Hydrogen chemisorption and thermal desorption on the diamond C(111) surface

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Temperature programmed desorption (TPD) and low energy electron diffraction (LEED) were utilized to study the interaction of atomic hydrogen with single crystal diamond C(111) surface. From isotherm and isostere analysis of TPD spectra acquired at various sample heating rates ranging from 0.6 K/s to 30 K/s, the kinetic parameters were extracted. It is found that molecular hydrogen desorption from the C(111) surface exhibits the first-order kinetics. This result is confirmed by no apparent shift in peak temperatures of TPD spectra for hydrogen coverage above 0.2 ML. At lower coverage regime, the isothermal desorption experiment also indicates the first-order desorption kinetics. A nearly coverage-independent activation energy of $(3.7 \pm 0.1)$ eV and a prefactor of $(9.5 \pm 4.0) \times 10^{13}$ s$^{-1}$ are obtained except at relatively low coverages (below $0.2$ ML). In addition, the half-order LEED spots intensity decreases linearly with increase of the hydrogen coverage and drops to zero at $0.5$ ML. These results are interpreted with a model that during adsorption hydrogen atoms segregate to form metastable, highly hydrogenated domains from where hydrogen atoms recombine and desorb concertedally as the substrate surface is heated up. The comparison of this work with the hydrogen adsorption and desorption on silicon surfaces is also discussed. © 1997 American Institute of Physics. [S0021-9606(97)03342-4]

I. INTRODUCTION

Diamond is one of the most important materials in industry. Because of its many outstanding physical and chemical properties, such as high thermal conductivity, extreme hardness, high transparency for ultraviolet-infrared (UV-IR) radiation, chemical inertness, and low friction coefficient, it has been a very useful material for various technological applications. Chemical vapor deposition (CVD) has been widely used for making diamond thin films because of the active chemical interactions between the feed gas and the substrate surfaces. In this process, in addition to hydrocarbons (C$_x$H$_y$) which are the source species for the C, H atom is also an important ingredient from the point of view of quality control. It is believed that H atoms not only can preferentially etch away graphite component and assure the smoothness of diamond surfaces, they can also terminate the surface C atoms to maintain the $sp^3$ hybridization so that graphite formation can be prevented. On the other hand, gas phase H atoms can abstract top layer H atoms and open the available sites for C addition to the lattice. Diamond growth sites also can be created by thermal desorption of H atoms. Therefore, the flux of H atoms and the H surface coverage critically affect the diamond growth process. Consequently, the interaction between H and diamond surfaces becomes an important issue for both diamond technology and surface science study.

Many theoretical and experimental works have been performed in the reaction of H with diamond surfaces by using various methods. For H adsorption on diamond surfaces, the vibrational spectroscopic techniques such as electron energy loss spectroscopy (EELS), infrared spectroscopy (IR), sum frequency generation spectroscopy (SFG), and second-harmonic generation (SHG) have been employed to yield valuable information about surface species as well as their bonding geometry on the surfaces. Theoretically, the normal mode analyses and molecular dynamic calculations have provided the
features of surface vibrational spectra and possible surface structures. For hydrogen desorption from diamond surfaces, temperature programmed desorption (TPD)\textsuperscript{30–37} and isothermal desorption\textsuperscript{58,39} have been performed. In spite of these efforts and the abundant phenomenological reports for the hydrogen-assisted diamond CVD process, a basic understanding of chemical interactions between hydrogen and diamond surfaces, in particular, the low index diamond faces, still remains elusive.

The diamond C(111) surface is one of the principal faces along which diamond films have been grown. The interaction of atomic hydrogen with the C(111) surface is the subject of the present study. The ideal bulk-terminated C(111) surface has a $(1 \times 1)$ structure with only one dangling bond on each top layer C atom. However, the bare C(111)-(1 $\times$ 1) surface is unstable and is able to reconstruct to form a $(2 \times 1)$ structure. Molecular dynamic calculations by Brenner\textsuperscript{12} and Far-lori et al.\textsuperscript{42} predict that the $\pi$-bonded chain reconstruction as proposed initially by Pandey\textsuperscript{43} is the most stable structure on the bare diamond (111) surface which shows $(2 \times 1)$ configuration. The most direct support for the $\pi$-bonded chain structure of the clean C(111) surface comes from the ion scattering study by Derry et al.\textsuperscript{40} and the dynamical low energy electron diffraction (LEED) work of Sowa et al.\textsuperscript{41} Upon hydrogen adsorption, a bulk-truncated surface with $(1 \times 1)$ configuration is more stable than the $(2 \times 1)$ reconstruction.\textsuperscript{12,14} Both crystallographic patterns are easily distinguished by LEED technique.\textsuperscript{44–46} The study of hydrogen-diamond interaction by high resolution electron energy loss spectroscopy (HREELS) also indicates that the vibrational mode characteristic of the as-polished C(111)-(1 $\times$ 1) surface reappears when the reconstructed $(2 \times 1)$ surface is exposed to atomic hydrogen.\textsuperscript{44} Moreover, sum frequency generation (SFG) experiment\textsuperscript{25} has shown the complete disappearance of surface phonon peak representative of $(2 \times 1)$ features when atomic hydrogen is exposed onto the $(2 \times 1)$ reconstructed surface. Based on these results, it is clear that in addition to chemical effects, the influence of the adsorbate on the surface structure is an important issue in hydrogen–diamond interaction.

During the course of this study, some other works on the thermal desorption of H$_2$ from the C(111) surface have been published.\textsuperscript{27,47} Here, we report more detailed studies of the interaction of atomic hydrogen with the diamond C(111) surface mainly using TPD and LEED among other techniques. Section II describes the experimental apparatus and sample preparation which is one of the major challenge in the study of low index diamond plane. Section III presents experimental results for the adsorption and thermal desorption of hydrogen on the C(111) surface, and how kinetic parameters for hydrogen desorption can be derived. To explain the unusual hydrogen desorption behavior from the C(111) surface, a novel model which is consistent with both experimental LEED and SFG data are proposed and discussed in Sec. IV.
time. The deuterium coverage described here is the relative coverage assuming that the saturation coverage is equal to 1 ML. We note that in prior studies, the saturation H coverage has been estimated to be around 0.83–0.95 ML. During hydrogenation the filaments were sheltered by a tantalum cover to minimize the adsorption of atomic hydrogen on sample assembly other than the diamond surface. Prior to hydrogenation, the Ta-cover was thoroughly outgassed by electron beam (EB) heating. In this way, the background signal during the desorption process was greatly reduced. This background minimization is crucial in this experiment since the hydrogen desorption from diamond surface occurs at temperature above 1200 K. Under this high temperature condition, the entire sample holder assembly was heated up as well. Nevertheless, a significant amount of D₂ molecules desorbing from sample holder was still detected by QMS. This spurious signal could be removed by preheating the crystal at the temperature just below the onset of D₂ desorption temperature for 1 min. As temperature was raised beyond 1400 K, a small amount of D₂ desorption still appeared as high temperature background which could be removed by a linear function. This linear subtraction is appropriate for such low background spectrum.

