



TOF-SARS study of hydrogen adsorption and desorption kinetics on Si(1 0 0)

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Abstract

The kinetics of atomic hydrogen isothermal adsorption and desorption on a Si(1 0 0) surface was studied using the time-of-flight scattering and recoiling spectrometry technique at temperatures below and above the thermal desorption threshold. A continuous decrease in saturation coverage with temperature under constant atomic hydrogen exposure has been observed in both regions for temperatures in the range 325–820 K. For $T_S = 500$ –650 K, the decrease is described by a kinetic model where Eley–Rideal (ER) abstraction is responsible for hydrogen removal from the surface and hydrogen coverage depends on the temperature due to the changing rate of migration from precursor to primary monohydride sites. For $T_S = 650$ K and higher, in addition to the ER abstraction, the thermal desorption from primary monohydride sites leads to a further decrease of the saturation coverage. The first-order desorption rates after source shut-off have been measured and an activation barrier of 1.89 eV has been obtained.

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1. Introduction

Adsorption and desorption of hydrogen from the Si(1 0 0) surface has received much attention in recent years [1–14]. Technologically, the presence of hydrogen in the gas phase and as a surfactant plays an important role in crystal growth on silicon substrates. Examples of how hydrogen affects epitaxial growth processes are an increase in island density [15,16] and decrease in anisotropy [16,17] during H-assisted homoepitaxy and hydrogen coverage dependence of the growth behavior

of silicon [18] and germanium [19] overlayers. From a theoretical standpoint, the H/Si(1 0 0) system displays many unique properties, such as sticking probabilities that are greater than expected for Langmuirian adsorption [1], first-order thermal desorption kinetics [2,3], and Eley–Rideal (ER) abstraction by atomic hydrogen from the gas phase [4]. Despite the efficient abstraction, a high degree of passivation of the Si(1 0 0) surface can be achieved by exposure to atomic hydrogen due to the existence of “reservoir” adsorption sites [4,5] that help in maintaining a finite sticking probability at high coverages. Once the existence of dihydride and monohydride species on Si(1 0 0) was established [6], a generally accepted view of

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hydrogen phases on Si(100) was developed. It is known that H/Si(100) has a 3×1 structure at 400 K consisting of alternating monohydride and dihydride units [7,8] with a coverage of 1.33 ML and a 2×1 monohydride structure at 600 K with a coverage of 1 ML [9]. At lower temperatures, 1.5 ML [10] at 373 K and 1.6 ML [3] at 110 K deuterium coverages were measured, although the (1×1) phase to which they correspond is not well defined [7,8].

Currently, no measurements of H adsorption kinetics on Si(100) exist for a continuous range of temperatures between 325 and 820 K. This paper presents measurements of H atom adsorption and desorption dynamics and steady-state saturation values on Si(100) in this temperature range. The data reveal a continuous change in the hydrogen atom saturation coverage, in contrast with a widely accepted view of the Si(100)/H surface as having three fixed coverage states within certain temperature windows in the pre-desorption region. The adsorption dynamics for temperatures between 500 and 820 K is interpreted by means of a kinetic model that includes adsorption, abstraction, thermal desorption and migration of H atoms between two types of adsorption sites.

2. Experimental

2.1. Setup

A detailed description of the basic experimental setup has been given elsewhere [20]. Briefly, a time-of-flight (TOF) analysis of scattered and recoiled particles was performed in a stainless steel ultra-high vacuum chamber with a base pressure $\sim 2 \times 10^{-10}$ mbar. A primary 4 keV Ne^+ ion beam pulsed at a rate of 30 kHz with a 50 ns pulse width and a ~ 0.1 nA/cm² average ion flux was used for scattering from a Si(100) target. The scattered and recoiled particles were velocity analyzed through a 90 cm-long TOF drift region and detected by a channeltron multiplier. TOF analysis allowed detection of both neutral particles and ions with high efficiency. The system contains LEED optics and a sputter ion gun for sample cleaning. The channeltron detector could be rotated in the

scattering plane (the plane formed by the sample normal and beam line), allowing a continuous change in the scattering angle. The samples were mounted on a conventional manipulator that provides reproducible rotation in both azimuthal δ and incident α angles to within $\pm 1^\circ$. The sample temperature was measured by a calibrated infrared pyrometer and a thermocouple attached to the back of the sample.

