Sublimation of the Si(111) surface in ultrahigh vacuum

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We investigated sublimation of a Si(111) surface using a 70-μm-wide (111) plane created at the bottom of a crater during ultrahigh-vacuum heating. Step spacing on the plane is determined by nucleation of macrovacancies in the center of the plane while steps move in a step-flow manner. The step spacing is related to the adatom diffusion length and decreases with increasing temperature of up to 1190 °C. Around 1200 °C, the spacing shows a transitionlike behavior and increases to 2.5 times the value at 1190 °C. Step flow is maintained above the step-spacing transition. [S0163-1829(97)51616-X]

Sublimation of silicon surfaces has attracted much attention because it is useful for testing theories. Reflection electron microscopy has been used to investigate the step velocities during sublimation for Si(111) (Refs. 1 and 2) and Si(001),[3,4] and macrovacancy (monolayer-deep hole) formation has been discussed on Si(001).[4–6] Step bunching under an electric current has been analyzed taking into account the influence of sublimation.[7,8] Sublimation has technological significance because large terraces are formed during sublimation of Si(111) and Si(001) surfaces. We found the formation of wide (111) planes as large as several tens of micrometers at the bottom of a crater on a vicinal Si(111) surface.[9] Recently, Tanaka *et al.* reported similar phenomena on a Si(001) surface.[10] Initially we interpreted the phenomena as filling in the holes or growth of the Si(111) plane at the bottom of the crater,[9,11] but actually it is due to step-flow sublimation of the Si(111) surface, as already discussed by Tanaka *et al.*[10] The step-flow sublimation takes place so as to expand a low-index plane at the very bottom of a crater.

The Si(111) plane formed at the crater bottom has step spacing as large as 10–30 μm, so it provides a very good basis for investigating surface phenomena while avoiding effects caused by a high density of steps. We have already reported a current effect on a 7×7 domain formation on a wide Si(111) terrace.[12] In this paper, we present experimental results of sublimation of a Si(111) surface at high temperatures based on step distribution observations on a wide (111) plane. So far, macrovacancy formation has mainly been observed on Si(001) (Refs. 3 and 4) because it needs very large terraces on Si(111). Our results show that it only occurs in the center of a wide bottom terrace and that step flow is maintained up to much higher temperatures than on Si(001).

A Si(111) wafer (boron doped, about 5 Ωcm) 0.15° miscut from the (111) plane was used as the substrate. A specimen 5×15 mm was cut from the wafer. The long side of the specimen was nearly parallel to the miscut orientation, around the $[\bar{2}11]$ direction. Square craters with sides 150×150 μm and a depth of about 1 μm were formed on the surface by O_2^+ beam raster scanning in a secondary ion mass spectrometry instrument. The beam energy was 10.5 keV and the beam diameter was about 30 μm. The specimen was then repeatedly oxidized using a H_2SO_4:H_2O_2 (4:1) solution and etched using dilute HF for several cycles to remove possible contamination caused by the crater formation process. After the final oxidation cycle, the specimen was introduced into an ultrahigh-vacuum scanning electron microscope (UHV-SEM) (Refs. 13 and 14) and resistively heated using direct current. The temperature was measured using an infrared pyrometer, which was calibrated using a disappearance filament pyrometer taking into consideration the temperature dependence of emissivity.[15] Since the specimens were clamped using tantalum foil spacers with uniform force, the temperature was uniform in the central region of the specimens, and the reproducibility of the temperature was quite high. Nevertheless, we estimate the accuracy of temperature measurements as $\pm20°$ for around 1200 °C.

The step distribution was observed *in situ* in the UHV-SEM. To observe atomic steps at low magnifications, we radiation quenched the surface by turning off the heating current. The cooling rate was about 150 °C/s from above 1200 °C to 600 °C. At this cooling rate, continuous 7×7 regions could nucleate mainly at steps. Steps were thus decorated with 7×7 bands about 1 μm wide. As reported previously,[13,16] 7×7 regions appear brighter than 1×1 regions in a SEM image, so we could easily observe atomic step distributions even in a 70-μm-wide terrace.

