Thermal desorption of hydrogen from the diamond C(100) surface

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Abstract

Temperature-programmed desorption (TPD) is used to measure the kinetics of hydrogen desorption from the C(100) surface. Two major desorption channels, attributed to hydrogen desorption from (2×1) domains (a sites) and disordered domain boundaries sites (b sites) were observed. The change in the morphology of the C(100) surface upon hydrogen adsorption/desorption leads to a variation in the intensity ratio between the two hydrogen desorption peaks. The degradation results in smaller (2×1) domains, as evidenced by deteriorated LEED patterns in which the characteristic (2×1) half-order spots disappear. The (2×1) LEED pattern can be restored on the degraded C(100) surface by repeated hydrogenation–annealing cycles in the temperature range 300–1100 K. Fitting the experimental TPD data with simulated curves from the two-site model shows that desorption from the a site obeys first-order kinetics with a prefactor of $1.4 \pm 0.9 \times 10^{13}$ s$^{-1}$ and an activation energy of $80.3 \pm 1.3$ kcal mol$^{-1}$, whereas the process giving rise to the b peak follows second-order kinetics with a prefactor of $2.3 \pm 0.9 \times 10^{13}$ s$^{-1}$ (expressed in first-order units) and an activation energy of $75.1 \pm 0.5$ kcal mol$^{-1}$. Possible mechanisms for first-order recombinative hydrogen desorption from the C(100)-(2×1) surface are also discussed.

Keywords: Diamond; Hydrogen; Thermal desorption

1. Introduction

Synthetic diamond is a material of great potential in industry. Because of their useful properties (such as high thermal conductivity, extreme hardness, high transparency for ultraviolet-infrared (UV-IR) radiation and chemical inertness), diamond thin films play an important role in various commercial applications. These include machine tools, optical coatings and high-temperature electronics. The epitaxial growth of single-crystal diamonds has been a long-standing goal of diamond technology. Until now, chemical vapor deposition (CVD) has been the most well-developed technique used to fabricate diamond films. The usual chemical sources for diamond CVD are hydrogen atoms and certain hydrocarbon-based species (C$_x$H$_y$). While more carboneous precursors such as halocarbon species (C$_x$X$_y$ or C$_x$X$_y$H$_z$) have been developed recently, atomic hydrogen is the obligatory ingredient in diamond CVD. It is generally agreed that the role of hydrogen atoms in this process is to enhance the growth rate of the diamond film by creating vacant sites through abstraction, and to improve the quality of the diamond film by suppressing graphite formation [1,2].
of hydrogen to remove non-diamond carbon was presented by Mucha et al. [3]. Theoretical calculations suggest that rehybridization is the principal channel by which hydrogen “removes” non-sp³ carbons [4, 5]. In the recently developed atomic layer epitaxy (ALE) method, which is a novel approach for growing diamond homoepitaxially at low pressure, hydrogen is used to saturate the surface dangling bonds and keep them capped between alternating growth cycles [6]. Since hydrogen is such a critical element in the diamond growth mechanism and in determining the quality of diamond films, both experimental and theoretical efforts to achieve a better understanding of the interaction of hydrogen with diamond surfaces have increased in the last few years.

The studies reported here were performed on a type-IIa natural diamond (100) single crystal. The C(100) face was chosen because C(100) films could be used more widely in electronic applications than other low-index diamond faces. It has been found that growth of the diamond C(100) face showed a lower defect concentration. As demonstrated by various microscopy techniques (atomic force microscopy (AFM) [7], scanning tunneling microscopy (STM) [8] and scanning electron microscopy (SEM) [9]), homoepitaxial diamond films tend to be smoother and more defect-free in the (100) orientation. Many theoretical and experimental works have been performed using various methods to investigate the reaction of H with diamond surfaces. For H chemisorption on the diamond C(100) surface, techniques such as low-energy electron diffraction (LEED) [10, 11], high-resolution electron energy-loss spectroscopy (HREELS) [12, 13], infrared spectroscopy (IR) [14–16], sum frequency generation spectroscopy (SFG) [17] and X-ray photoelectron spectroscopy (XPS) [18, 19] have been employed to yield valuable information about the adsorbed species as well as their bonding geometry on the surface. Theoretically, molecular mechanism calculations and ab initio studies have provided possible structures of the hydrogenated species on the C(100) surface [15, 20–25]. For hydrogen desorption from the C(100) surface, temperature-programmed desorption (TPD) [26–28] and isothermal desorption [29] have been performed.

The clean, bulk-terminated C(100) diamond surface nominally has two dangling bonds at each surface carbon atom. In order to lower the surface free energy, the surface may reconstruct by dimerization of the surface carbon atoms to form a re-bonded surface structure. This surface reconstruction results in a (2 × 1) symmetry in the LEED pattern. An alternative way to relieve the surface stress is to cap the surface dangling bonds with foreign atoms, such as atomic hydrogen originating from the sample preparation procedure by either wet chemistry or H-plasma cleaning. Variations in the hydrogen surface concentration may lead to different surface structures. For example, a low hydrogen coverage is only sufficient to form a monohydride phase in which a reconstructed structure with (2 × 1) symmetry is preserved. With higher hydrogen concentrations, however, a dihydride phase could be formed by de-reconstructing the surface back to the ideal bulk-terminated structure exhibiting a (1 × 1) LEED pattern. In fact, the existence of the dihydride phase in the C(100) surface is still controversial. Theoretical calculations indicate a substantial barrier for breaking the dimer bond by the addition of atomic hydrogen [10, 30, 31]. Yang et al. [20] have argued that steric constraints severely limit the ability of the surface to saturate in the dihydride phase. Moreover, this intriguing surface normally possesses intrinsic instability due to the large number of surface dangling bonds as well as its naturally high chemical reactivity. On the (100) face, there are two dangling bonds per surface carbon atom, while there is only one dangling bond for each surface carbon atom on the (111) or the (110) face. As a result, a consensus about the nature of the diamond C(100) surface is still lacking. In addition, the unstable characteristics leading to surface degradation also provide a major difficulty in the study of the C(100) surface.

The present study was undertaken to investigate how the initial conditions of the diamond C(100) surface influence the hydrogen surface chemistry, especially the kinetics of hydrogen desorption from this particular system. The result provides kinetic data for hydrogen desorption from the C(100)-(2 × 1) surface. This study was carried out mainly using LEED, HREELS and TPD. LEED was used
to examine the surface structure, HREELS to monitor the H–D exchange process, and TPD to probing the desorbing hydrogen molecules. A simple model based on the assumption that the C(100) surface is constituted of two surface sites with different populations is proposed and used to simulate quantitatively the hydrogen desorption kinetics.

