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Structure of the Si(011)-(16 × 2) surface and hydrogen desorption kinetics investigated using temperature-programmed desorption

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Abstract

D₂ temperature-programmed desorption (TPD) was used to probe the structure of the Si(011)-(16 × 2) surface. Deuterium was adsorbed at 200 °C to coverages θ_D ranging up to complete saturation (approximately 1.1 ML) and the sample heated at 5 C s⁻¹. TPD spectra exhibited three second-order desorption peaks labelled β_2 , β_1^* and β_1 centered at 430, 520 and 550 °C. Of the proposed models for the Si(011)-(16 × 2) reconstruction, the present TPD results as a function of θ_D provide support for the adatom/dimer model with the β_2 peak assigned to D₂ desorption from the dihydride phase, while the β_1^* and β_1 peaks arise from adatom and surface-atom monohydride phases. © 1997 Elsevier Science B.V.

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Initial low-energy electron diffraction (LEED) studies of the Si(011) surface revealed a variety of reconstructions including (2 × 1), (5 × 1), (9 × 1), (4 × 5) and (16 × 2) [1]. However, subsequent LEED and Auger electron spectroscopy (AES) results demonstrated that all but the (16 × 2) structure are due to Ni contamination [2]. From scanning tunneling microscopy (STM) measurements [3,4] the Si(011) unit cell is known to consist of an upper and lower terrace of equal widths, separated by a single-atom height step along the [01 $\bar{1}$] direction, as first proposed by Ampo et al. [5]. However, the detailed atomic configurations on these terraces are still unclear. Proposed configura-

tions include reconstructions in which the surface atoms form dimers and trimers [6], adatoms [7,8] or adatoms and dimers [9–11].

Determining the Si(011) surface reconstruction is of interest both scientifically as well as for technological applications. The growth of Si_{1-x}Ge_x on Si(011) rather than the usual Si(001) substrates, for example, provides additional degrees of freedom for bandgap engineering in heterojunction devices. The maximum film/substrate conduction-band offset is predicted to be larger for Si_{1-x}Ge_x(011) than for Si_{1-x}Ge_x(001) [12], the optical bandgap of strained Si_{1-x}Ge_x(011) decreases more rapidly with Ge fraction [12], and optical selection rules allow hole-intersubband transitions to be excited by light parallel to Si_{1-x}Ge_x/Si(011) multiple quantum-well layers [13]. However, understanding and controlling Si

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and $\text{Si}_{1-x}\text{Ge}_x$ film growth kinetics on Si(011) requires detailed knowledge of the surface reconstruction. Moreover, for film growth by gas-source molecular beam epitaxy (GS-MBE) or chemical vapor deposition (CVD), knowledge of hydrogen desorption kinetics from the (011) surface is also essential.

In this Letter, we present initial results of an investigation of D_2 desorption kinetics from the Si(011)-(16×2) surface using temperature-programmed desorption (TPD) as a function of deuterium coverage θ_{D} . Deuterium rather than hydrogen was used to reduce the background signal and obtain greater sensitivity. Si(011) TPD spectra exhibit three peaks, with the lowest centered at 430°C, similar to the case for Si(111), for which coverage-dependent D_2 TPD spectra were also measured. In contrast, only two desorption peaks are observed for Si(001) [14].

The experiments were carried out in the analytical chamber of an ultra-high vacuum GS-MBE system [15] with a base pressure of 5×10^{-11} Torr. The chamber is equipped with AES, LEED and a quadrupole mass spectrometer (QMS) which is differentially pumped using a turbomolecular pump with a molecular drag stage. Clean Si(111) and Si(011) substrates held at 200°C were exposed to controlled fluxes of D_2 delivered as molecular beams through a tubular doser located 3 cm from the sample. A hot W filament in the gas stream was used for dissociation. The substrates were then placed 2 mm from the 5 mm diameter hole in the skimmer cone of the mass spectrometer and heated at a linear rate of 5°C s^{-1} by direct current, while the temperature was determined by a thermocouple calibrated using optical pyrometry.

All substrates used in these experiments were 1 cm × 3 cm plates cleaved from p-doped ($5 \times 10^{15} \text{ cm}^{-3}$) Si(111) or Si(011) wafers. Initial cleaning consisted of solvent degreasing, multiple wet-chemical oxidation/etching cycles, and a 20 s etch in 2% HF. The substrates were then exposed to a UV/ozone treatment [16] and introduced, through a sample-exchange loadlock, into the analytical chamber, where they were degassed at 300°C for 4 h, then rapidly heated at 20°C s^{-1} to 1100°C for 2 min. No residual C or O was detected by AES, and LEED patterns from the Si(011) and

(111) substrates were (16×2) and (7×7), respectively. Following saturation exposures, the intensities of all Si(111) and Si(011) LEED superstructure reflections decreased and, consistent with previous reports [5,17], only those near the fundamental reflections remained visible.