In TPD experiments, a differentially pumped QMS was employed to monitor molecules desorbing from the surface. The QMS was situated in a copper tube and separated from the main chamber through a 3 mm diam Mo cone, and pumped with one turbomolecular pump (60 /s) and two small ion pumps (20 /s). During TPD cycles, the C(111) surface was positioned approximately 2 mm from the Mo cone in order to prevent the Mo aperture from being heated up by the radiation from the sample holder. We found that the desorption of D₂ from the Mo aperture would appear as a low temperature shoulder in the real D₂ desorption spectra if the distance between the crystal holder assembly and the Mo cone was too small. This unwanted feature was especially pronounced for TPD cycles with low heating rates.

In quantitative LEED experiments, the patterns at different partial D coverages were acquired and analyzed by a CCD camera/VG SMARTLEED system. In order to achieve the good pattern contrast/resolution, it is necessary to constantly optimize the LEED condition. Additionally, the SMARTLEED software allows us to readjust the contrast of the obtained LEED pattern so that the half-order spots with vague intensity could be displayed more clearly. The advantage of SMARTLEED software is to digitize the spots intensity by integrating the intensity over the spot area. As will be mentioned in Sec. II C, the change of half-order spots intensity can be used to access the progress of the phase transition from the (2×1) to (1×1) surface. Thus, in order to quantitatively compare the coverage-dependent half-order spots intensity, we have integrated the intensity for all observable spots and normalized to that of either the specular beam spot or the primary spot.

**B. Diamond sample assembly and temperature measurement**

The C(111) sample used in this study was a natural, type IIa diamond single crystal (5 mm diam, 0.25 mm thickness, Drukker International) with a typical miscut of less than 3° in orientation. Prior to mounting the diamond on the indirect heating source and the sample holder, the crystal was mechanically polished with 0.25 μm DP-paste, followed by a H₂SO₄-HNO₃(3:1) cleaning at 90 °C, H₂O rinsing and ultrasonic cleaning in acetone and methanol solvents to remove any metallic and graphitic contaminants on the surface. The crystal was then mounted on a 1 mm thick molybdenum (Mo) cup and held by three Mo wires as shown schematically on Fig. 2. The sample assembly was heated by two resistively heated tungsten wires (0.3 mm diam) wedged into a 0.5 mm slot encompassing the side face of Mo cup. Extreme care must be exercised when tungsten wires were wrapped around the Mo cup. Due to the brittle nature of tungsten, it is facile to break apart when extra force is applied. However, it is important to tighten the tungsten wires to assure good thermal contact with Mo cup so that the current used for sample heating at high temperature can be reduced as much as possible. Overheating of tungsten wires may cause tungsten evaporation and, hence, surface contamination. Tantalum is an alternative material for heating wires since it has better flexibility. Hamza et al. has found the significant amount of atomic H (or D) being absorbed into the tantalum clamps which hold the crystal. Therefore, it is generally accepted that Ta is not appropriate material for hydrogen desorption study. The current for the heating of the sample is provided by a programmable power supply under the control of a personal computer. We have developed a 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 is monitored by a W(5% Re)–W(26% Re), C-type thermocouple (TC) spot-welded onto a tiny Pt tab on the back of the Mo holder. The thermocouple temperature readings were confirmed with an optical pyrometer (Optex, Thermo-Hunter, Model VF-1600S @ 5°C, 0.7–1.1 μm wavelength) for temperatures between 900 K and 1500 K. It was found that the temperature readings measured by these two methods were in good agreement (within ±10°C). However, as the emissivity of diamond is nearly zero, the true sample temperature can not be obtained by an optical pyrometer. Thus, in a separate test chamber, we clamped tightly a second pair of C-type TC directly onto the diamond surface to calibrate the temperature readings. We found that the diamond surface temperature could deviate as much as 300 K at 1300 K from that of the Mo holder. Similar observation was reported by Smentkowski et al. To maximize the intimate contact between the sample and Mo cup, two thin layers of 0.001 in. wrinkled platinum (Pt) foils were used as a heat transfer media at the rear of diamond crystal. Thermal desorption of D₂ from a C(100) surface was performed with the same design. It was found that the desorption peak temperature was in excellent agreement with the value obtained by Yang et al. for the same chemisorption system. In their study, Yang et al. performed a very careful temperature calibration by placing a diamond sample in a tubular furnace. AES measurements showed no Pt contamination on the diamond surface even after repeated high temperature heating (up to 1500 K).

The Mo cup was fastened onto two tungsten rods with tungsten heating wires and Mo wires (Fig. 2). The tungsten rods were then clamped to a 1.33 in. copper feedthrough which was in turn attached to the end of a dewar. The dewar itself was mounted on a rotary platform (Thermionic Northwest, Inc. model RNN-150/FA), which in turn was mounted on an XYZ translation stage (VG, model MX200). With such a configuration, the sample temperature could be raised as high as 1700 K. In addition, the sample could be positioned to different focal points of the various surface diagnostic instruments.

C. Diamond surface treatment in UHV

The investigation of the surface structure and reaction on low index diamond planes has been hampered by difficulties in sample preparation. Due to its extreme hardness, a diamond sample is usually difficult to be well polished, and contains significant defect sites. The traditional surface treatment procedure such as Ar⁺ sputtering and high temperature annealing technique cannot be utilized because of the instability of diamond form of carbon which is facilely converted to graphite. Hydrogen microwave plasma etching shows a smoothing effect on the diamond surfaces as evidenced by improved sharpness in the LEED patterns after prolonged etching. Upon surface degradation the diffraction spots in the LEED pattern become more diffuse. Treatment of diamond with atomic hydrogen produced by a hot filament can also produce smooth surfaces. This provides a convenient method to reproduce a good diamond surface for in situ surface study.

In this work, for the C(111) surface, right after the as-polished sample was introduced into the vacuum chamber, a (1×1) LEED pattern with diffuse background was observed. Upon heating to 1500 K to remove surface oxygen as well as adsorbed hydrocarbons, it displayed the vague (2 × 1) pattern with bright background which is the characteristic feature of a not so well-ordered surface after structural reconstruction. Figure 3(a) shows a clear LEED (2 × 1) pattern of the reconstructed surface obtained after prolonged hydrogen etching of C(111) at 1100 K. Improved sharpness and intensity of the half-order spots was evident, indicating an increase in the domain size as etching proceeded. The purpose of surface treatment by hydrogenating the C(111) surface at 1100 K is to etch away the nondiamondlike surface component as well as the rough steps among terraces. Given this treatment procedure, a well-ordered C(111) surface can be prepared repeatedly which allows the surface chemistry and physics to be investigated under a well defined condition. When a bare C(111)-(2 × 1) surface is exposed to...
H(D) atoms at a dosage sufficient to saturate the surface, the structure completely transforms to (1×1) configuration [Fig. 3(b)]. This phase transition between (1×1) and (2	imes1) structures is completely reversible and strongly surface coverage-dependent. The LEED pattern showed little degradation of the diamond surface after at least fifteen repetitive D exposures and the TPD cycles. The degraded surface, when detected, can always be recovered by the treatment procedure mentioned above.