The surface oxide of the specimens was desorped by heating them to 1200 °C. A wide (111) plane was formed by heating the specimen for 20 min at 1220 °C.[17] The width of the (111) plane reached more than 60 μm after the heating. The step distributions on the (111) plane were observed at various heating temperatures. The heating time was set to obtain a steady-state step distribution at each temperature.

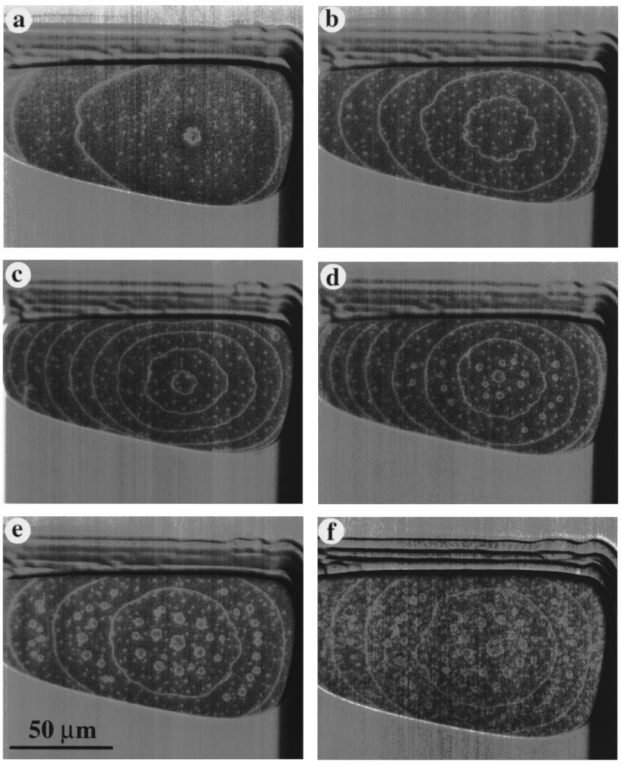

FIG. 1. SEM images of step distributions on a wide (111) plane quenched from (a) 1066 °C, (b) 1123 °C, (c) 1180 °C, (d) 1200 °C, (e) 1230 °C, and (f) 1277 °C. Continuous 7×7 domains nucleated at steps during quenching and appear brighter than the rest on the ''1×1'' surface.

Figure 1 shows SEM images of the quenched surfaces after heating at various temperatures. For most cases, concentric circles are seen. They are the bilayer (0.31 nm high) steps of the (111) plane decorated with 7×7 regions. The concentric circular shape is due to the step-flow sublimation of the surface; steps are created at the center of the widest part of the (111) plane. The step spacing depends on the temperature. Below 1200 °C it increases with decreasing temperature. Below 1060 °C the (111) plane of this width was step free. At 1200 °C smaller circles appeared in between the concentric circles. They are macrovacancies surrounded by bilayer steps; this was confirmed by atomic force microscopy in air. Similar circles are seen on the surfaces heated at higher than 1200 °C. The spacing of the concentric circles becomes larger for temperatures $\geqslant$1210 °C. The concentric shapes imply that the step-flow sublimation is maintained even at these temperatures. Furthermore, the concentric step distributions appeared regardless of the heating duration. Therefore, the macrovacancies between the concentric steps must be formed in the middle of wider terraces during quenching. Other bright patchy contrast seen on the (111) plane is probably due to boron precipitation on the surface. This is caused by the use of the boron-doped wafer ($\sim$5 Ωcm); such a contrast was not observed with a lightly boron-doped wafer (30–50 Ωcm).[9]

The average step spacing between the first and second concentric circles was derived from several images at each temperature and plotted in Fig. 2. The step spacing monotonically decreased from more than 30 μm to 10 μm up to 1190 °C. Then, it showed a transitionlike increase around 1200 °C and reached 2.5 times the value at 1190 °C. The temperature dependency of the step spacing is not clear above 1210 °C because of the large scatter of the data.