2. Experimental

The experiments were carried out in a two-stage ultrahigh vacuum (UHV) apparatus with a base pressure of $2 \times 10^{-10}$ Torr. A detailed description of the system design and experimental capability, including the hydrogen atom source, the crystal mounting and surface temperature measurement/calibration, has been given previously [2]. Briefly, the UHV apparatus was equipped with the following capabilities: digital LEED optics for surface structure determination, an Auger electron spectrometer (AES) for surface chemical characterization, a high-resolution electron energy-loss spectrometer (HREELS) for surface vibration detection, and a quadrupole mass spectrometer (QMS) for probing the thermal desorption species from the surface. The quadrupole mass spectrometer (UTI 100 C) was situated in a separate, differentially pumped chamber with two small ion pumps ($20 \text{ l s}^{-1}$). Sample heating was programmed by controlling the heating current via a personal computer. We have developed some novel software which allows us to program the sample temperature as any linear function of time and simultaneously record multiple QMS signals during the TPD experiments. The sample temperature was measured by a W(5%Re)-W(26%Re) C-type thermocouple connected via an isolation amplifier to the A/D channel of the computer interface card. As in previous studies, the desorbing molecules were sampled through a 3 mm diameter Mo cone situated approximately 2 mm away from the sample surface.

The C(100) sample used in this study was a natural type-Ia diamond single crystal (5 mm diameter, 0.25 mm thickness; Drukker International) with a typical miscut of less than 3° in orientation. Two sample preparation methods were employed prior to mounting the diamond on the manipulator. In the first method, the crystal was treated by the standard sample preparation procedure, i.e. mechanical polishing with 0.25 μm DP paste and cleaning the surface with acid solution ($\text{H}_2\text{SO}_4$:$\text{HNO}_3$, 3:1, at 90°C for 20 min), followed by rinsing in $\text{H}_2\text{O}$ and ultrasonic cleaning in acetone and methanol to remove any metallic and graphitic contaminants on the surface [32]. After this treatment, the C(100) surface exhibited a visible (1 x 1) LEED pattern with diffuse spots and background after being introduced into the vacuum chamber. This observation is consistent with other LEED measurements on the as-polished C(100) surface [27]. As measured by nuclear reaction techniques, one monolayer of hydrogen on the C(100) surface was suggested to correspond to two hydrogen atoms per surface carbon atom [33]. Therefore, the (1 x 1) configuration is explained by the dihydride termination on the diamond C(100) surface. Nevertheless, the assignment of a dihydride phase is controversial. Atomic hydrogen appears to be relatively inefficient in breaking the C–C dimer bonds on the C(100)-(2 x 1) surface according to Thomas et al. [26]. Even if the C–H bond strength is greater than the C–C bond strength, theoretical calculations by several groups have indicated that there is a substantial energy barrier to breaking of the dimer bond by the addition of atomic hydrogen [10,30,31,34]. Yang et al. [15,20] have also argued that the dihydride phase is highly strained due to H–H repulsion, and was predicted to be thermodynamically unstable with respect to dehydrogenation to monohydride [15,20]. If the dihydride structure exists, one would expect a complete change in the C–H bond orientation in order to stabilize the surface, or it would only appear on specific surface sites such as defect sites, step edges or domain boundaries, which normally have more free space. Another explanation for the (1x1) LEED pattern is that polishing the diamond surface produces repeated microcleavage along (111) planes, leaving a rough but crystalline surface which is visible in electron microscopy [35].

Upon heating the surface to over 1200 K, half-order spots start to appear and the LEED pattern
exhibits two rotated (by 90°) domains of (2×1) symmetry. In the initial stages of this study, this surface transformation phenomenon was not very reproducible. Hamza et al. [27] found that approximately 60% of the polished diamond C(100)- (1×1) surface reconstructed to the (2×1) structure after annealing the sample to 1300 K. In Ref. [27], an ESD-TOF experiment was performed to show the correlation between this structure transformation and the surface oxygen concentration. It was concluded that as-polished (1×1) surfaces producing the most intense (2×1) LEED pattern had the lowest oxygen ESD-TOF signal.

The effect of surface contamination on the surface reconstruction has been also noted in the case of the Pt surface [36]. Küttel et al. [35] utilized ECR hydrogen-plasma treatment to prepare an oxygen-free C(100) surface which showed a consistent (1×1) LEED pattern for electron energies higher than 40 eV [35]. Upon annealing the sample at 1320 K in UHV, however, in only one case could very weak half-order spots indicating a (2×1) reconstruction be observed.

Smentkowski et al. [19] reported an XPS and LEED study of the interaction of atomic deuterium with the diamond C(100) surface. A stepwise heating schedule (in steps of ~50 K) was applied in the course of sample annealing. It was found that at a temperature of ~1135 K, the C(100)- (1×1) surface started to reconstruct. With this strategy, we were able to repeatedly obtain a very vague (2×1) pattern with a bright background after initial heating of the as-polished C(100)- (1x1) surface at about 1200 K. As the temperature was further increased to 1350 K, where the surface was free of hydrogen as indicated by HREELS spectra [19], the (2×1) LEED pattern improved, but the half-order spots were still diffuse. However, annealing the as-polished C(100) surface beyond 1450 K led to the disappearance of the (2×1) structure. In this case, only primary spots were observed, which might result from the severely degraded surface, as suggested by Küttel et al. [35]. When exposing the annealed C(100) surface to atomic hydrogen, the (2×1) LEED pattern remained intact from low coverage to saturation coverage. Assuming the same sticking probability as that on the C(111) surface, the hydrogen-saturated C(100) surface was obtained by exposing the bare surface to 5×10^{-6} Torr of hydrogen for at least 10 min in the presence of a hot tungsten filament (1800 K). Surface charging effects were sometimes present when trying to obtain LEED patterns for the hydrogen-free surface. Thomas et al. [26] also observed (2×1) diffraction patterns before and after hydrogen desorption. Smentkowski et al. [19] reported that a (2×1) LEED pattern persisted even for a very intense atomic D exposure (1 000 000 L). Conversion of the surface back to the (1×1) state by hydrogen exposure, however, was observed by Hamza et al. [27]. AFM study revealed a huge morphological change for those surfaces which converted back to the (1×1) structure by hydrogen adsorption/desorption cycles.