2.2. Sample preparation

The 2×2 cm Si samples were cut from 0.005 to 0.02 Ω cm p-type silicon wafer and mounted on a two-axis goniometer for polar and azimuthal angle rotations with respect to the primary ion beam. Annealing was accomplished by electron bombardment or radiative heating from behind the sample. Before each adsorption run, the sample was repeatedly flushed to 1500 K for 10–15 s and gradually cooled to 800 K with the ambient pressure remaining at 9×10^{-10} mbar or lower throughout the cleaning cycle. The surface quality was monitored by LEED and the cleaning procedure was repeated until a sharp (2×1) two-domain LEED pattern characteristic of the clean Si(100) surface was observed. TOF spectra obtained from the sample at room temperature are shown in Fig. 1 for two cases: immediately following the cleaning procedure and after 40 min inside the chamber with ambient pressure 4×10^{-10} mbar. Only the scattered Ne and recoiled Si peaks are observed upon cleaning the surface in UHV. The emergence of recoiling peaks from carbon, oxygen and hydrogen, as well as the decrease of the Si recoil peak are attributed to contamination from the ambient hydrocarbons and water. The inset shows details of the hydrogen intake dynamics by the initially clean surface that was cooled down to room temperature with a residual gas pressure at 4×10^{-10} mbar. The measurement was started at $T_S = 800$ K, dropping to 400 K within first 5 min. Even in UHV conditions, rapid adsorption of hydrogen from the surrounding gas places restrictions on the time during which the deposition of adsorbate should start before the surface contamination begins. Under current vacuum conditions, the passivation

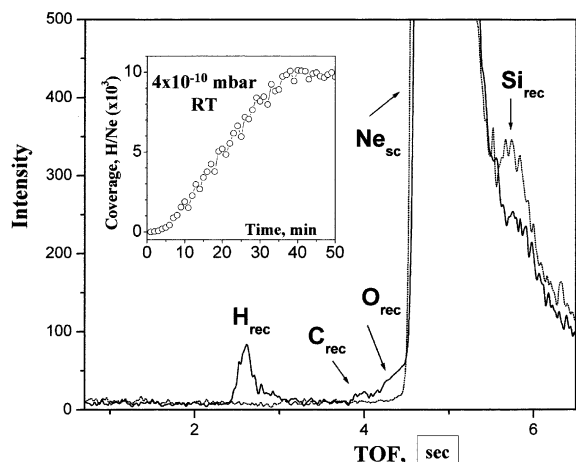


Fig. 1. TOF spectra obtained by scattering 4 keV Ne from the Si(100) surface at room temperature immediately following the cleaning procedure (dotted line) and after 40 min inside the chamber with ambient pressure 4×10^{-10} mbar (solid line). Inset: details of the hydrogen adsorption dynamics from the residual gas onto the initially clean surface. The signal from recoiled hydrogen was normalized by the scattering Ne intensity.

by deposition of adsorbate should begin within 5 min of the cleaning procedure.

After several heating-cooling cycles, irreversible damage to the surface occurred, and the sample had to be replaced due to etching by hydrogen at room temperature [8,11]. In order to avoid such damage, the sample was maintained at an elevated temperature between experiments. The clean surface quality was also checked by measuring the incident angle dependence of the scattered Ne ion fraction, $\text{Ne}^+ / (\text{Ne}^0 + \text{Ne}^+)$.

The monohydride Si(100)- 2×1 -H surface was prepared by cooling the sample to 600 K and dosing it until saturation with atomic hydrogen (molecular hydrogen pressure was 2.7×10^{-7} mbar). Atomic hydrogen was produced by dissociation of H₂ at a hot spiral W filament with the area 1 cm² placed ~ 10 cm in front of the sample and heated to 2100 K. Adsorptions at other temperatures were performed in a similar manner. In order to prevent contamination of the highly reactive Si surface with the ambient gas, hydrogen exposure was carried out immediately after the sample was cooled down to the required temperature.

3. Results

In order to measure the relative amount of adsorbed hydrogen, the ratio of H atoms recoiled from the surface to scattered primary Ne particles was monitored as a function of hydrogen exposure. Since time-of-flight scattering and recoiling spectrometry (TOF-SARS) has equal detection efficiencies for ions and neutrals in this energy range, the signal from recoiled hydrogen does not depend on the chemical environment at different adsorption sites. The only factors that should be taken into account when comparing the recoiling intensities from different sites are scattering/recoiling cross-sections and possible shadowing/blocking of trajectories. Our simulations have shown that for H atoms adsorbed above the first layer of the substrate, the predominant mechanism leading to forward recoiling of hydrogen is a single direct encounter with the incoming Ne projectile, independent of the atom position in the surface unit cell. Therefore, the scattering/recoiling cross sections are constant and the shadowing/blocking of trajectories are nonexistent under these conditions. The hydrogen position near the top layer Si atoms, indicated by simulations [5] as a candidate for a secondary adsorption site, was also tested. In general, recoiling intensities from this site and the primary monohydride site differed; however, for the specific azimuth of 15° off the main channeling surface direction used in experiment, these two intensities were equal.