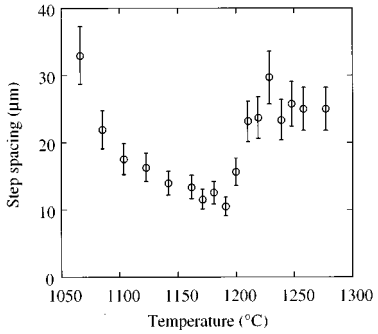

FIG. 2. Temperature dependence of step spacing on Si(111) surface. At temperatures $<$1060 °C, the 70-μm-wide (111) plane was completely step free.

The step distribution below 1200 °C can be explained by macrovacancy formation in the center of the bottom terrace followed by step-flow sublimation. The step-flow sublimation is the reverse process of the step-flow growth that is well described by the Burton, Cabrera, and Frank theory,[18] but it relates to both adatom and advacancy formation. Pimpinelli and Villain treated the evaporation of vicinal surfaces taking into account vacancy formation.[5] They showed that macrovacancies nucleate on an evaporating vicinal surface when the step-step spacing l roughly satisfies

$$\kappa l > \gamma/k_B T, \tag{1}$$

where γ is the step stiffness (energy per unit length), $1/\kappa=\lambda_s$ is the adatom diffusion length before desorption, k_B is the Boltzmann constant, and T is the absolute temperature.[5] Here, $\lambda=\sqrt{D\tau_v}$, where D is the adatom diffusion coefficient and τ_v is the adatom lifetime before desorption. On (111) $\gamma\approx0.39$ eV,[19] so $\gamma/k_BT\approx3$ in the present temperature range. Thus $l>3\lambda_s$, which means that macrovacancies nucleate when the terrace size is roughly three times larger than the adatom diffusion length. Their model is for a terrace between two parallel steps. Although the bottom terrace has a circular shape in the present case, the criterion for macrovacancy nucleation can be used as a rough estimation; macrovacancies nucleate when the radius of the terrace becomes larger than the order of the adatom diffusion length and then step flow is maintained without macrovacancy formation until the next ones appear in the center of the terrace. Therefore, the step spacing in Fig. 2 gives a rough measure of adatom diffusion length λ_s. Since $\lambda_s^2=a^2\exp[(W_v-W_{sd})/k_BT]$, where a is the interatomic spacing, W_v is the desorption barrier for adatoms and W_{sd} is the surface diffusion barrier for adatoms,[6] we have

$$l\approx(\gamma/k_BT)a\exp[(W_v-W_{sd})/2k_BT]. \tag{2}$$

Hence, the Arrhenius plot of Tl vs $1/T$ gives $(W_v-W_{sd})/2$. The plot is shown in Fig. 3, and it yields an activation energy of 1.2 eV, or $W_v-W_{sd}=2.4$ eV. This value is in good agreement with the reported value of 2.3 ± 0.3

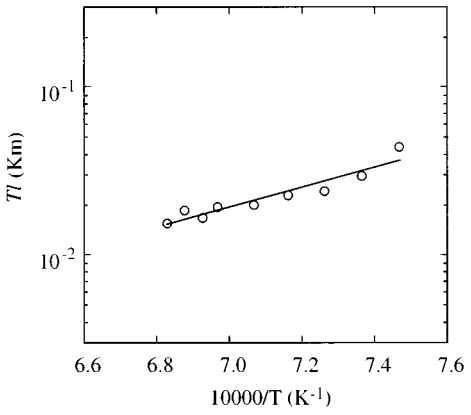

FIG. 3. Arrhenius plot of step spacing multiplied by absolute temperature for the data below 1200 °C. The activation energy 1.2 eV gives $(W_v - W_{sd})/2$.

eV,[6] indicating that inequality (1) is valid for the present case. The decrease in the step spacing with increasing temperature reflects an increase in the desorption of adatoms.