The intensity of the half-order spots of the LEED pattern for the first C(100)-(2×1) surface obtained from the as-polished surface was not very distinct even after the surface hydrogen had been completely desorbed. This indicated that the average size of atomically flat domains with (2×1) structures was not large enough, and further surface treatment was certainly needed. Johansson et al. [37] found that treatment of the diamond surface with atomic hydrogen produced by hot W filaments showed a smoothing effect [37]. Smentkowski et al. noted a significant sharpening of the FWHM of the C 1s transition in the XPS spectrum after re-exposure of a clean C(100) surface to ~2000 L of atomic D followed by heating to 1450 K (twice). Some modification of this cleaning cycle has been made in this study. It was found that moderate and repeated hydrogenation–annealing cycles greatly improved the (2×1) LEED pattern. In this treatment, the chamber was back-filled with 5×10^{-6} Torr of H2 or D2, and the C(100) surface was exposed to the H (D) flux generated by hot tungsten filaments. During hydrogenation, the crystal was linearly heated at 10 K s^{-1} from 300 to 1100 K followed by slow.
cooling to 300 K (about 5 min) before another heating cycle took place. Heating in vacuum can remove surface hydrocarbons [38]. Flashing to 1100 K followed by instant cooling will only remove the hydrocarbon species at defect sites or steps, without desorbing hydrogen adsorbed on the terraces. Such defect-site hydrocarbons can be generated again by another exposure to atomic hydrogen at a lower surface temperature. Therefore, repeated hydrogenation-annealing cycles would readily strip off the defect carbon atoms from the diamond surface. Given the above treatment procedure for the diamond C(100) surface, it was possible to restore a good (2 × 1) LEED pattern without breaking the system vacuum. This is very important for studies on the C(100) surface, since the LEED pattern would quickly deteriorate with repeated hydrogen adsorption and desorption. Even the study of hydrogen desorption started with an extremely smooth surface condition (as presented in Section 3), the (2 × 1) pattern could only survive for a few hydrogen adsorption/desorption cycles.

An alternative and better way to prepare a smooth and well-ordered C(100) surface is to treat hydrogenated diamond surface has been demonstrated to be fairly conductive [40]. In the hydrogen adsorption and substitution experiments, the HREELS spectra were acquired for every 300 L of D atom exposure. LEED measurements were performed concurrently to verify the surface structure after complete D substitution.

3. Results and discussion

In presenting and discussing the results for the interaction of hydrogen with the C(100) surface, we begin with the LEED measurements. LEED patterns were undertaken to characterize the symmetry of the diamond surfaces in various stages of the study. The H–D exchange process was monitored by HREELS measurements. Hydrogen desorption from the C(100) surface was then determined by TPD. Finally, the results from fitting the experimental TPD curves with a two-site kinetic model are presented.
3.1. Low energy electron diffraction

The state of the diamond surface after insertion into the UHV chamber was examined by LEED. It is generally agreed that the order of the C(100) surface is very sensitive to the sample preparation procedure \cite{11,41}. Two initial sample preparation methods were discussed in Section 2, i.e. (i) initial stepwise heating and (ii) hydrogen microwave plasma treatment of the as-polished C(100) surface. Both methods lead to the \((2 \times 1)\) LEED pattern which is characteristic of the surface reconstruction. Here, we present the data from the surface prepared by method (ii), since it provides a better initial condition in terms of surface smoothness, as indicated by the LEED measurement. Fig. 1a is a typical \((2 \times 1)\) LEED pattern for a plasma-treated C(100) surface after normal chamber bakeout (~24 h at 150°C). No oxygen or other contamination could be detected by AES.

The plasma treatment procedure produced a fully hydrogen-terminated C(100) surface. Since deuterium is the required element in the TPD experiments, the hydrogenated surface was then exposed to deuterium atoms created by passing molecular deuterium over a tungsten filament. In this way, the surface hydrogen could be completely substituted by deuterium atoms. HREELS was used to confirm that this procedure produced a fully deuterated surface. In Fig. 2, the exchange between D and H on the C(100) surface is shown. The H-terminated sample shows a C–H stretching peak at 360 meV and a broad band with a peak center at 151 meV which is assigned to a mixture of the C–H bending and substrate C–C stretching modes according to Aizawa et al. \cite{13}. As D–H exchange

![Fig. 1. LEED patterns (\(E_p = 164\,\text{eV}\)) and TPD spectra of \(\text{D}_2\) desorption from various diamond C(100) surfaces. The initial surface conditions for the first, second and third TPD runs (or the TPD spectra of (b), (d) and (f)) are manifested by the LEED patterns shown in (a), (c) and (e), as indicated by the direction of the arrows. The LEED pattern in (a) was taken after hydrogen microwave plasma treatment. The fitted TPD spectra are also shown in (b), (d) and (f). Note that the time-integrated mass spectrometer signal for each TPD run has been normalized to 1, assuming unity for the saturation hydrogen coverage.](image-url)
background were observed. This indicates that the long-range order of the (2 × 1) surface structure is lost after hydrogen desorption, although the short-range structure may not be largely perturbed [13]. In other words, the surface (2 × 1) domains may shrink upon hydrogen desorption. In addition, the long-range order could not be recovered simply by hydrogen readsorption. As mentioned above, the C(100) surface is inherently unstable as compared to other diamond faces. The instability of the C(100) surface is presumably due to the high concentration of surface dangling bonds and the difficulty in forming highly strained C–C dimers. Evans [42] associated the observed degradation with a pure thermal effect. Recently, Hoffman et al. [43,44] have suggested that cycles of deuterium adsorption–desorption would result in a degraded surface consisting of a disordered top layer in which the carbon atoms are most probably bonded in an sp² configuration. The degradation phenomenon of the diamond surface by repeated deuterium adsorption–desorption may also be due in part to hydrogen etching. The desorption of hydrogen from the amorphous deuterium/hydrogenated surface [43,44]. It has also been reported that prolonged hydrogenation of a C(100) surface at elevated temperatures would result in etching anisotropy and {111}-oriented facet formation [16]. Whether C(100) surface degradation is due to a thermal effect or etching, these experimental results show how sensitive the surface condition is to hydrogenation, and careful attention has to be paid to the study of the interaction of hydrogen with the C(100) surface. This is also the possible major reason for inconsistent results in previous studies, as summarized and compared in Section 3.2. Complete recovery of the initial
Fig. 3. LEED patterns ($E_p = 164$ eV) and TPD spectra of D$_2$ desorption from various diamond C(100) surfaces. The initial surface conditions for the first, second and third TPD runs (or the TPD spectra of (b), (d) and (f)) are manifested by the LEED patterns shown in (a), (c) and (e), as indicated by the direction of the arrows. The LEED pattern in (a) was taken after 15 cycles of hydrogen adsorption–annealing treatment on the C(100) surface after the TPD run of Fig. 1f. The fitted TPD spectra are also shown in (b), (d) and (f). Note that the time-integrated mass spectrometer signal for each TPD run has been normalized to 1, assuming unity for saturation hydrogen coverage.