Figs. 1a and 1b show typical D_2 TPD spectra from Si(111) and Si(011) surfaces, respectively, dosed for successively longer times t_{D} with the upper curves corresponding to saturation coverage. TPD spectra from Si(111) exhibit two peaks, β_2 at 430°C and β_1 at 530°C, in good agreement with literature data [18,19]. The Si(111)-(7×7) surface has the dimer/adatom/stacking-fault structure [20], in which Si adatoms have three backbonds to surface atoms. Each of the two triangular-shaped subunits are bounded by three Si dimers and have corner holes. At low coverages, hydrogen adsorbs on the single dangling bonds of adatoms and rest atoms (first-layer atoms not bonded to

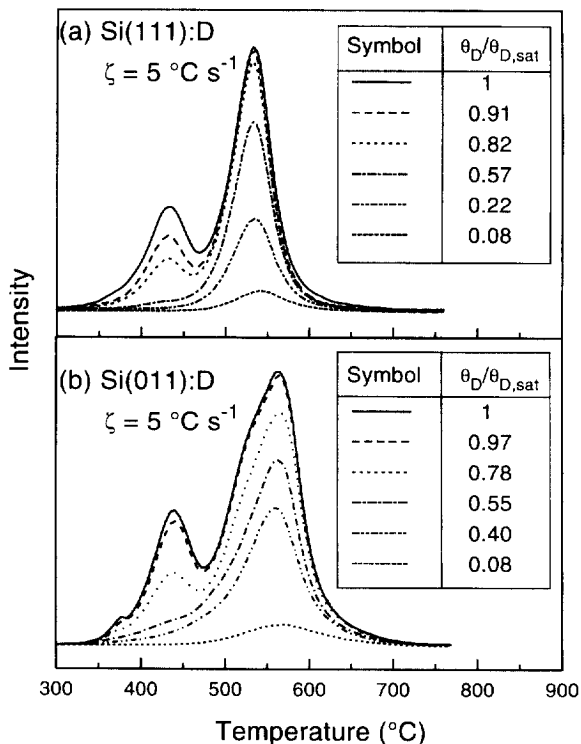


Fig. 1. D_2 TPD spectra, obtained with a heating rate $\zeta = 5^\circ\text{C s}^{-1}$, from (a) Si(111) and (b) Si(011) surfaces exposed to deuterium for $t_{\text{D}} = 1, 3, 5, 10, 20$ and 30 min at 200°C.

adatoms), giving rise to the high-temperature β_1 monohydride feature. Detailed analyses have shown that the two second-order monohydride components are separated by $\sim 10^\circ\text{C}$, with the higher temperature component attributed to hydrogen desorption from rest atoms [19]. At higher coverages, hydrogen inserts into adatom backbonds. The dihydride-bonded adatoms are mobile on the surface and form disordered islands in which the majority species are SiH_2 with some isolated trihydride units [21]. H_2 desorption from these species gives rise to the second-order β_2 peak.

D_2 Si(011) TPD spectra as a function of θ_{D} (Fig. 1b) are similar to those from Si(111). The low-temperature peaks, except for the addition of a small shoulder near 375°C , are almost identical, while the splitting in the high-temperature feature is more obvious in the (011) spectra. Fig. 2 shows that for a given exposure time, deuterium coverages normalized to their saturation values $\theta_{\text{D,sat}}$ on Si(111) and Si(011) are essentially equal.

We have fitted the experimentally obtained spectra using a standard Polanyi–Wigner analysis [22] in which the desorption rate $d\theta_{\text{D}}/dT$ is expressed as

$$\frac{d\theta_{\text{D}}}{dT} = -\left(\frac{v\theta_{\text{D}}^n}{\zeta}\right) \exp(-E_{\text{a}}/kT), \quad (1)$$

where v is the attempt frequency, θ_{D} is the instantaneous D coverage, n is the order of the desorption reaction, ζ is the sample heating rate, E_{a} is the desorption activation energy, and k is

Boltzmann's constant. Readsorption can be ignored due to the high pumping speed and the low D_2 sticking probability. Thus [23]

$$\ln\left(\frac{\theta_{\text{D}}(T)}{\theta_0}\right) = -\frac{v}{\zeta} I(T), \quad (2)$$

for first-order desorption, and

$$\theta_{\text{D}}(T) = \frac{\theta_0}{1 + \left(\frac{v}{\zeta}\right) \theta_0 I(T)}, \quad (3)$$

for second-order desorption. θ_0 in Eqs. (2) and (3) is the initial coverage and $I(T)$ is given by

$$I(T) = \frac{E_{\text{a}}}{R} \left| \frac{e^{-\epsilon}}{\epsilon^2} \sum_{n=1}^{\infty} \frac{(-1)^{n+1} n!}{\epsilon^{n-1}} \right|_{T_0}^T, \quad (4)$$

in which $\epsilon = E_{\text{a}}/kT$.