III. RESULTS

The results on the adsorption and desorption of deuterium from the C(111) surface are presented in two parts. First, we present the transformation of surface structure upon D atom adsorption by LEED measurements. Secondly, we describe the kinetics of thermal desorption of D2 from the C(111) surface.

A. Low energy electron diffraction of hydrogenated C(111)

In our study of deuterium adsorption and desorption on the C(111) surface, the experiments was started with a bare (2×1) surface. As mentioned earlier (Sec. II C), exposing the bare C(111) surface to hydrogen atoms can convert the surface structure from (2×1) to (1×1) as indicated by LEED. We have investigated this phase transformation phenomenon in more details by quantitative LEED and established the correlation between the surface structure and the deuterium surface coverage. Each LEED measurement was made with the surface being exposed to a different amount of atomic deuterium, followed by TPD experiment. Hamza et al. observed the electron-stimulated desorption (ESD) of hydrogen from the diamond C(111) surface. Compared to the reported condition used for ESD, this effect is negligible during our LEED measurements.

Typical LEED images for partial D coverages were acquired by a VG SMARTLEED system with the same incident beam energy (E0) of 141 eV. It is observed that the half-order spots intensity fades away gradually as the D surface coverage increases. The half-order spots intensity at different D coverage reveals the different stages of transformation from (2×1) reconstructed surface to the unreconstructed (1×1) surface. Figure 4 depicts the normalized half-order spots intensity (I1/2) as a function of D surface coverage (θ). Obviously, I1/2 declines gradually as θ increases and cuts off at ~0.5 ML.

Mitsuda et al. observed the same phase transition for D adsorption on C(111)-(2×1) from both LEED and optical second harmonic generation (SHG) techniques. In that work, the transition was observed to occur at approximately 5% of the saturation coverage. The discrepancy in the amount of D to cause phase change might be due to the following reasons. First, for LEED measurements, the detection sensitivity in LEED optics as well as the data acquisition method is the major concern. As noticed in the LEED patterns from both studies, the brighter background for partial D coverage on the C(111) surface will interfere with the detection of half-order spots. In the present study, the VG SMARTLEED system in conjunction with a CCD camera allows us to digitize the spots intensity by integrating the area of selected spots and more accurately determine the spots intensity as a function of D coverage. One important feature for digitizing the image is to adjust the image contrast for the acquired LEED pattern so that the half-order spots with vague intensity can still be observed. Second possibility is the different sample preparation procedure. As mentioned in Sec. II C, in order to achieve the best surface condition by removing nondiamondlike surface structure, the “as-installed” diamond surface needs to be treated by prolonged hydrogenation at elevated temperature. The excellent spot profile with low background has assured a better surface to begin with in this study. Other differences in the experimental setup including the construction of the sample holders may also affect the surface coverage measurement which are based primarily on thermal desorption spectra in both studies. Yet, in view of the instability of the (2×1) structure which is easily influenced by surface defect, the difference in the sample treatment in the UHV resulting in the different surface condition is most likely the major reason for such discrepancy of reported values.

The desorption of hydrogen precedes the surface reconstruction back to the (2×1) configuration, indicating that the phase transition between (1×1) and (2×1) structures is reversible. Therefore, an alternative way to observe the LEED pattern under the various partial D coverage is to thermally desorb the hydrogen from a fully saturated D/C(111)-(1×1) surface. We have utilized the heating rate of 10 K/s to heat the fully hydrogenated C(111) surface up to different temperature. When the desired sample temperature is reached, the heating power is turned off right away and leave the C(111)-(1×1) or C(111)-(2×1) surface with partial deuterium coverage. True D coverage is estimated from the
time-integrated TPD spectra (Sec. III B). We have observed the discernible half-order spots even for D coverage up to \( \sim 0.5 \) ML, which agrees well with the results obtained from different D exposure on a freshly made bare C(111)-(2 \( \times \) 1) surface.

Another important observation for the LEED pattern is the appearance of brighter background with increasing D coverage, which implies the structure complication during the phase transformation. Nevertheless, low LEED background is observed as D coverage approaches saturation coverage. The vibrational spectra obtained from the sum-frequency-generation (SFG) technique have provided more insight for the adsorbate-induced phase transition for H chemisorption on the C(111) surface.\(^{27}\) The SFG spectrum for H on a fully relaxed saturated C(111)-(1 \( \times \) 1) surface is dominated by a sharp peak at \( \sim 2830 \) \( \text{cm}^{-1} \) which is identified to be due to the C–H stretch from atomic hydrogen chemisorbed perpendicularly on top sites. For partial coverage, the spectra on a freshly converted, but unrelaxed, C(111)-(1 \( \times \) 1) surface shows a peak at \( \sim 2860 \) \( \text{cm}^{-1} \) with H coverage \( \leq 0.42 \) ML, which can be gradually replaced by the peak at \( \sim 2830 \) \( \text{cm}^{-1} \) by either annealing the crystal or increasing hydrogen coverage to above 0.42 ML. An intermediate metastable (1 \( \times \) 1) surface structure is thus proposed to exist in the adsorbate-induced phase transition of C(111)-(2 \( \times \) 1) to C(111)-(1 \( \times \) 1). If there exists a metastable phase it is apparently not to be identified from our LEED measurements.

Recently, molecular-dynamics simulations of diamond surface annealing together with vibrational spectra calculations yield insight into the pathway of transformation between the (2 \( \times \) 1) \( \pi \)-bonded chain reconstruction and (1 \( \times \) 1) bulk-terminated structure.\(^{28}\) It is suggested that the hydrogen-desorption-induced (1 \( \times \) 1)\( \rightarrow \) (2 \( \times \) 1) phase transition would be mediated by a defect-free intermediate structure. Although the definitive structure for this intermediate state still remains unclear, the brighter background observed in our LEED results may be partially attributed to this metastable state formation. Downsizing of the (2 \( \times \) 1) domains may also contribute to the diffuse background as will be discussed later. More detailed information of hydrogen interaction with the C(111) surface is given by TPD study in next section which provides more insight to the mechanism for both adsorption and desorption of hydrogen on this surface.