LEED pattern is difficult. While insufficient treatment cycles cannot fully smooth the degraded portion of the (2×1) terraces, extensive surface treatment may result in irreversible {111}-oriented facet formation [14]. In this study, it was found that the faceting phenomenon began to appear after about 200 cycles of hydrogenation–annealing. We repeated a series of consecutive deuterium TPD experiments on the as-treated C(100) surface, with the LEED pattern shown in Fig. 3a. The effect of cumulative damage to the surface by hydrogen desorption is again evidenced by LEED measurements, as shown in Fig. 3c and e, which are LEED patterns taken after the first and second deuterium adsorption–desorption cycles. These patterns are presented to show the initial surface conditions for the TPD spectra which will be presented and discussed in Section 3.2.

3.2. Temperature programmed desorption

Temperature-programmed desorption (TPD) was performed to elucidate the kinetics of hydrogen desorption from the C(100) surface, which has been investigated by several research groups [15,26,27,41]. However, a consistent conclusion has not yet been reached. This is obviously due to the inherent instability of the C(100) surface giving rise to inconsistent surface conditions in these previous studies. Our LEED results (Section 3.1) showed that the C(100)-(2×1) surface structure is extremely sensitive to the hydrogen
adsorption–thermal desorption process. In this section, the effect of the initial surface condition on the hydrogen adsorption and desorption kinetics will be explored and discussed.

At the beginning of each TPD experiment, the surface was exposed to 3000 L of D2 to ensure saturation coverage. D2 was the only detectable desorption product from the deuterated C(100) surface within the detection limit of the quadrupole mass spectrometer. However, the surface degradation and H-etching effect (Section 3.1) indicated that the desorption of hydrocarbon species should take place concurrently. Prior to most TPD cycles, the deuterated surface was annealed at 1030 K for 1 min. The main purpose of the surface pretreatment was to minimize background desorption from both the sample assembly and defect sites to improve the signal-to-background ratio. Hydrogen desorption from molybdenum and other metal substrates normally occurs at about 500–800 K.

Bobrov et al. [45] found that hydrogen desorption from a severely degraded portion of a diamond C(111) surface occurred as broad desorption peaks ranging from 800 to 1110 K. Therefore, with such a pretreatment procedure, we probed only the diamond-like portion of the bonding sites. A typical deuterium desorption spectrum is shown in Fig. 4. Clearly, hydrogen desorption from the C(100) surface displays a broad feature in the temperature range 1000–1400 K. The large background rising at the end of each spectrum is attributed to deuterium desorption from the sample assembly and the low pumping speed in the differentially pumped QMS chamber. It was noticed that the whole sample support was indirectly heated at such high temperatures. The background for all the TPD curves could be fitted by a single exponential function, which was then removed from the experimental raw data. Both the raw data and the resultant curve after background subtraction are displayed in Fig. 4. Some uncertainty in the background fitting was introduced by the arbitrary assignment of the limits of the desorption peak.

The dotted curves in Fig. 1b, d and f show a series of TPD spectra obtained from H-plasma treated and degraded diamond surfaces exposed to a saturation coverage of D atoms using a heating rate of 5 K s⁻¹. The absolute hydrogen coverage after saturation is assumed to be one monolayer. It should be emphasized that Fig. 1b was the very first TPD spectrum from the hydrogen-plasma treated C(100) surface. It can be seen that deuterium desorption from the well-defined C(100) surface shows a peak at 1260 K (Tmain, α) with a shoulder at 1170 K (Tshoulder, β).

The second and the third TPD curves, as shown in Fig. 1d and f reveal that the intensity of the high-temperature peak (α channel) decreases while the intensity of the low-temperature shoulder (β channel) increases. The surface condition was monitored by LEED measurements between TPD cycles. The initial surface conditions for the first, second and third TPD runs (or the TPD spectra of Fig. 1b, d and f) are manifested by the LEED patterns shown in Fig. 1a, c and e, as indicated by the direction of the arrows. Clearly, the α state is gradually replaced by the β state as the half-order spot intensity fades away. This occurred even for only a few TPD cycles. Hoffman et al. intentionally destroyed the C(100) surface by electron irradiation and several deuterium adsorption–desorption cycles. TPD study of such a severely degraded C(100) surface showed that the main desorption peak appeared at 983 K, while at 1188 K only a shoulder was observed. The result in this work...
should be compared with other work on the thermal desorption of D₂ from the C(100) surface [15, 26, 27, 41]. The deuterium desorption temperature, the sample heating rate, the surface cleaning methods and the kinetic parameters obtained from each of the TPD studies found in the literature are summarized in Table 1. The result of this work for a well-defined C(100) surface is in reasonable agreement with that of Yang et al. [15] using the same heating rate (1250 K (T_{\text{main}}) and 1125 K (T_{\text{shoulder}})), and with those of Hoffmann et al. [41] at a heating rate of 35 K s⁻¹ (1188 K (T_{\text{main}}) and 983 K (T_{\text{shoulder}})). However, it deviates from those of Thomas et al. [26] (1175–1200 K, heating rate 20 K s⁻¹, single peak) and from those of Hamza et al. [27] (1200 K, T_{\text{peak}} at low coverage (heating rate of 6 K s⁻¹, single peak). The major discrepancies between these studies are: (i) the peak temperature variation, which is possibly due to thermal contact between the diamond crystal and the sample holder, and (ii) the difference in the number of desorption peaks assigned, which is probably due to the vastly distinct initial surface conditions controlling the kinetics of hydrogen adsorption/desorption on the C(100) surface in a very sensitive manner, as discussed throughout this article.

After the C(100) surface was destroyed by deuterium adsorption/desorption, the surface treatment procedure developed in this laboratory (Section 2) was applied in order to recover the surface smoothness or (2×1) domains on the C(100) surface. After 15 treatment cycles on the previously degraded C(100) surface, the LEED pattern of Fig. 3a was obtained. Fig. 3 also shows the results for the following consecutive TPD experiments on the as-treated C(100) surface. The initial surface conditions for the first, second and third TPD runs (or the TPD spectra of Fig. 3b, d and f) correspond to LEED pattern shown in Fig. 3a, c and e, as indicated by the direction of the arrows. The same conclusion as above can be drawn for this series of TPD experiments, i.e. there is a strong correlation between the surface order and the intensity ratio of the two desorption peaks. It is also evident that only the TPD peak at the higher temperature results from desorption from the (2×1) domains (z sites). Yang et al. [15] assigned the asymmetrically shaped peak centered at 1250 K which is characteristic of first-order desorption kinetics to monohydride desorption [15]. For first-order desorption kinetics, the peak temperature is independent of the initial deuterium coverage. As demonstrated in our study, hydrogen desorption from the C(100) surface is very sensitive to the initial surface condition, and it is extremely difficult to achieve the same initial conditions for C(100) surfaces by any surface preparation method. Therefore, we have not yet been able to establish the dependence of the peak temperature on the deuterium coverage.

