Si-adsorption induced phase transition on the 3C–SiC(001) surface

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Abstract

The formation of Si-rich surfaces on the 3C–SiC(001) crystal using Si molecular beam epitaxy has been investigated using scanning tunneling microscopy. We observed a surface phase transition from the c(4 × 2) reconstruction to the (3 × 2) reconstruction by the adsorption of Si atoms. The adsorbed atoms formed one-dimensional (1D) strings, followed by narrowing the width of the adjacent strings with increasing adsorption. We find that the adsorption by narrowing of the 1D strings is in Langmuir-type adsorption. The Si adsorption saturated at the surface with (3 × 2) reconstruction having the Si coverage of 5/3 monolayer. No Si island was observed on the saturated (3 × 2) surface. We discuss the Si adsorption mechanism in terms of the structural phase transition. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Silicon carbide (SiC) has been established as a substrate material superior to silicon in high power electronic devices [1]. Most efforts in the SiC research have been concentrated on bulk SiC crystal growth and epitaxy, where it is well known that Si-rich ambience in the growth reactor is necessary during the growth. In the sublimation growth method for the SiC bulk growth, the Si-rich ambience prevents the crystal surface from graphitization [2]. Also, in molecular beam epitaxy (MBE) growth, the Si-rich surface with the (3 × 2) surface atomic reconstruction was found to be required for the growth of a 3C–SiC film with good crystallinity [3]. Too much excess of Si over carbon in the growth ambience, in turn, has been reported to precipitate Si islands on the surface [3]. Understanding the Si atom behavior on the SiC surface is thus very important for further improvements of the growth techniques.

So far, single SiH4 gas supply, it has been found that the Si growth onto a carbon-terminated c(2 × 2) surface saturated at the Si-rich (3 × 2) surface [4]. Further interests are the Si growth saturation in the MBE method and the surface atomic structure during the Si irradiation. In this paper, we report the formation of the Si-rich surfaces of the 3C–SiC(001) crystal in the Si MBE,
where we use scanning tunneling microscopy (STM) to observe the details of the surface phase transition from the Si-terminated c(4 × 2) reconstruction to the Si-rich (3 × 2) reconstruction. We discuss the Si adsorption mechanism in terms of the structural phase transition.

2. Experimental

The experiments were performed in an ultra-high vacuum (UHV) STM system with a base pressure below \(8 \times 10^{-11}\) Torr. A flux of Si atoms was generated from a direct-current heated Si substrate. A single-domain 3C-SiC(001) crystal was grown on an Si(001) wafer misoriented by 0.5° ± 0.05° toward the [110] direction [5]. Before introducing the samples into the UHV-STM system, samples were degreased by trichloroethylene, followed by HF dipping to remove native oxide.

We formed a clean Si-rich (3 × 2) surface by UHV anneal [6], a carbon-terminated c(2 × 2) surface was formed by C\(_2\)H\(_2\) dosing [4], and an Si-terminated c(4 × 2) surface by Si molecular beam [7], sequentially to improve the surface crystallinity. We irradiated the Si molecular beam flux onto the c(4 × 2) surface at 1303 K with an irradiation rate of \(1.8 \times 10^{13}\) atoms/cm\(^2\)/s (= 1.0 ML/min). After the irradiation, the Si flux supply was stopped, and we observed a surface reconstruction using STM at room temperature. We repeated the irradiation and the following STM observation five times.