The isothermal hydrogen adsorption and desorption at different temperatures with constant atomic H flux was carried out in a series of experiments. All data were normalized to the reference signal from a 1 ML monohydride obtained from a saturated surface at $T_S = 600$ K.

Fig. 2 shows plots of the measured hydrogen coverage versus the exposure time for four substrate temperatures, $T_S = 420, 638, 720$ and 743 K. Uptake slopes at the initial stages of adsorption at different temperatures indicate constancy of the initial sticking coefficient over a wide range of temperatures. In all cases, the H₂ source was turned off after saturation was achieved and the hydrogen surface population was monitored for some time after the shut-off. For $T_S = 420$ and

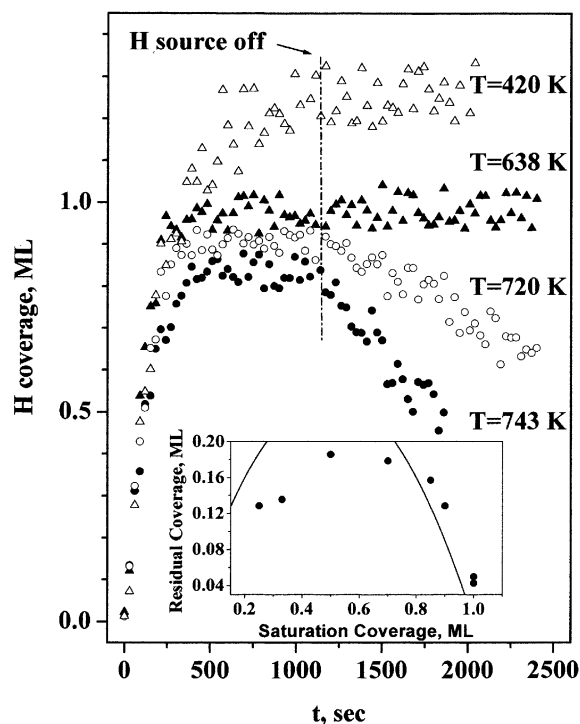


Fig. 2. Hydrogen adsorption dynamics on Si(100) at 420 K (open triangles), 638 K (filled triangles), 720 K (open circles), and 743 K (filled circles). The hydrogen source was turned off at $t = 1140$ s. Inset: symbols—residual coverage n_{res} for $T_S > 650$ K after the H source shut-off plotted against saturation n_{sat} value with the source on. The solid curve is $n_{\text{sat}}(1-n_{\text{sat}})$.

638 K, no change in hydrogen coverage was detected after the H atom shut-off, but the saturation values were different.

Under identical conditions, the adsorption and subsequent thermal desorption of H from Si(100) has been monitored for T_S between 680 and 820 K. The measured H coverage as a function of dose is shown in Fig. 2 for $T_S = 720$ and 743 K; similar dependencies were obtained for other temperatures from the interval. A further diminishing of the saturation coverage n_{sat} when the H source is on as well as a region of exponential coverage decrease due to thermal desorption after the source shut-off are observed. When the transition is complete, a new steady-state nonzero value of the residual H coverage n_{res} is attained. This residual coverage was found to vary with temperature, just as the steady-state coverage with the

H source on. However, the trend of the variation is opposite to n_{sat} : for $n_{\text{sat}} > 0.5$ ML, n_{res} increases with increasing temperature. The inset in Fig. 2 shows values of n_{res} plotted against corresponding values of n_{sat} obtained in several adsorption/desorption measurements at different temperatures. For temperatures slightly above the desorption threshold when n_{sat} is close to unity, almost a complete desorption of hydrogen is observed after the H source is turned off. As temperature increases, n_{sat} starts to drop, but at the same time the residual coverage grows. This behavior can be explained considering the possibility that molecular hydrogen desorbs only from doubly occupied dimers at these temperatures.