**B. Temperature programmed desorption of deuterium from the C(111) surface**

While LEED was utilized to explore the hydrogen adsorption process, the temperature programmed desorption (TPD) was performed to elucidate desorption kinetics and possible desorption products from the hydrogenated diamond C(111) surface. At the beginning of each experiment, the surface was exposed to the D atom for 3000 langmuir [1 langmuir (L) = \( 10^{-6} \) Torr s] of D\(_2\) to ensure the saturation coverage. The heating effect of the radiation from high temperature tungsten filaments (1800 K) results in an increase of surface temperature to \( \sim 500 \) K during the exposure. Within our detection limit of quadrupole mass spectrometer, D\(_2\) is the only detectable desorption product from the deuterated C(111) surface. Prior to each TPD cycle, deuterated surface is annealed at 1030 K for 1 min. This pretreatment procedure can remove background desorption from supports and improve signal to background ratio.\(^{31}\) Bobrov et al. have found that hydrogen desorption from degraded and edge sites of diamond surface occurs as broad desorption peaks ranging from 800 K to 1110 K.\(^{47}\) Pretreatment at 1030 K, therefore, would eliminate any uninteresting hydrogen desorption from these bonding sites. The study of hydrogen desorption from the diamond planes is thus simplified. In fact, we have acquired TPD spectra with no pretreatment which shows insignificant amount of deuterium desorption at temperature below 1200 K except the desorption peak from sample holder. This indicates that the diamond C(111) sample used in this study is basically free of the graphitic component. This is very likely due to the unique surface treatment mentioned in the Experiment. The typical desorption spectra of D\(_2\) from the fully deuterated C(111) surface after background subtraction are shown in Fig. 5, in which the average heating rate was varied from 0.6 K/s to 30 K/s. Obviously, D\(_2\) desorbs in a single asymmetric peak. Increasing the heating rate tends to shift the spectra to higher temperature and increase the desorption rate, or equivalently the intensity. In addition, no desorption is observed after the acquisition of a TPD spectrum if the sample is not exposed to the D atom flux again.

No TPD signals for hydrocarbon species were observed within the detection limit. This indicates surface decomposition or etching, if any at all, is insignificant during desorption. Surface condition is verified by LEED pattern measurements between TPD cycles. It is found that the C(111) surface at saturation coverage preserves good (1 \( \times \) 1) structure for at least 15 TPD runs due to the inherent stability of this surface.
To analyze this set of TPD spectra, a method developed by Taylor et al. for determining the coverage dependence of the pre-exponential factor and the desorption energy was applied. The relations used to describe desorption in a single state system are a mass balance on the surface [Eq. (1)] and a heating program [Eq. (2)],

\[ -\frac{d\theta}{dt} = R_d(\theta, T) = \nu(\theta, T) \cdot \theta^n \cdot \exp[-E_d(\theta, T)/kT], \]  
\[ T = f(t), \]  

where \( \theta \) is the number of adsorbed D atoms, \( T \) the sample temperature, and \( t \) the time. The desorption rate \( R_d \) depends on the reaction order \( n \) and two rate parameters, namely, the pre-exponential factor \( \nu(\theta, T) \) and the activation energy for desorption \( E_d(\theta, T) \). Use of this expression is based on the assumption that desorption occurs through a one-step mechanism or through one dominant, rate-determining step. Read- sorption of the desorbed species onto the surface is negligible.

To extract the coverage dependence of the rate parameters, it should be realized that a desorption spectrum correlates with the temporal variation of surface coverage. Under the equilibrium assumption, the number of molecules desorbing to gas phase per unit time is proportional to the mass spectrometer signal \( (I) \); and therefore, the surface coverage \( \theta \) is proportional to the integral of the mass spectrometer signal with time. Figure 6 shows the variation of normalized D surface coverage as a function of surface temperature at different heating rates obtained from the time-integrated TPD spectra. Note that the initial coverages have been normalized to unity for all curves.

Chin et al. has shown that the equilibrium coverage of H on the C(111) surface is 0.83 ML at room temperature. Another study demonstrates that the saturation coverage is about 0.95 ML. Here, we have ignored the abstraction effect and assumed that the saturation coverage of D on the C(111) surface is equal to one monolayer. Since the spectra are measured by altering the heating schedule, the desorption rates and the sample temperature may be varied for any particular coverage. Therefore, an Arrhenius plot of \( \ln(-d\theta/dt) \) vs \( 1/T \) at a fixed coverage gives a straight line with slope of \( -E_d(\theta)/k \) and intercept of \( \ln(\nu(\theta)^n) \), assuming \( \nu, n, \) and \( E_d \) are temperature independent in this temperature range. It should be pointed out that both signal intensity and sample temperature are monitored as independent functions of time. Thus, no special form for the heating schedule need to be assumed in the analysis, although a linear heating schedule is used throughout this study. The advantage of varying the heating rate is that a large dynamic temperature range for any coverage is produced. A hundredfold variation in heating rate generates at least a 130 K temperature range for all coverages (Fig. 6).

Figure 7(a) is the Arrhenius plot for D\textsubscript{2} desorption from the C(111) surface for various D coverages. The straight lines are the best fit to each plot from which the activation energy \( (E_d) \) can be calculated. In Fig. 7(b), the desorption activation energy is plotted as a function of coverage. The averaged results were determined from two sets of TPD data. The desorption energy is essentially independent of D coverage as shown in Fig. 7(b). At the very low coverage regime (<0.1 ML), the drastic decrease of activation energy may correspond to the manifestation of new desorption features. For example, there might be more population for sites with lower desorption barrier at very low surface coverages. Since the observed desorption energy is just an ensemble average, it will be reduced under this condition. Further discussions for this point will be presented in Sec. IV B.

Although the desorption activation energy can be extracted from the above procedure, the reaction order \( n \) must be known first to determine the pre-exponential factor. The desorption order \( n \) can be obtained from the slope of the plots of \( \ln(-d\theta/dt) \) vs \( \ln(\theta) \) at points of constant temperature. This method is based on the assumption of coverage independent or weakly dependent activation energy and pre-exponential factor, which happens to be the case in this system. Figure 8(a) shows the order plots for D\textsubscript{2} desorption from a C(111) surface at different surface temperatures. Figure 8(b) depicts the desorption order vs surface temperature. Obviously, from 1250 K to 1350 K, the desorption follows the first-order kinetics. Due to the insufficient dynamic range, the order plot may not be valid in higher and lower temperature regimes.

The first-order kinetics should manifest itself in the non-shifting desorption peak temperatures in TPD spectra at various initial surface coverages. To verify this, we have performed the desorption experiments with different initial deuterium exposure to the sample and a fixed heating rate of 10 K/s. Since the surface can be heated up by radiation from hot tungsten filaments during D exposure, to assure the same
surface condition, each D exposure is finished within 2 min which is feasible by adjusting the back-filled D2 pressure. The maximum surface temperature during the D exposure is \( \sim 500 \, \text{K} \). Note that the dissociation efficiency of deuterium molecule to atomic D by hot tungsten filaments at different back-filled deuterium pressure is unknown. Thus, there is no simple correlation for the surface D coverage to the exposure of molecular deuterium. Nevertheless, based on the assumption of 1 ML for saturation D coverage, the value of relative \( \theta \) under various exposure condition can be determined from time-integrated TPD curves. Figure 9 shows the relative coverage of deuterium as a function of exposure to atomic deuterium.