One intriguing and undetermined feature in Yang’s TPD spectrum is the desorption shoulder.

### Table 1: Comparison of TPD results, extracted kinetic parameters and experimental conditions for deuterium desorption from a well-defined C(100)-(2×1) surface

<table>
<thead>
<tr>
<th>Source</th>
<th>Peak temperature (K)</th>
<th>Heating rate (K s⁻¹)</th>
<th>Sample preparation</th>
<th>In situ</th>
<th>Kinetic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Primary</td>
<td>Shoulder</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[27]</td>
<td>1200</td>
<td>–</td>
<td>6 Polish with DP in olive oil</td>
<td>Heat stepwise to 1300 K</td>
<td>First order, n = 3 × 10⁵ s⁻¹, E_a = 37 kcal mol⁻¹</td>
</tr>
<tr>
<td>[15]</td>
<td>1250</td>
<td>1125</td>
<td>5 Polish with DP in olive oil</td>
<td>Heat up to 1400 K</td>
<td>First order, n = 10⁵ s⁻¹, E_a = 79.5 kcal mol⁻¹</td>
</tr>
<tr>
<td>[26]</td>
<td>1175–2000</td>
<td>–</td>
<td>20 Polish with DP in DI water and organic solvents</td>
<td>Heat stepwise to 1423 K (10 K s⁻¹)</td>
<td>First order, n = 10⁵ s⁻¹, E_a = 72.7 kcal mol⁻¹</td>
</tr>
<tr>
<td>[41]</td>
<td>1188</td>
<td>983</td>
<td>35 Acid–hydrogen H plasma</td>
<td>–</td>
<td>First order, n = 4 × 10⁻¹ s⁻¹, E_a = 80.3 kcal mol⁻¹</td>
</tr>
<tr>
<td>This work</td>
<td>1200</td>
<td>1170</td>
<td>5 Acid–organic solvent → microwave H plasma</td>
<td>–</td>
<td>First order, n = 10⁵ s⁻¹, E_a = 71 kcal mol⁻¹</td>
</tr>
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This work: Microwave H plasma
at the lower temperature. From the detailed study presented here, the desorption from this shoulder ($\beta$ channel) appears to be real. As a matter of fact, a two-peak assignment for the preannealed surface is further supported by the computer simulation presented in Section 3.3. The $\beta$ peak is tentatively assigned to desorption from dihydride species bonded in the disordered portion of the C(100) terraces, i.e. the domain boundaries ($\beta$ sites). Hydrogen desorption from $\beta$ sites was observed (even in small amounts) in the very first TPD run on the H-plasma treated surface which possessed atomically flat domains larger than 300 Å, as indicated by an LEED pattern (Fig. 1a) as good as that of Thoms et al. [11]. Therefore, the $\beta$ sites are considered to exist inherently in the domain boundaries of the C(100)-(2×1) terraces. Moreover, desorption from steps or defect sites should appear in an even lower temperature region, as discussed below. Further evidence for the $\beta$ site assignment is that AES (Fig. 5) showed the absence of the characteristic graphitic feature at 250 eV [32] even for the “degraded” surface shown in Fig. 3e. In other words, the degraded surface still remains pretty much diamond-like. This assignment is not unreasonable because of the less steric hindrance for dihydride formation on these surface sites. In fact, careful HREELS measurements were performed in order to detect any CH$_2$ groups on the hydrogenated C(100) surface. No significant difference could be observed in HREELS before and after surface degradation. The characteristic vibrational frequencies for CH$_2$ scissor (≈140 meV) [46] and stretching (≈370 meV) modes [17] are expected to be close to those for CH bending (≈151 meV) and stretching (≈365 meV).

Our spectral resolution was about 16-20 meV, and therefore CH$_2$, if present, probably could not be detected in this study. Since it is impossible to determine the exact hydrogenated structure of the degraded C(100) surface in our study, the existence of other possible hydrocarbon species (CH$_x$) on the C(100) surface cannot be completely ruled out. Nevertheless, the CH$_2$ groups have been observed to locate at either the unreconstructed C(100)-(1×1) island surface or step sites by Sato et al. [17] from vibrational sum-frequency generation (VSFG) experiments on a homoepitaxially grown diamond C(100) surface [17]. Therefore, the adsorbed species on the domain boundaries could be mainly dihydrides, based on the VSFG results. Incidentally, similarly to the case of the H/Si(100)-(2×1) surface, hydrogen desorption from the dihydride phase is about 100 K lower in temperature than from the monohydride phase [47].

One of the important steps prior to the TPD experiment was to anneal the deuterated C(100) surface at 1030 K for 1 min. The purpose of this pretreatment was to remove the uninteresting deuterium desorption feature which might hamper the analysis of the TPD spectra. This unwanted feature includes thermal desorption from the sample holder, steps, edges, and any graphitic carbon component. However, it might also cause the rearrangement of adsorbed D on surface sites during annealing. To examine the redistribution of chemisorbed deuterium between $a$, $\beta$ and other adsorption sites, TPD experiments were carried out without any preannealing procedure. Fig. 6b shows the TPD spectrum of D$_2$ desorption from the C(100) surface without preannealing. The initial surface condition was represented by the LEED pattern shown in Fig. 6a. Since this was the first TPD run after the hydrogen surface treatment, the half-order spots were clear and the TPD
spectrum was mainly dominated by the $\alpha$ peak. Nevertheless, an obvious shoulder still appears. This is consistent with the previous finding for annealed surfaces, and hence no obvious site redistribution effect is concluded. It can be seen that the shoulder shifts by $\sim 40$ K to a lower temperature, which might be due to the existence of a third desorption peak ($\gamma$ channel) broadening the leading edge of the TPD spectrum. Indeed, a third peak has to be included at a lower temperature in order to obtain the best fit to the original experimental curve, as shown in Section 3.3. As a matter of fact, the population of the $\gamma$ site deduced from the fitting (Section 3.3) remains almost constant (5–10\%) for both the well-defined and the degraded surface, while the populations of $\alpha$ and $\beta$ change significantly. Thus, the $\gamma$ peak might correspond to the desorption of deuterium bonded at defect sites or steps, which normally have a lower binding energy, as reported by Su et al. [2].