Best fits to the D_2 TPD Si(011) spectra, ignoring the small shoulder at $\sim 375^\circ\text{C}$ which we attribute to surface defects at high deuterium coverages, were obtained using one low-temperature and two high-temperature second-order desorption peaks. An example is shown in Fig. 3a for a sample exposed to saturation coverage. The low-temperature peak is labeled β_2 and the two high-temperature peaks are β_1^* and β_1 . Frequency factors and activation energies obtained are: $1 \times 10^{15} \text{ s}^{-1}$ and $2.22 \pm 0.02 \text{ eV}$ for β_2 , $2 \times 10^{15} \text{ s}^{-1}$ and $2.55 \pm 0.02 \text{ eV}$ for β_1^* , and $2 \times 10^{15} \text{ s}^{-1}$ and $2.68 \pm 0.02 \text{ eV}$ for β_1 . Equally good fits using these same parameters were obtained at all deuterium coverages. Typical results are shown in Fig. 3b.

The bulk-terminated Si(011) surface consists of zig-zag in-plane rows of atoms along $[01\bar{1}]$ directions, as shown in Fig. 4a. Each surface atom has one dangling bond at an angle of 36° with respect to the surface normal. Proposed models for the Si(011) reconstruction include dimers and trimers [6], adatoms [7,8] and adatoms plus dimers [9–11] as the building blocks. The existence of the strong β_2 desorption peak in our high-coverage (011) TPD spectra at the same temperature as the β_2 peak in the (111) spectra, together with the fact that bulk-terminated (011) surface atoms have only one dangling bond, argues strongly in favor of the presence of adatoms on the reconstructed (011)

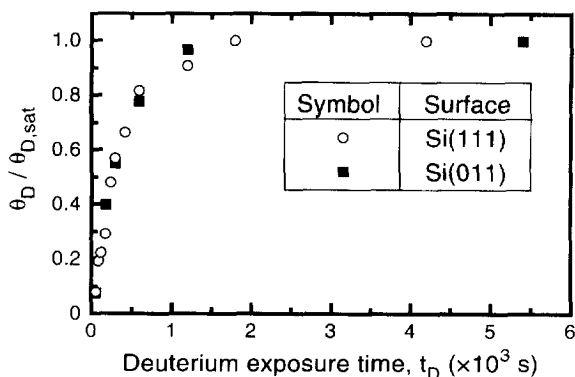


Fig. 2. D coverage θ_{D} normalized to the saturation coverage $\theta_{\text{D,sat}}$ on Si(111) and Si(011) as a function of t_{D} .

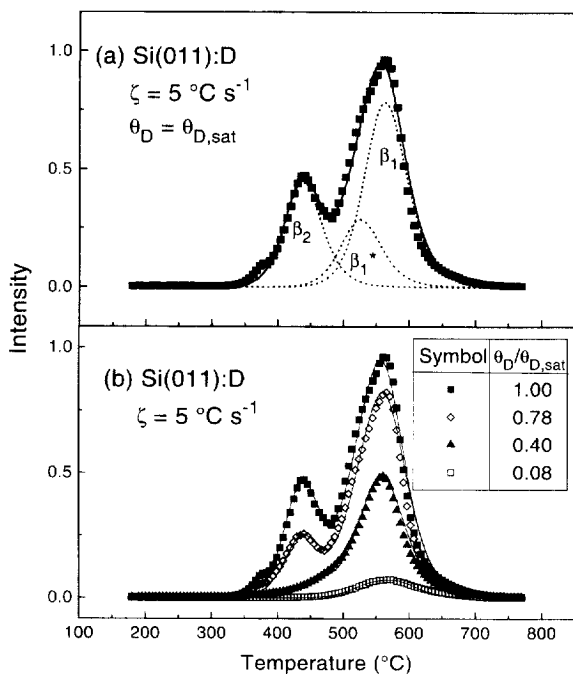


Fig. 3. Fitted D_2 TPD spectra (solid lines) from Si(011) with (a) saturation deuterium coverage and (b) $\theta_D/\theta_{D,sat} = 1.0, 0.78, 0.40$ and 0.08 .