A series of TPD spectra for different D exposure are shown in Fig. 10. The D2 desorption signal increases with the increase of D exposure up to a saturation level (3000 L) beyond which the signal is independent of the D exposure. There is no evidence of a shift in desorption peak temperatures (\( T_{\text{peak}} \)) for D exposure above 300 L \( (T_{\text{peak}} = 1300 \, \text{K} \) at coverage above 0.3 ML), supporting the conclusion of first-order desorption kinetics. Note that at low surface coverage regime (below 0.3 ML), the peak temperature shifts to the lower temperature with decrease of the initial surface coverage \( (T_{\text{peak}} = 1246 \, \text{K} \) at 0.05 ML) as shown in the inset of Fig. 10. This is due to either the fractional desorption order\(^{61}\) or the decrease of desorption energy as indicated by the coverage-dependent activation energy in Fig. 7(b). To check this, we have carried out the isothermal desorption experiment which is an alternative way to directly measure the desorption order.

FIG. 7. (a) Arrhenius plots for D2 desorption from the C(111) surface at different D surface coverages. The straight lines show the best fit to each plots for obtaining the activation energy. (b) Variation of activation energy for D2 desorption from the C(111) surface. No obvious coverage dependent desorption activation energy was observed except at relatively low coverage regime.

FIG. 8. (a) Reaction order plots for D2 desorption from C(111) surface at various surface temperatures. (b) The reaction order at different surface temperatures for D2 desorption from the C(111) surface which shows the consistent first-order desorption kinetics.
In the isothermal desorption experiment, an initial D exposure of 50 L $D_2$ was first dosed onto the C(111) surface, and the temperature was quickly ramped to 1200 K where less than 10% of D atoms desorb from the surface. The $D_2$ desorption rate is then monitored by the mass spectrometer as a function of time at 1200 K as shown in Fig. 11(a). In order to derive the kinetic parameters, we have analyzed the data by the same desorption rate equation [Eq. (1)].

Under the isothermal condition, the simplest way to obtain the desorption order is to plot ln(rate) vs ln(coverage) from analysis of spectrum in (a). The coverage was determined by integrating the curve of the desorption rate over the time shown in (a) without any further normalization. The result of first-order desorption kinetics is consistent with another TPD study performed recently by Bobrov et al. Even the surface was not pretreated in that work to reduce the interfering signals from the supports and the degraded parts of surface, the hydrogen desorption from diamond C(111) plane was also concluded to be first order. In addition, Chin et al. have observed the first-order kinetics with a similar activation energy of 4.0±0.4 eV for hydrogen...
desorption from the C(111) surface utilizing sum frequency generation (SFG) technique. In SFG experiment, instead of measuring the hydrogen desorption from the C(111) surface, the H surface coverage is monitored following isothermal desorption.25 The first-order kinetics seems to be unusual for a recombative thermal desorption process which normally would follow a second-order kinetics. Obviously, it requires a model to explain the dynamics of recombative hydrogen desorption from the C(111) surface. This point will be further discussed in Sec. IV B.

IV. DISCUSSION

The thermal desorption study shows that the hydrogen desorption from the C(111) surface follows the first-order kinetics while the LEED measurements reveal the gradual change of the (2×1) surface structure upon hydrogen adsorption. In this section, we will interpret our results in terms of a novel model for the recombative desorption from the diamond C(111) surface and compare to the hydrogen desorption from the Si(100)-(2×1) surface which is the representative system in the study of covalently bonded surfaces.

A. Hydrogen adsorption on diamond C(111) surface

Among the possible structures proposed for clean diamond C(111) surface, the Pandey π-bonded chain is the most widely accepted model to represent the bare C(111)-(2×1) surface structure as shown in Fig. 12.10,43,62 When the C(111)-(2×1) surface is exposed to hydrogen atoms, the π-bonds open up and simultaneously make available surface dangling bonds for further hydrogen adsorption. There are many possible distributions for hydrogen adsorption on this surface. First, atomic hydrogen or hydrogen pairs may randomly populate on the (2×1) surface without perturbing the (2×1) surface structure. In other words, even the surface π-bonds are broken, the surface geometry remains the same. In this case, the half-order spots intensity should not vary as a function of hydrogen coverage, as in the cases of H/Si(100)-(2×1)63,64 and H/C(100)-(2×1) in the monohydride phase.30,31,51,65

Secondly, hydrogen atoms randomly distribute on the surface and considerably perturb the nearby surface structure. In this case, the half-order spots intensity should decrease drastically as the hydrogen coverage increases. Only when the size of ordered domain is larger than the coherence length of the incident electron beam, then LEED will present clear spots.61 On the other hand, the LEED spots will become blurred and hence the intensities decrease if the domain dimension is reduced. If the hydrogen atoms are randomly distributed on the surface, whether they form singly H-bonded surface dimer or are paired up on the surface, the size of ordered (2×1) domains should be reduced instantly as long as the local π-bonded (2×1) structure is perturbed as proposed in Fig. 12. As a result, the LEED pattern should display a more drastic change for half-order spots intensity. Note that the detectable (2×1) LEED pattern indicates the existence of large enough portion of the surface which still remains as ordered (2×1) reconstruction. In our experiment, a gradual decrease of half-order spots intensity in the LEED pattern up to D coverage as high as 0.5 ML strongly suggests that the D atoms are not randomly distributed on the C(111) surface. Instead, a segregation mechanism leading to domain formation for hydrogen adsorption on the C(111) surface is thus proposed to explain the LEED results. The situation may be quite similar to hydrogen adsorption on a W(100) surface at room temperature. In that system, a sequence of LEED patterns with “extra” ½ ½ spots were observed.66 Measurements of such spots intensity (integrated over the spot area) showed that it increased linearly with coverage, which was explained by the “island” model. If hydrogen atoms segregate together to form highly hydrogenated domains when they adsorb on the C(111) surface, the size of the remaining ordered (2×1) domains should be larger than that expected for randomly distributed hydrogen atoms at any fixed coverage.

The half-order spots intensity cuts off at about 50% of deuterium saturation coverage. This is probably because at high coverage the (2×1) domains are too small to have enough observable half-order spots intensity and/or the complete dismantling of (2×1) domains takes place under this condition. In the case of H/Si(111), Chabal et al. reported that the spontaneous (1×1)→(2×1) reconstruction occurred after electron-stimulated desorption of hydrogen and the observable minimum atom number to maintain the (2×1) domain was about 10 surface sites.69 In other words, there may need a critical number of surface sites to stabilize a (2×1) domain among tetrahedral (1×1) environment due to the marked structure difference as shown in Fig. 12. The
H-induced dereconstruction should also take place in the surface region where the local density of adsorbed H atoms exceeds some critical value. As a matter of fact, the (2 × 1)→(1 × 1) conversion upon hydrogen adsorption on a freshly cleaved Si(111)-(2 × 1) surface has been investigated by Henzler et al.88 They reported that during H exposure the half-order spots intensity became weaker and weaker and were completely distinguished after 0.5 ML of hydrogen coverage. This is strikingly similar to our results. An assumption of random distribution for H adsorption on Si(111)-(2 × 1) surface was taken to explain the gradual decrease of half-order spots intensity. This model could only be true if the remaining bare (2 × 1) domains could be stable at any size. However, from the size dependence of the domain stability observed by Chabal et al. (see above), we believe that the domain formation may also occur in the H/Si(111)-(2 × 1) system.