The saturation values for various substrate temperatures with H source on from the interval $T_S = 323$ –820 K are plotted in Fig. 3, which can be separated into regions corresponding to coverages characteristic of the three phases existing on the H-saturated Si(100) surface [7–9]. The main 1 ML (2×1) monohydride phase, the 1.33 ML (3×1) phase, and a disordered 1.5–2 ML (1×1) phase can be assigned to temperatures centered around 600, 400, and 300 K, respectively. Contrary to the accepted view that the coverage associated with the (2×1) monohydride phase is constant and

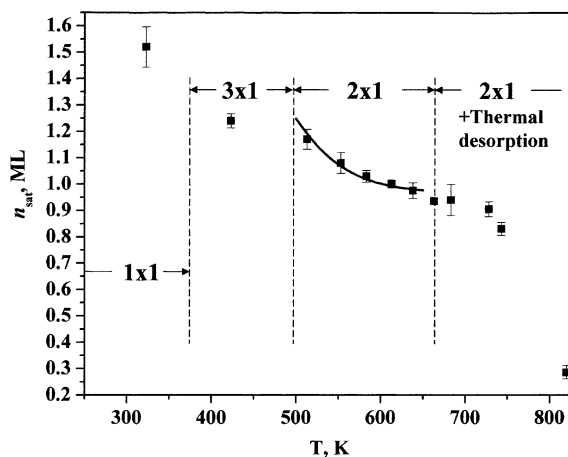


Fig. 3. Experimental measurements (squares) of H saturation coverage as a function of substrate temperature. Three regions corresponding to (1×1), (3×1), and (2×1) phases of H on Si(100) are shown. The solid line shows coverage variations obtained from the kinetic model.

equal 1 ML, Fig. 3 shows that the saturation coverage inside the (2×1) region (500–650 K) actually varies with temperature. There is no thermal desorption in this temperature range and variations cannot be caused by change in the thermal desorption rate, as it is in the case [12] for $T_S > 650$ K.

4. Discussion

A kinetic model with two types of adsorption sites has been created to describe adsorption of H on Si(1 0 0) from which coverage variations for the interval $T_S = 500$ –650 K were obtained [21]. These are shown in Fig. 3 by the solid line. In order to apply the model for $T_S > 650$ K, a modification should be made by adding a term responsible for the first-order thermal desorption to the kinetic equations. With the hydrogen source off, the terms that describe the gas-surface reactions vanish from the equations, and the thermal desorption constant c can be determined from the following first-order equation.

$$\frac{dn}{dt} = -cn, \quad (1)$$

where n is the total surface coverage. By fitting the desorption curves in Fig. 2 with solutions to Eq. (1), the desorption activation energy of 1.89 ± 0.3 eV was obtained. This value falls into the range of previously reported activation energies for this process [2,3,13,14]. Existence of the residual coverage after the completion of desorption implies that Eq. (1) actually applies to only a part of the total surface population, while the rest of the adsorbed atoms remain on the surface. It can be argued that for $T_S = 650$ –820 K, molecular hydrogen desorbs only from dimers that are doubly occupied, and desorption from singly occupied dimers occurs at higher temperatures. Assuming random filling of monohydride bonds during adsorption and no migration between sites, the number of filled sites that have an adsorbed hydrogen on a next neighbor dimer atom is n_{sat} [2], and the number of sites with an empty site next to them is $n_{\text{sat}}(1-n_{\text{sat}})$ for any given saturation coverage n_{sat} . In the inset of Fig. 2, the $n_{\text{sat}}(1-n_{\text{sat}})$ curve is plotted along with residual coverages

measured for various saturation values. It is seen that this simple reasoning can be used in explaining the observed dependence of the residual coverage as a function of the saturation coverage.

5. Conclusions

Due to its unique capabilities, the TOF-SARS method allows determination of the hydrogen coverage and studies of the dynamics of hydrogen adsorption on Si(1 0 0). In this work, TOF-SARS measurements of isothermal H adsorption on Si(1 0 0) for a continuous range of temperatures $T_S = 325$ –820 K have been performed. The saturation coverage was found to monotonically decrease with temperature from ~ 1.5 to 0.29 ML. A kinetic model describing competing processes of adsorption, abstraction, and migration between two types of adsorption sites is used to explain the observed dependencies in the range 500–650 K. For $T_S > 650$ K, the thermal desorption reaction was included in the model and a desorption activation energy of 1.89 ± 0.3 eV was obtained.

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