3. Results

Phase transitions from the c(4 × 2) reconstruction to the (3 × 2) reconstruction by successive Si irradiations were observed as shown in Fig. 1. Fig. 1a–f show STM topographical images corresponding to (a) a surface with the c(4 × 2) reconstruction before the Si irradiation, (b) a surface with an (n × 2) reconstruction with \(n \geq 15\), (c) and (d) surfaces with mixed reconstructions of the (3 × 2) and (5 × 2), (e) a surface with a defective (3 × 2) reconstruction, and (f) a surface with the (3 × 2) reconstruction after the saturation of the Si coverage. Fig. 1c was obtained from another sample under the same conditions of temperature and Si irradiation rate as those in the other STM images in Fig. 1. In the initial stage of the Si irradiation, the Si atoms formed one-dimensional (1D) strings [6,8] as shown in Fig. 1b. The 1D strings ordered well with almost the same width between the adjacent strings with the periodicity of \(n \geq 15\). According to the additional dimer row model for the \((n \times 2)\) reconstructions proposed by Hara et al. [6], the atomic structure of the 1D string has two Si dimers in each oval-shaped protrusion. The model was supported by experiments with STM [6,9,10] and photoelectron spectroscopy [10,11]. For the ideal (3 × 2) surface without any defects, the full coverage on the Si-terminated c(4 × 2) surface is 2/3 monolayer (ML). The defect densities, defined as the rate of missing Si dimer pairs for the full 2/3 ML, are 10% in Fig. 1e and 9% in Fig. 1f. We have estimated the average saturation defect density at 7 ± 2% from STM images of six (3 × 2) saturated surfaces formed by repeating the Si flux and C\(_2\)H\(_2\) gas irradiations. We observed no Si island formation by scanning electron microscopy (SEM) and several STM observations with a wide scanning area of 3μm × 3μm.

Counting the numbers of Si dimer pairs and missing dimers on the surfaces in Fig. 1, the Si additional coverage, \(\theta_{\text{adSi}}\), on the Si-terminated c(4 × 2) surface is plotted by open circles in Fig. 2a as a function of the irradiated Si dose. It is found that \(\theta_{\text{adSi}}\) gradually saturates with increasing Si dose. If the saturation is exponential, it is the Langmuir-type adsorption (LTA) [12,13]. We fitted our experimental plots to the LTA model using the equation to express the model, \(d\theta_{\text{adSi}}(dt) = sF(3/2 - \theta_{\text{adSi}})\). Here, \(s\) the sticking probability of the irradiated Si atoms, \(F\) the irradiation rate of the Si flux as \(1.8 \times 10^{13}\) atoms/cm\(^2\)/s (= 1.0 ML/min), and \(t\) the Si irradiation time. Solving the equation, we obtain: \(\theta_{\text{adSi}} = 2/3[1 - \exp(-st)]\). This equation indicates that the logarithmic \(\theta_{\text{adSi}}\) is proportional to \(t\). We plot ln(1 - 1.5\(\theta_{\text{adSi}}\)) versus \(t\) in Fig. 2b. Also, we obtain the ideal Si coverage \(\theta_{\text{Si}}\) by subtracting the observed defect density in \(\theta_{\text{adm}}\) as plotted by closed circles in Fig. 2a and b.
The solid line in Fig. 2b is the result of fitting it to three experimental plots from (b) to (d). We find that $s=0.111$. Since the solid line fits very well in the regime from (b) to (d), the adsorption in this regime is LTA. In the regime, the widths between the 1D strings are narrowing as shown in Fig. 1. It is found that LTA is applicable to the 1D string narrowing as well as the site-by-site adsorption and the adsorption forming two-dimensional islands. The experimental plot of (a) is out of the LTA line. This indicates that the 1D string forms very slowly at the initial stage, not obeying LTA.

The actual experimental coverage $\theta_{\text{ads}}$ is also plotted in Fig. 2b. The deviation from the LTA line indicates the effect of the defect density. In the saturation regime (e) and (f), the deviation is prominent because the narrowing of the string is terminated and the annihilation rate of the missing Si dimers is dominant.

In the Si irradiation onto the surface whose temperature was reduced from 1303 K to 1233 K, the defect density of $4\pm1\%$ was obtained. The reduced defect density is comparable to that reported by Semond et al. [14]. The surface with the small defect density, however, has Si islands with the size from 0.2 to 1 μm as shown in a wide scale image by SEM in Fig. 3. The islands form because of a higher sticking probability under the lowered substrate temperature. In the irradiation at 1173 K, the surface has the $(3 \times 2)$ reconstruction in the atomically-flat area and large Si islands.