In this set of experiments, no surface pretreatment was performed, and hence deuterium desorption from the $\beta$ sites and $\gamma$ sites was combined. Combined desorption from multiple sites will lower the apparent activation energy for a higher desorption energy peak, as one might expect. In particular, when the concentrations of individual sites are comparable to each other, as in the case of the TPD run in Fig. 6b, the multiple site effect is more apparent.

Normally, the thermal desorption of deuterium from the C(100) surface after about five or six TPD runs exhibits a single desorption peak, as shown in Fig. 7. A similar broad and symmetric peak from 1000 to 1450 K centered around 1170–1200 K was also observed by Thomas et al. [20]. Such a TPD spectrum could be reproduced on the degraded C(100) surface with truly vague half-order spots.

**Fig. 6.** (a) LEED pattern ($E_p = 164$ eV) taken after 11 cycles of hydrogen adsorption–annealing treatment on the C(100) surface after the TPD run of Fig. 3f. (b) TPD spectrum of D$_2$ desorption from a C(100) surface with the initial condition shown in (a). Also shown are the fitted TPD spectra. The dotted curve was obtained by subtracting from the original TPD curve the background signal from the metallic sample assembly, which is normally the lower temperature range. Note that the time-integrated mass spectrometer signal for each TPD run has been normalized to 1, assuming unity for saturation hydrogen coverage.

**Fig. 7.** TPD spectrum of deuterium desorption from the C(100) surface conditioned after six hydrogen adsorption–desorption cycles.
3.3. Kinetic parameters extracted from the TPD spectra

Temperature-programmed desorption (TPD) was performed to obtain kinetic information on hydrogen desorption from the C(100) surface. Most previous work in analyzing TPD spectra was based on Redhead’s method [48], in which a general relationship between the maximum desorption temperature, the linear heating rate, the activation energy \((E)\) and the prefactor \((v)\) was established by solving the desorption rate equation. A value of \(v\) (usually \(10^{18} \text{s}^{-1}\)) was assumed in order to calculate the activation energy for each desorption peak. This was somewhat problematic because of the compensation effect between \(E\) and \(v\), which can give an incorrect desorption energy if the value of the prefactor is not properly chosen.

In this work, the TPD spectra were analyzed by computer simulation of the desorption profile for the multiple-site desorption pathway. The result yields valuable kinetic information \((E, v\) and desorption order\) for hydrogen desorption from the C(100) surface under different initial surface conditions.

We begin by defining the model system. \((2 \times 1)\) LEED patterns with clear or diffuse spots and near-\((1 \times 1)\) patterns with bright fuzzy background were observed on the clean and H-dosed C(100) surfaces, respectively, at different experimental stages of this study. The correlation between the TPD curves and the LEED patterns implies that the high-temperature desorption peak \((\beta)\) can be attributed to domain boundaries. The subsequent simulations were therefore made on the basis of desorption from these two surface components. For those TPD spectra without preannealing, deuterium chemisorbed at step or defect sites \((\gamma)\) was also included.

The general features of the desorption of surface adsorbates can be expressed in an Arrhenius form

\[
\text{Rate} = -\frac{d\theta}{dt} = v\theta^a \exp(-E/kT), \tag{1}
\]

where \(\theta\) is the fractional surface coverage, \(T\) is the sample temperature, and \(a\) is the desorption order (usually \(a=1\) or 2). Since the desorption rates in our TPD spectra contain contributions from multiple binding sites, the overall rate via these desorption channels is therefore given by

\[
\text{Rate} = v_1\theta_1^a \exp(-E_1/kT) + v_2\theta_2^b \exp(-E_2/kT), \tag{2}
\]

where the subscripts \(x\) and \(\beta\) refer to the \(x\) state and the \(\beta\) site, respectively, on the C(100) surface. It is assumed that the reaction order, \(E\) and \(v\) are independent of the surface temperature and coverage. We have tested different desorption orders for the \(\alpha\) and \(\beta\) sites, and conclude that the best choice for modeling the experimental TPD curves is to combine a first-order process for the \(x\) state and second-order kinetics for \(\beta\) state. First-order kinetics for deuterium desorption from the C(100) surface is supported by the asymmetric peak shape, with the high-temperature side of the peak sloped more steeply. This feature is particularly distinguishable for the first TPD run after hydrogen plasma treatment or cycles of hydrogen adsorption/desorption on the C(100) surface. Although first-order kinetics is not intuitively recommended for recombinative molecular desorption, it has been found to occur on metal surfaces and other covalently bonded semiconductor surfaces [47,49,50]. To produce the simulated TPD spectra using this model, the surface coverage is first evaluated as a function of the surface temperature by integrating Eq. (2) using a linear function for the temperature sweep.

\[
\int_{T_0}^{T_f} \frac{dT}{T} = \frac{\theta(T_f)}{\theta(T_0)} \Rightarrow \frac{T_f}{T_0} = \int_{\theta_0}^{\theta_f} \frac{d\theta}{\theta^a} = \left[ \frac{\theta^{1-a}}{1-a} \right]_{\theta_0}^{\theta_f} = \ln(\theta_f/\theta_0) \quad \text{for } n=1, \tag{1}
\]

\[
\int_{T_0}^{T_f} \frac{dT}{T} = \frac{\theta(T_f)}{\theta(T_0)} \Rightarrow \frac{T_f}{T_0} = \int_{\theta_0}^{\theta_f} \frac{d\theta}{\theta^2} = \left[ \frac{\theta^{-1}}{-1} \right]_{\theta_0}^{\theta_f} = \theta_f^{-1} - \theta_0^{-1} \quad \text{for } n=2,
\]

where \(\eta\) is the sample heating rate, \(\theta_0\) is the initial coverage, and \(\theta_f\) is the coverage at temperature \(T_f\). By substituting the integrated coverage varia-
tion as a function of the surface temperature into Eq. (2), an equation describing the shape of the desorption rate curve can be obtained. The TPD spectra for deuterium desorption from C(100) surfaces were simulated numerically using Eq. (2) with \( n_a = 1 \) and \( n_b = 2 \). Adjustment of the parameters to give the best fits to the experimental TPD curves provides an insight into the kinetics of hydrogen desorption from both well-defined and degraded C(100) surfaces, and hence yields the best and consistent values for the kinetic parameters.