The transitionlike increase in the step spacing at $\geqslant$1200 °C suggests the occurrence of some change in surface structure. One likely surface structure change at such a high temperature is the ''incomplete surface melting,'' which has been predicted theoretically[20] and actually observed on Ge(111) near the melting point (T_m).[21,22] On the Ge(111) surface only the first surface bilayer melts at about $0.9T_m$.[22] Recently Kandel and Kaxiras pointed out that a similar phenomenon should occur on the Si(111) surface because of the structure similarity between Ge and Si.[8] They also predicted that surface steps are still well defined even above the transition temperature (T_c) because, except for the subsurface region, the rest of the material retains its crystallinity.[8]

We believe that the transitionlike behavior around 1200 °C is a piece of evidence for incomplete surface melting of the Si(111) surface. A reflection high-energy electron diffraction (RHEED) study suggested the occurrence of surface melting at 1414 K (1141 °C) on Si(111).[23] The RHEED intensity dropped at this temperature but still kept a finite intensity after the transition indicating that the surface region retained crystallinity. There is a discrepancy of about 60 K between that transition temperature and ours. However, it is not surprising to find this amount of uncertainty in temperature measurements in such a high-temperature regime. Moreover, we found that the electric current effect on step bunching changes at around 1200 °C. We observed step bunching with a step-down current at 1210 °C, and with a step-up current at 1180 °C.[24] Kandel and Kaxiras suggested that incomplete surface melting changes the effective charge of adatoms, causing a transition in the current effect.[8]

A first-principles molecular-dynamics calculation of Ge(111) showed that the outermost bilayer becomes diffusive, while the second bilayer remains completely solid.[25] So, after the surface melting transition, the topmost surface consists of atoms in the melting first bilayer in addition to adatoms, and steps and vacancies are defined on the second bilayer. It is natural, therefore, to assume that the discussion on inequality (1) is still valid even after the transition. A recent Monte Carlo simulation of Si(111) surface melting showed that the cohesive energy of atoms in the melting layer is greater than the adsorption energy of adatoms, while the diffusion coefficients are almost the same for both cases.[26] This means that the lifetime of atoms before evaporation in the melting layer is longer than that of adatoms, so the diffusion length of melting layer atoms is longer than that of adatoms.[26] This result, in conjunction with inequality (1), explains the increase in step spacing after the transition, if we assume γ remains almost the same after transition.

There are two possible explanations for macrovacancy formation between steps on the surfaces quenched from above T_c. One is that they are formed when the substrate temperature passing through the minimum step-spacing temperature of about 1190 °C (scenario I). According to inequality (1), macrovacancies nucleate between concentric steps with larger spacing than the minimum stable terrace size (i.e., about 20 μm). The other is that they are formed because the number of atoms in the melting layer is smaller than that required to form ordered layers below T_c (scenario II). In other words, the number of vacancies is greater in the melting layer than on the normal surface. Vacancies near the concentric steps are incorporated into steps during quenching but those in the middle of the terrace form macrovacancies. Or both of the scenarios contribute to macrovacancy formation. From Figs. 1(e) and 1(f) the fraction of the macrovacancies is about 0.1 of a terrace excluding regions near steps. In scenario I, this means that 10% of the surface atoms are sublimated during quenching. In scenario II, the surface atom density decreases by 10% when surface melting occurs. An estimated fraction of sublimated atoms during quenching is comparable with 10%. But we cannot rule scenario II out based on the present results. A precise measurement is necessary to clarify the formation process of macrovacancies during quenching.

It should be emphasized again that these macrovacancies between steps are not formed during step-flow sublimation. Macrovacancy formation during sublimation only occurred at the center of the bottom terrace. This differs from the Si(001) surface where macrovacancies nucleate between steps, and step flow breaks down.[4]

In conclusion, we investigated sublimation of the Si(111) surface at a high temperature regime by SEM observation of step distribution on a wide (111) plane created at the bottom of a crater. The step spacing on the wide (111) plane depended on the heating temperature; it decreased from more than 30 to 10 μm with increasing temperature up to 1190 °C. This could be understood in terms of the macrovacancy formation during step-flow sublimation, which is the reverse process to step-flow growth. Above 1200 °C, we observed a transitionlike increase in the step spacing to 25 μm. The electric current direction that induced step bunching changed around the transition temperature. We attributed these phenomena to incomplete surface melting on the Si(111) surface.

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