The intrinsic driving force for the segregation and domain formation comes from the inherent difficulty in the structure transformation and energy dissipation. When H chemisorbs on the bare C(111)-(2 × 1) surface as depicted in Fig. 12, it will immediately open up the chemisorbs on the bare C~3 face adjacent to an already chemisorbed hydrogen adatom. In this radical site to cause the rearrangement of carbon skeletons by which the reconfiguration between the π-bonded chain reconstruction and the bulk-terminated structure is accomplished. Any pair of electrons can move to an adjacent site of electron deficiency and the group attached to the pair of electrons goes along.69,70 Therefore, the effect of adsorbed hydrogen is to initiate this 1,2-alkyl shift resulting in sp3 hybridized carbon atoms singly backbonded to the underlying layer. Since this reconfiguration is likely required to overcome a potential barrier due to the structure constraint, the adsorption of another hydrogen atom in this radical site or vicinity of an existing CH bond is expected to be more favorable from both energetics and structure points of view. In other words, once the (1 × 1)-like center has been created by first adsorption of H on the C(111)-(2 × 1) surface, the subsequent coming H atoms would have a much higher probability of adsorption at a site adjacent to an already chemisorbed hydrogen adatom. In the case of Si(100)-(2 × 1) surface, hydrogen atom indeed has higher sticking probability in the singly H-bonded surface dimer and consequently, the surface hydrogen adsorption tends to pair on the surface.71 Indeed clustering of hydrogen paired dimer units on the Si(100) surface has been observed by scanning tunneling microscopy (STM) following a brief anneal at 630 K after hydrogen exposure. This clustering phenomena appears to occur due to the effect of thermal diffusion, unlike the case with diamond C(111) surface in which the domain formation is believed to be driven by bond strain. In other words, on the C(111) surface, randomly distributed CH pairs are not expected to be stable on the (2 × 1) structure. Thus, the relaxation of the local surface structure upon hydrogen adsorption will bring more hydrogen atoms to adsorb around the hydrogenated region. In this way, separate domains will be formed and grow during H adsorption process.

In this description of adsorption, a conversion from the (2 × 1) structure to the bulk-truncated (1 × 1) surface involves many C–C bonds and at least the two top layers of C–C bonds need to be broken and reformed in the phase transition process. Thus, before the final (1 × 1) phase is completely formed, a transition state with a set of bond angles and bond distances slightly different from those of the fully relaxed structure may exist. Such intermediate deformed surface structure may correspond to the freshly transformed metastable (1 × 1) phase proposed by Chin et al.,27 and probably contributes to the diffuse background observed in the LEED pattern with partial D coverage as described in Sec. III A. Based on this segregation model, the individual domain is highly hydrogenated. While the exact structure of such hydrogenated domain cannot be determined from the LEED study, judging from the gradual replacement of the SFG peak at 2860 cm⁻¹ by the peak at 2830 cm⁻¹ with further H exposure,27 we believe that when the domain size is big enough, the transformation to a fully relaxed (1 × 1) structure would occur. The SFG peak at 2860 cm⁻¹ also can be thermally converted to the peak at 2830 cm⁻¹ which is characteristic of bulk-terminated (1 × 1) structure. The outcome of this thermal annealing effect lends a strong support for the model of domain formation, since it is difficult to visualize that CH bonds with sp3 characteristics could be randomly distributed in a sp²-like (2 × 1) structure. Note that diffusion to form separate domains during thermal annealing is not expected, as will be discussed later. Therefore, from both LEED and SFG results, we here propose that domain formation definitely takes place upon H adsorption. When these neighboring chemisorbed hydrogen atoms are thermally activated, they will recombine and desorb concertedly. This picture accounts for the unusual first-order kinetics for the molecular hydrogen desorption from the C(111) surface.

The requisite condition for the proposed domain formation is the ability of H atoms to roam over the surface and encounter as many sites as possible before they finally chemisorb or bounce back into gas phase. Based on thermodynamic estimation, to form a CH bond from a gas phase hydrogen atom with the C(111) surface could release energy as much as 8.4 eV (Fig. 14). Considering the difficult momentum exchange between H(D) and substrate lattice, H(D) atoms could experience many hoppings before they finally chemisorb at preferred sites, which would subsequently lead to the observed domain formation. Actually, similar concept has been proposed as a hot-precursor mechanism in the case of H adsorption on the Si(100)-(2 × 1) surface by Weingberg and co-workers.71 It is thought that the incident hydrogen atoms excite surface phonons during the initial collisions and become dynamically trapped in highly excited vibrational states in which the hydrogen atoms wander about on the surface during the time necessary for energy dissipation until they are finally localized by the diffusion barrier.

The picture in Fig. 13 depicts the process for hydrogen segregation mechanism discussed above. In this mechanism, hydrogen atoms segregate during the adsorption to form the separate domains. The open circles represent the hydrogen atoms which hop around on the surface to hunt the most
stabilized adsorption sites. Different circled regions are the inherent (2×1) domains populating on the surface. Since the step sites or the boundaries of these inherent (2×1) domains have less structure strain and better coordinating capability, compared to other adsorption sites in the middle of terraces or domain center, they might serve as the initial nucleation sites for hydrogen adsorption. We, however, have no clear data to support this picture from the present experiment.

B. Hydrogen desorption from the diamond C(111) surface

The results from the TPD study show that the thermal desorption of D₂ from the C(111) surface follows the first-order kinetics in the D coverage. This result was verified over a temperature range from 1200 K to 1350 K. The first-order kinetics indicates that the probability of encounter of two D atoms and their subsequent associative desorption does not go as the square of the D atom coverage as one might expect. A second important result is the nearly constant value of the measured desorption activation energy \( E_a \), 3.7±0.1 eV except at low coverage regime where \( E_a \) decreases drastically with decrease of the hydrogen coverage. The kinetic parameters determined here are compared with those measured by other groups and summarized in Table I. Most prior studies were performed by temperature programmed desorption technique as employed in this work. It is clear from this comparison that the measured activation energy for hydrogen desorption from diamond may be varied from 1.6 eV to 4.1 eV, while the variation in prefactor value may be up to ten orders of magnitude. It is true that the activation energy in hydrogen desorption may differ for the various low-index diamond single crystal surfaces and polycrystalline diamond film surfaces. Different sample preparation may also be responsible for the disparate results, as desorption from steps and defect sites might occur at slightly different rates and might give rise to anomalously broad TPD peaks. Different analysis method for extraction of kinetic parameters can lead to different conclusion as well. For example, Schulberg et al. have studied hydrogen desorption from diamond films. They reported a single first-order desorption feature at approximately 1300 K using a heating rate of 6 K/s. To extract kinetic parameters, the desorption spectra were fitted to the desorption rate equation by varying \( E_a \) and prefactor value. When a single peak was assumed, they obtained the optimal \( E_a \) of 2.2 eV and prefactor of 5×10⁷ s⁻¹. If multiple desorption sites with a Gaussian-

<table>
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<th>Authors</th>
<th>( E_a ) (eV)</th>
<th>( \nu ) (s⁻¹)</th>
<th>Sample</th>
<th>Source</th>
<th>Method</th>
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<td>Ref. 37</td>
<td>TPD</td>
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<td></td>
<td>C(100)</td>
<td>Ref. 12</td>
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FIG. 14. One dimensional potential energy diagram for the interaction of deuterium with the diamond C(111) surface, which illustrates the relative bond energies for C–D and D–D as well as the possible reaction energy paths along the hydrogen adsorption/desorption coordinate.