4. Discussion

We discuss the behavior of the Si atoms on the surface with the 1D strings. In an adsorption-obeying LTA, an incoming atom onto the empty
area adsorbs while another atom on the adsorbed area desorbs. Si atoms incoming directly onto the 1D string on the c(4×2) surface immediately desorb, whereas those directly onto the empty area are incorporated and migrate around to form a nucleus of the 1D string. Once the 1D nucleus forms, it grows rapidly to extend in the [110] direction until the end of the string meets a terrace edge or step. The ends of the strings were always observed at the steps in our all experiments. This supports the rapid extension of the 1D string. We always observed almost equivalent distances or almost the same n value in the (n×2) reconstructions on a surface. The new 1D string thus narrows the average width of 1D strings on the terrace. Once the narrowing terminates by the formation of the perfect (3×2) reconstructions with n≥5, the vacancy annihilation of the missing Si dimer pairs becomes dominant. The distances between the Si islands formed at the lower substrate temperature in Fig. 3 are 1 to 3 μm. This indicates that the migration length of the Si atoms on the perfect (3×2) surface is also a few microns. This suggests that the Si migration on the 1D strings of the sparse (n×2) surface drastically increases when the coverage attains the perfect (3×2) surface. The migration traversing the strings in the [110] direction along the 3×periodicity should be dominant because the Si atom immediately desorbs on the sparse 1D string. Even in the long migration length, almost all Si atoms result to desorption since the surface has no Si islands. This indicates that the global sticking

Fig. 2. (a) The Si coverage of the 3C–SiC(001) surface as a function of the number of the irradiated Si atoms. Each plot labeled (a–f) corresponds to the STM images in Fig. 1a–f. The Si coverages were estimated by counting protrusions and defects in the STM images. The ideal Si coverage \( h_{adSi} \) is obtained by subtracting the defect density from the actual experimental coverage \( h_{exp} \). The adsorption of Si saturates at \( h_{adSi} = 0.62 \pm 0.01 \) ML with the defect density of \( 7\pm2 \)%. The curve shown in the figure is the logarithmic form of the solid straight line in (b). (b) Empty sites expressed as ln(1−1.5\( h_{adSi} \)) in the Langmuir-type adsorption model. A best fit to \( h_{adSi} \) in the regime between (b) and (d) is shown by the solid line. The sticking probability on an empty site is 0.111, obtained from the slope of the line.

Fig. 3. A SEM image showing Si islands on the 3C–SiC(001) surface. The Si islands are formed when the sample temperature is decreased from 1303 K to 1233 K without changing the Si irradiation rate of 1.0 ML/min. The (3×2) reconstruction is observed by STM on the flat area.
probability $p_G$, which is the rate of the total amount of adsorbed atoms on the SiC surface for the total amount of supplied atoms, is nearly zero. The estimated $x_G$ from Fig. 2a is 0.0005 on the perfect $(3 \times 2)$ surface.

In a simultaneous supply of Si and carbon in the MBE growth reported by Kitabatake et al. [3], the total amount of supplied Si and carbon atoms is almost the same as that in the volume of the grown 3C-SiC film. They grew the epitaxial films so as to maintain the $(3 \times 2)$ reconstruction on the surface. $x_G$ is around unity for both Si and carbon atoms. The irradiated Si atoms inevitably encounter irradiated carbon atoms to form the SiC crystal, leading to the low desorption rate or $x_G$ of unity. In our single Si supply, absence of irradiated carbon atoms to encounter the irradiated Si atoms leads to $x_G$ of nearly zero.

5. Conclusion

We found that Si molecular-beam adsorption on the 3C-SiC(001) crystal saturates at the $(3 \times 2)$ surface having the Si coverage of 5/3 ML. No Si island on the saturated $(3 \times 2)$ surface formed at 1303 K under the Si irradiation rate of 1.0 ML/min. Irradiated Si atoms onto the Si-terminated $(4 \times 2)$ surface form 1D strings with the width between adjacent 1D strings, $n$, narrows with increasing Si dose. The narrowing phenomenon of the 1D strings obeys Langmuir-type adsorption. The irradiation onto the substrate at a lower temperature of 1233 K forms the $(3 \times 2)$ surface with Si islands.

References