The solid lines in Fig. 1b, d and f and in Fig. 3b, d and f show the best-fit results to the experimental TPD spectra of D\(_2\) desorption from the C(100) surface as well as the individual simulated desorption curves for \( x \) and \( y \) desorption channels. The values of the parameters used for the TPD curve fitting were optimized by a trial and error method until best fits were achieved. The best-fit values are listed in Table 2. The averaged desorption energy for the \( x \) site is 80.3 ± 1.3 kcal mol\(^{-1}\) with a prefactor of 1.4 ± 0.9 \times 10^{13}\) s\(^{-1}\), while the averaged desorption energy for the \( y \) site is 75.1 ± 0.5 kcal mol\(^{-1}\) with a prefactor of 2.3 ± 0.9 \times 10^{13}\) s\(^{-1}\) (expressed in first-order units). It can be seen that the values of \( E_a \) and \( v \) for different initial surface conditions are in excellent agreement. The prefactor for \( y \)-site desorption can be converted to standard units by dividing by the absolute hydrogen saturation coverage. The surface carbon density on the C(100) surface is 1.58 \times 10^{15}\) atoms cm\(^{-2}\). The hydrogen saturation coverage has been determined by several research groups.

Thoms et al. [51] determined \( \theta \) on poly-crystalline diamond using HREELS, and verified that \( \theta = 0.95 \). Koleske et al. [52] obtained \( \theta = 0.96 \) by employing Na\(^{+}\) ion beams to probe the same surfaces. Recently, Chin et al. [53] used SFG to study H adsorption/abstraction on the single-crystal C(111) surface, and a maximum coverage of \( \theta = 0.83 \) was determined at room temperature. If we take the averaged value of \( \theta = 0.90 \) from all these measurements, the saturation coverage for hydrogen on the C(100) surface would be equal to 1.42 \times 10^{15}\) atoms cm\(^{-2}\), and a prefactor of \( v = 1.6 \pm 0.6 \times 10^{13}\) cm\(^2\) s\(^{-1}\) is thus obtained.

Once the best fits were achieved for the experimental TPD curves with different initial surface conditions, the composition of these two surface components on the C(100) surface were obtained. As expected, the initial coverage \( (\theta_{0,x}) \) of dihydride species in the \( y \) site increases with decreasing initial coverage \( (\theta_{0,x}) \) of the \( x \) site as degradation proceeds. The same method was applied to the TPD spectrum without preannealing the sample, and the results are shown in Fig. 6b. It should be pointed out that the peak temperatures and the extracted kinetic parameters for the \( x \) and \( y \) sites from the preannealed surfaces were found to be consistent with those from surfaces without the preannealing treatment.

The apparent activation barrier of 80.3 kcal mol\(^{-1}\) for hydrogen desorption from the \( x \) site or from the C(100)-(2 × 1) domains is somewhat lower than the upper limit of the reaction endothermicity (88 kcal mol\(^{-1}\)), which is equal to the difference in bond energy between two C–H bonds and one H–H bond. This number is, however, higher than the theoretical prediction of

<table>
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<th>Run no.</th>
<th>( t_1 ) (ML)</th>
<th>( v_x ) (10^{13}) (s(^{-1}))</th>
<th>( E_a ) (kcal mol(^{-1}))</th>
<th>( t_2 ) (ML)</th>
<th>( v_y ) (10^{13}) (s(^{-1}))</th>
<th>( E_{xy} ) (kcal mol(^{-1}))</th>
</tr>
</thead>
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<tr>
<td>1(b) first</td>
<td>0.97</td>
<td>1.0</td>
<td>80.6</td>
<td>0.13</td>
<td>1.2</td>
<td>75.0</td>
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<td>0.57</td>
<td>2.0</td>
<td>81.6</td>
<td>0.43</td>
<td>3.8</td>
<td>75.5</td>
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<tr>
<td>1(f) third</td>
<td>0.35</td>
<td>3.0</td>
<td>82.0</td>
<td>0.65</td>
<td>3.0</td>
<td>75.8</td>
</tr>
<tr>
<td>3(b) first</td>
<td>0.47</td>
<td>0.8</td>
<td>79.6</td>
<td>0.53</td>
<td>2.0</td>
<td>74.5</td>
</tr>
<tr>
<td>3(d) second</td>
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<td>0.8</td>
<td>79.0</td>
<td>0.69</td>
<td>2.0</td>
<td>75.0</td>
</tr>
<tr>
<td>3(f) third</td>
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<td>0.8</td>
<td>79.0</td>
<td>0.80</td>
<td>2.0</td>
<td>75.0</td>
</tr>
</tbody>
</table>

\( t_1 \) is the averaged value for \( v_x \) is 1.4 ± 0.9 \times 10^{13}\) s\(^{-1}\), for \( E_{xy} \) it is 80.3 ± 1.3 kcal mol\(^{-1}\), for \( v_y \) it is 2.3 ± 0.9 \times 10^{13}\) s\(^{-1}\), and for \( E_{xy} \) it is 75.1 ± 0.5 kcal mol\(^{-1}\).
67–72 kcal mol$^{-1}$ determined by ab initio calculations [54] and by empirical bond-order analysis [1] in which $\pi$-bonding formation is included. It implies that there a barrier probably exists to H chemisorption from gas-phase $\text{H}_2$. Nevertheless, the activation barrier measured for the C(100) surface is slightly lower than the desorption energy of 85.1 kcal mol$^{-1}$ for hydrogen desorption from the C(111) surface [2]. Indeed, the surface structure is expected to have a significant effect on the degree of $\pi$-bond formation between carbon atoms on the surface. The hydrogen-terminated C(100) surface has a similar structure to the hydrogen-free C(100) surface, with a slight difference in the bond distance of the C-C dimer. For the C(111) surface, there is a great structural difference between the hydrogen-terminated C(111)-(1 $\times$ 1) surface and the bare C(111)-(2 $\times$ 1) surface. Therefore, $\pi$-bonding would be expected to occur more facilely on the C(100) surface, and in turn the energy barrier for hydrogen desorption should be lower than that on the C(111) surface.