Distributed population was assumed, however, the average kinetic parameters of $E_d = 3.6$ eV and prefactor of $9 \times 10^{12}$ s$^{-1}$ were obtained.

Regardless of the effect from different surfaces, most of the values for activation energy are substantially lower than the estimated H$_2$ desorption energy based on simple bond energy calculation. Figure 14 is the simple one-dimensional potential energy diagram that illustrates the relative bond energies for the interaction of hydrogen with diamond surface as well as the reaction energy path along the hydrogen adsorption/desorption coordinate. The reaction products of hydrogen molecule and an ideal bare diamond surface (no $\pi$-bond formation) is set to be the energy zero. The dissociation energy of the D–D bond is 4.5 eV (Ref. 72) for the D$_2$ molecule and the C–D bond energy for the monohydrride diamond is 4.2 eV. Forming one C–D bond lowers the system energy to 0.3 eV, and forming one more C–D bond lowers the total energy to $-3.9$ eV. This gives an enthalpy change of 3.9 eV for D$_2$ desorption from the diamond surface. If we assume that there is no barrier to D$_2$ adsorption, the heat of adsorption calculated from the bond energy is the lower limit value of activation energy for hydrogen desorption from the fully-relaxed D/C(111)-(1×1) surface (A state). The change of C–C bonding may occur after desorption of hydrogen and needs to be included in the thermodynamic prediction. For example, hydrogen desorption may result in the $\pi$-bond formation as well as surface structure transformation. Koleske et al. have estimated $\sim 1$ eV of energy correction for this $\pi$-bond formation using an empirical bond order analysis. The predicted endothermicity is thus brought down to 2.9 eV.

The kinetic apparent activation energy for hydrogen desorption is not necessarily equal to the thermodynamic reaction endothermicity. No D$_2$ was detected during TPD measurement if the C(111) surface was first exposed to deuterium gas without turning the W filaments on. This indicates that there should be a barrier to dissociative chemisorption for molecular hydrogen on the C(111) surface, which is depicted as state B or C in Fig. 14. This energy barrier may be complicated by the possible existence of a precursor state or a metastable state on atomic H(D) adsorption. Indeed, as proposed from the result of the SFG study, such intermediate states may exist on a freshly formed C(111) surface at any partial hydrogen coverage. During the initial adsorption, hydrogen atoms may partially induce the relaxation of the (2×1) surface structure and result in a C(111)-metastable (1×1) state (A* state). Either sufficiently high H(D) exposure or thermal annealing can lead to the complete relaxation of this surface structure to a more stable bulk-truncated (1×1) surface (A state). The influence of precursor state (A* state) on the measured activation energy for hydrogen desorption is described as follows. Since hydrogen desorption follows first-order behavior, a simple kinetic scheme can be expressed by the following reaction equation:

$$\frac{k_d}{k_c} = \frac{k^*}{k_c} \Rightarrow A^* \rightarrow A_{gas}. \quad (3)$$

From the steady-state approximation for the $A^*$ state, it can be readily shown that the desorption rate can be expressed as:

$$R_d = \frac{k^* k_d \theta}{k_c + k_d (1 - \theta)}. \quad (4)$$

where $k_c$, $k_d$, and $k^*$ are the rate constants corresponding to the individual step shown in Eq. (3). As defined by Fig. 14, $E_d$ is the activation energy barrier from the chemisorbed state to the precursor and $E_c$ is the activation energy for chemisorption from the precursor, $E^*$ is the desorption activation energy from the precursor. Two limiting cases may be considered here. In case one, $k^* \gg k_c$, Eq. (4) can be reduced to $R_d = k_d \theta$. In case two, $k^* \ll k_c$, then the rate equation is equal to $R_d = (k^* k_d / k_c) [\theta / (1 - \theta)]$. Case one is simply the normal first-order desorption process. In this case, however, the $A^*$ state should locate further out from the surface than the B or C state in the potential energy curve. This normally describes the molecular precursor state in a dissociative chemisorption system with $E_c > E^*$, instead of the metastable state mentioned above. The metastable state may be described more appropriately in case two, where the $A^*$ state locates somewhere between state A and B or C state as depicted in Fig. 14. It can be readily shown that in this case the desorption energy is equal to $(E_d + E^* - E_c)$ or the energy difference between state A and state B or C. The determination of the exact position of state $A^*$ with respect to state A needs a theoretical calculation. The reaction pathway of hydrogen desorption depends on the favorable state of the final product. For hydrogen desorption accompanied with the C–C $\pi$-bond formation, the transition state is designated as B in Fig. 14. For hydrogen desorption without $\pi$-bonding, the transition state is designated as C which is positioned higher than state B. It should be emphasized again that in addition to the energy correction for $\pi$-bond formation, a significant barrier which is purely due to the structure constraint also exists between the C(111)-(1×1) and the recon-
structed C(111)-(2×1) surface. When two adjacent H atoms desorb from the C(111)-(1×1) domain, the realization of the subsequent π-bond formation depends on the local structure of the desorption sites. In other words, it might or might not support the π-bond formation. For example, the structure in the domain center would hinder π-bond formation after hydrogen desorption, because it would create enormous strain for π-bonding to occur in a very “unfriendly” tetrahedral-like sp³ environment (favorable desorption pathway is through transition state C). On the other hand, the hydrogen desorption near the edge of the segregated domain would probably result in π-bond formation more easily (the reaction pathway is along transition state B). The structure in the domain boundary region is expected to be less tetrahedral-like, since it requires vigorous rebonding to merge (1×1) and (2×1) structures. Consequently, the H₂ desorption from the domain edge requires lower activation energy compared to that from the domain center. Note that the measured activation energy is actually an ensemble-averaged value. One, therefore, would expect higher measured activation energies above certain coverage, where the desorption from domain center sites may dominate that from minority boundary sites. On the other hand, lower values of the measured activation energy are expected at low H(D) coverage regime. At low coverages, the hydrogenated (1×1) domains are so small that edge and center are essentially indistinguishable. In addition to π-bonding, easiness of structure transformation from (1×1) to (2×1) at low coverage regime may also play an important role in lowering the measured desorption energy. In their excellent ESD study on H/Si(111), Chabal and co-workers reasoned that when a critical number of H atoms have been desorbed, the Si(111) surface tends to lower its free energy through a spontaneous phase transition to the (2×1) structure, desorbing the remaining hydrogen in the converted area due to the fact that atomic hydrogen would be very unstable on the Si(111)-(2×1) surface. The same mechanism should apply here due to the identical structures existing between unreconstructed C(111) and Si(111) surfaces. This may explain the observed coverage-dependent activation energy at low θ regime in this study.