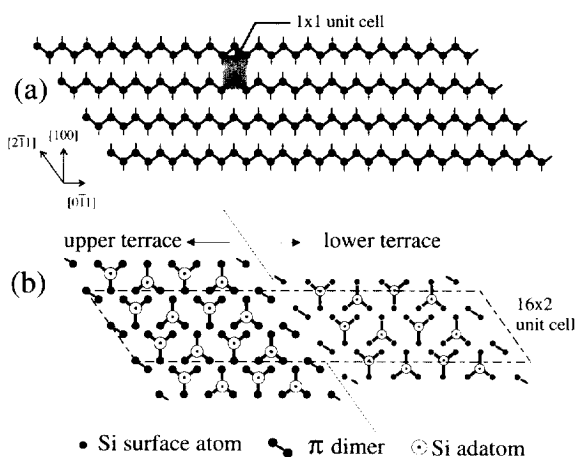


Fig. 4. (a) Bulk-terminated Si(011). (b) Adatom/dimer model of the Si(011)-(16 \times 2) reconstructed surface [9].

surface and against the dimer/trimer [6] reconstruction model. By analogy with the Si(111) case, we propose that adatom backbonds are broken to form dihydride with some trihydride species during deuterium adsorption on Si(011).

After desorbing the dihydride β_2 phase, the remaining deuterium on the Si(011) surface is present as a monohydride. However, the TPD spectra in Figs. 1b and 3 clearly show that the high-temperature desorption feature is composed of two peaks, indicating the presence of two types of monohydrides. The proposed Si(011) reconstruction which is most consistent with our TPD results is the adatom/dimer model [9–11], a schematic drawing of which is given in Fig. 4b. A similar reconstruction has been proposed for Ge(011) based upon STM observations [24]. Each Si adatom in Fig. 4b has three backbonds and one dangling bond. For Si(111), the difference in activation energies for D_2 desorption from the two monohydride phases, where the Si–H bond directions on both adatoms and rest atoms are normal to the surface, is only 0.04 eV [19]. Based upon the (011) reconstruction model in Fig. 4b, where the adatom Si–H bond direction is close to normal but the surface Si–H bond is far from normal, a larger splitting in the monohydride desorption peaks would be expected. This is consistent with our experimental results, where the difference in β_1^* and β_1 activation energies is 0.13 eV.

Adsorption of deuterium on the Si(011)-(16 \times 2) surface shown in Fig. 4b leads to 16 adatom monohydride units plus an additional 16 surface-atom monohydride species per unit cell generated by the D-induced breaking of the π -bonded dimers. D can also insert itself into adatom backbonds and generate more surface-atom monohydride species while forming adatom dihydrides or trihydrides. Thus, we assign the β_1 peak to the surface Si monohydride phase and the smaller β_1^* peak to the adatom Si monohydride phase.

Since there have been no reports of adatom-island formation on Si(011), as observed for hydrogen-saturated Si(111), we assume that D backbond insertion leads to the formation of only isolated dihydride and trihydride species. There are two limiting cases. All adatom monohydride units can be converted to dihydride through the insertion of one D per adatom or to trihydride through the insertion of two D per adatom. In both cases, the newly formed surface-atom dangling bonds also become D-terminated. Complete dihydride formation corresponds to an expected

ratio of integrated areas under the dihydride and monohydride peaks, $\beta_2/(\beta_1^* + \beta_1)$, of $16/(16 + 32) = 0.33$ since, as is the case for Si(001) [25] and Si(111) [19], second-order desorption of dihydride species from Si(011) leaves the adatoms with monohydride termination. Similarly, complete trihydride formation yields $\beta_2/(\beta_1^* + \beta_1) = 32/(16 + 48) = 0.50$. From the saturated coverage TPD spectra in Fig. 3a, we obtain a ratio of 0.37, indicating that the dominate adatom phase contributing to β_2 is the dihydride as expected. Based upon these results, we estimate the saturation D coverage to be approximately 1.1 ML. From TPD spectra as a function of θ_D , it is clear that the dihydride β_2 peak emerges prior to the saturation of the monohydride phase (compare, for example, the $\theta_D/\theta_{D,\text{sat}} = 0.08$ and 0.78 curves in Fig. 3b), indicative of adatom backbond breaking, as in Si(111) [19]. The fact that the β_1^* peak is still present at the lowest coverage measured, $\theta_D/\theta_{D,\text{sat}} = 0.08$, suggests that deuterium adsorption on adatoms and surface atoms occurs in parallel.

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