullerene molecules reacted with the Si(1 1 1)-7×7 surface and created fluorine adsorption sites with localized distribution around the molecules. At 300 °C, creation of nanoscale etch pits in the nearest vicinity of the adsorbed $C_{60}F_x$ molecules was observed. High density of fluorine atoms around the $C_{60}F_x$ molecule creates highly fluorinated species, resulting in etching of the Si surface at relatively low temperatures. Annealing at 400 °C resulted in the delocalized fluorine distribution and healing of the etch pits which were created by preceding lower temperature etching at 300 °C, indicating the enhancement of the diffusion of fluorine and silicon atoms. Fluorine atoms desorbed at 500 °C as SiF$_2$ species, which resulted in the step-shape change and creation of etch pits on the terrace. The fluorine diffusion process observed at 400 °C should play an important role in this etching because the movement of adsorbed fluorine is essential for the formation of SiF$_2$.

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