The results presented above reveal first-order kinetics for hydrogen desorption from the C(100)-(2 $\times$ 1) domains. Since a unity order for hydrogen desorption from Si(100)-(2 $\times$ 1) and Ge(100)-(2 $\times$ 1) has also been observed, it is possible that there is a similar mechanism for the recombinative hydrogen desorption process from these covalently bonded semiconductor surfaces. The Si(100) surface is the most thoroughly studied system. Past studies of hydrogen desorption from the Si(100) surface have been reviewed in several publications [2,55]. Several possible mechanisms proposed to explain the first-order kinetics are briefly summarized here: the preparation mechanism [56], the generalized Eley–Rideal (ER) mechanism [47,57], the defect diffusion mechanism [58], the isomerization mechanism [59] and the H-atom diffusion mechanism [60]. Due to the similar structures for various possible dimer species on the C(100) surface (C–C, HC–C, and HC–CH), one would probably expect a random distribution for hydrogen chemisorbed on the C(100) surface. However, Hukka et al. [22] investigated the issue of the structure and energetics of hydrogen atoms on the dimer-reconstructed C(100)-(2 $\times$ 1) surface. It was found that the calculated $\pi$ bond energy provides a substantial driving force for the preferential pairing of surface hydrogen atoms and dangling bonds separately on dimers on the C(100)-(2 $\times$ 1) surface. Just as in the case of $\text{H}_2$/Si(100)-(2 $\times$ 1), even at the desorption temperature, equilibrium distributions might favor doubly occupied dimers, and hence the nearby hydrogen atoms would desorb concertedy. The preparation mechanism, with some modifications (domain formation), has been used to explain first-order kinetics for hydrogen desorption from the C(111) surface [2].

For the generalized ER mechanism, a hydrogen adatom is assumed to be irreversibly excited into a delocalized band state ($\text{H}^*$) and then reacts with a localized atom to produce molecular hydrogen. This two-step mechanism explains the first-order kinetics and reconciles with a significantly low measured activation energy (45 kcal mol$^{-1}$) for the reaction endothermcity of $\sim$75 kcal mol$^{-1}$. This mechanism can be considered as an alternative model for first-order kinetics, since hydrogen desorption from both the C(100) and C(111) surfaces presents the same reaction order. However, the measured activation energy for the H/C(100)-(2 $\times$ 1) system ($\sim$80 kcal mol$^{-1}$) is higher than the reaction endothermicity ($\sim$67–72 kcal mol$^{-1}$). If the delocalized band state does exist in the hydrogenated C(100)-(2 $\times$ 1) surface, the energy of the $\text{H}^*$ state relative to the chemisorbed C-H bond energy should be at least equal to 80 kcal mol$^{-1}$. Considering that the empirical bond energy of Si–H ($\sim$90 kcal mol$^{-1}$) is only slightly weaker than that of C–H ($\sim$104 kcal mol$^{-1}$), there is no obvious reason why the $\text{H}^*$ state in the silicon surface should be so much lower energetically than in the diamond surface.

The above three mechanisms are based on theoretical modeling and calculations, and involve the formation of the dihydride-like transition state from which the molecular hydrogen desorbs. These three mechanisms have been thoughtfully discussed and critically compared with the experimental results from the Si(100) and Ge(100) surfaces by Janda et al. [50]. While we cannot totally rule out any of these possibilities, it would be very interes-
ting to investigate theoretically the H/Si(100)-(2 \times 1) system.

At high hydrogen coverages, the Si(100) surface is dominated by a dihydride species which, however, has been shown to be highly unstable (Section 2) in the C(100)-(2 \times 1) surface. In our experiment, the LEED pattern of a good C(100) surface exhibited a (2 \times 1) structure, even at hydrogen exposures up to 3000 L. The (1 \times 1) pattern with very high background showed up only after the surface was totally destroyed by a number of hydrogen adsorption/desorption cycles. If the (1 \times 1) pattern represents the structure which can accommodate the dihydride phase, the possible bonding sites for the dihydride species are the diamond-like domain boundaries. If hydrogen desorption from the C(100)-(2 \times 1) domains is via a dihydride phase, it is at most the dihydride-like transition state, as in the isomerization mechanism. As the (2 \times 1) domains shrink or break into smaller domains, domain boundaries as well as the dihydride concentration is expected to increase. From our TPD simulation, hydrogen desorption from such a possible dihydride species shows second-order kinetics. The desorption of hydrogen molecules from the dihydride phase on the Si(100) surface was also found to be a second-order process. The mechanisms proposed for second-order kinetics are the recombinative desorption of two hydrogen atoms from adjacent silicon dihydride species (1,2 elimination) and the self-associated desorption of two hydrogen atoms on a single silicon atom (1,1 elimination) [61]. In the model proposed by Flowers et al., the chemical processes involving atomic hydrogen chemisorbed on the Si(100)-(2 \times 1) surface are governed by the “equilibria” existing between various surface dimer species and silicon dihydride [61]. This, however, may not be the case in the C(100) surface. Due to the fact that unstable dihydrides cannot exist on the C(100)-(2 \times 1) domains, no equilibria are expected to be established. Hence, the surface is tentatively assumed to be constituted by two basic components: (i) hydrogenated (2 \times 1) domains (\(x\) sites) which are purely in the monohydride phase, and (ii) disordered but still diamond-like domain boundaries (\(\beta\) sites) in which dihydride species exist. While monohydride desorption from the \(x\) state follows first-order kinetics, dihydride desorption from the \(\beta\) state exhibits a second-order process. The proposed model thus yields a consistent interpretation of the present experimental data.

Finally, the exact conditions giving rise to the surface degradation remain elusive. Whether the surface degradation is caused by the high surface temperature and/or the absence of surface hydrogen will clearly require more experimental and theoretical work.

4. Conclusions

In summary, the kinetics of hydrogen desorption from the diamond C(100) surface has been determined by TPD. On the well-ordered C(100) surface, the TPD spectra are dominated by hydrogen desorption from (2 \times 1) domains (\(x\) sites), while on the degraded C(100) surface hydrogen desorption from the disordered domain boundaries (\(\beta\) sites) becomes more significant. As hydrogen adsorption/desorption results in surface degradation, the ratio of \(x\) site concentration to \(\beta\) site concentration, which correlates with the intensity ratio of two desorption peaks, decreases after repeated TPD cycles. The degradation leads to smaller (2 \times 1) domains, as evidenced by the deteriorated LEED patterns in which the characteristic (2 \times 1) half-order spots disappear. Fitting the experimental TPD data with the simulated curves from the above two-site model shows that desorption from the \(x\) sites obeys first-order kinetics with a prefactor of \(1.4 \pm 0.9 \times 10^{13} \text{s}^{-1}\) and an activation energy of \(80.3 \pm 1.3 \text{kcal mol}^{-1}\), whereas the process giving rise to the \(\beta\) peak follows second-order kinetics with a prefactor of \(2.3 \pm 0.9 \times 10^{13} \text{s}^{-1}\) and an activation energy of \(75.1 \pm 0.5 \text{kcal mol}^{-1}\). The mechanism for the surface degradation is not clear, but the intensity of the half-order spots or corresponding (2 \times 1) domains on the diamond C(100) surface can be recovered readily in situ by repeated hydrogen adsorption-annealing treatments without the use of any complicated techniques.
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