Another important conclusion is the unusual first-order kinetics for recombinative desorption, which has also been observed in the case of H/Si(100)-(2×1). Several desorption mechanisms have been proposed to explain the first-order kinetics observed in the case of H/Si(100)-(2×1). Due to the strong bond energy as well as relatively short bond length between C–C, the diamond surface usually contains a high concentration of defect sites. If the hydrogen atoms preferentially diffuse to the defect sites from where hydrogen molecules desorb subsequently, the reaction kinetics is expected to be first-order. The H diffusion barrier on both Si(100) (about 60%–70% of the Si–H bond energy) and C(111) surface (about 70%–80% of the C–H bond energy) are shown to be very high. To make an order-of-magnitude estimation, only few number of surface sites are expected to be visited by hydrogen atoms before desorption (at desorption peak temperature, the number of visited sites is estimated to be less than 5). At low coverage regime, there may not be enough time for H atoms to reach defect sites before desorption. In our experiment, we have observed first-order kinetics even at H(D) coverage as low as 0.05 ML. It, therefore, is concluded here that hydrogen desorption from defect sites would be unlikely. Another possibility related to defect sites is presented as “defect diffusion/dihydride desorption” mechanism in which surface defects are converted into dihydride species from which H₂ desorption occurs. Since the H₂ desorption from the dihydride species is the rate-determining step, the kinetics of desorption is thus first-order. The main support for this mechanism is the calculation from density functional theory together with a cluster model on the H/Si(100)-(2×1) system. The existence of such surface defects has been detected by STM and supported by molecular dynamics study; yet, to date, no direct experimental observation for this intermediate dihydride species has been reported. Whether or not this mechanism can be applied to H/C(111) remains questionable. It, however, would be very interesting to theoretically investigate the role of defect diffusion in this system.

Another mechanism is a generalization of the Eley–Rideal reactions (generalized ER mechanism) on surfaces which explains first-order rate law. In this mechanism, the rate limiting step is an irreversible excitation of a hydrogen adatom into a delocalized band state (H*). The delocalized atom then reacts with a localized atom to produce molecular hydrogen which desorbs. The supporting evidence for this mechanism comes from the isotopic mixing experiments in which an Eley–Rideal mechanism was observed for an incoming H atom to directly abstract a localized chemisorbed D atom to produce a gas phase HD molecule even at low temperature, supporting the existence of a long-lived H* state. This mechanism is appropriate for hydrogen/diamond system only if the hydrogen desorption from any other diamond surface also follows first-order kinetics. Several groups have performed the study of hydrogen desorption from a C(100) surface and the reaction kinetics is described very crudely to be first order. More detailed studies have revealed the extreme inherent instability on the C(100)-(2×1) surface. The surface structure can be seriously degraded even by a single TPD heating process. The kinetics of hydrogen desorption from the nondegraded C(100)-(2×1) surface is not conclusively determined. Even if the unity desorption order exists for most diamond surfaces, this mechanism is still not compatible with this particular H/C(111) system from the energetics point of view. Within the theoretical framework proposed by Weinberg and co-workers, the energy level of the hypothetical rate-limiting delocalized H* state should exist between state A and state B (C), and it is very unlikely that the desorption activation energy should exhibit any coverage dependence. This is obviously inconsistent with our results at low coverage regime.

The preparing mechanism in which pairing of adsorbed hydrogen atoms on the silicon dimer prior to desorption is also proposed. This pairing phenomenon has been observed by scanning tunneling microscopy (STM) and was argued to result from hydrogen diffusion at high temperature.
mentioned above, Weinberg and co-workers have elegantly shown that hydrogen pairing on silicon dimers on the Si(100)-(2×1) surface can occur at surface temperature as low as 150 K which is proposed to be driven by “hot precursor” dominated adsorption kinetics rather than thermodynamics. Similar concept with some modification (domain formation) can be utilized to explain the first-order kinetics for hydrogen desorption from the C(111) surface. This modification is invoked from the consideration of structural factor in the particular case of the C(111) surface. As argued in the last section, hydrogen atoms prefer to adsorb on sites where the nearby structure has already been relaxed by preadsorbed hydrogen atoms. It can be readily conceived that in addition to possible prepairing, the hydrogenated domain is also formed during H(D) adsorption. The H₂ desorption reaction may then occur as the concerted desorption from the hydrogen atoms paired on two adjacent carbon sites in a highly hydrogenated domain. Due to the structural stability, the domains would shrink and remain highly hydrogenated as the hydrogen desorption proceeds. The kinetics of H₂ desorption would then be expected to follow a first-order rate law. The domain formation mechanism seems to be the most likely one in the hydrogen desorption from the C(111) surface, although some other mechanisms cannot be completely excluded. In fact, no experiments so far can provide the detailed and unequivocal description for the surface structure during the hydrogen desorption from the C(111) surface. Based on the similar vibrational and rotational energy distribution for desorbing hydrogen molecules from Si(100) and Si(111), Zare et al. have proposed a three-center dihydride-like structure as the transition state for hydrogen desorption from silicon surface. In the case of the diamond C(111) surface, due to the steric hindrance for smaller bond length of diamond compared to Si, the formation of the dihydride phase is unlikely except on the edge or defect sites. Diamond surfaces are generally thought to have a higher concentration of defects. If dihydrides do exist in our diamond sample, hydrogen molecules formed from such defect sites should have already been desorbed during the surface pretreatment prior to TPD cycles (Sec. III A). A more definitive determination of the mechanism for H₂ desorption from a C(111) surface will require further experimental and theoretical work.

V. CONCLUSION

In summary, we have determined the kinetics of recombinative deuterium desorption from the C(111) surface. From series of TPD spectra acquired at different heating rate, the desorption process was found to be first-order at all coverages with an approximately coverage-independent activation energy of 3.7±0.1 eV and a prefactor of (9.5±4.0)×10¹³ s⁻¹. No hydrocarbon desorption products were observed within the detection limit of the QMS. The diamond C(111) surface was observed to reconstruct reversibly following repeated hydrogen adsorption/desorption cycles. The dependence of the surface reconstruction, from a bare (2x1) reconstructed surface to a hydrogenated (1x1) bulk terminated surface was also investigated in details by quantitative LEED technique. It is observed that the half-order spots intensity which correlates with the size of the (2x1) domain gradually decreases as H(D) coverage increases. To consistently explain TPD, LEED, and SFG results, we propose here the domain formation model. According to this model, upon adsorption H atoms preferentially form highly hydrogenated domains from where hydrogen molecules desorb concerted when the surface temperature is raised. Although some unanswered questions remain, we are able to exclude a number of possibilities and to lend support to the preparing mechanism.

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