

## Photon-stimulated desorption of $H^+$ and $H^-$ ions from diamond surfaces: Evidence for direct and indirect processes

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Photon-stimulated desorption of positive and negative hydrogen ions from hydrogenated diamond film and  $Di(100)$  surfaces and amorphized diamond surface has been studied for incident photon energies in the 280–340 eV range. From comparison between the  $H^+$  yield as a function of photon energy and the near-edge x-ray absorption fine structure recorded by detecting secondary electrons of selected kinetic energies the processes leading to photodesorption are assessed. It is shown that desorption of  $H^+$  occurs through two different processes: an indirect process involving secondary electrons from the bulk and a surface process. The surface process is characterized by a resonance at 287.5 eV photon energy, which reveals the presence of C-H bonds on the diamond surface. Stimulated desorption of  $H^-$  is mainly the result of indirect processes that involve secondary electrons.  $H^+$  photodesorption from an amorphized diamond surface can be also induced by C ( $1s$ ) ionization. However, no  $H^-$  desorption from the amorphized surface could be detected. We suggest that this effect is associated with the reduced secondary electron emission yield of the amorphized diamond surface. Our results demonstrate that ion photodesorption may be used as a sensitive probe for hydrogen on diamond surfaces. [S0163-1829(99)05603-9]

### INTRODUCTION

Photon-stimulated desorption of ions and neutrals from surfaces is a consequence of primary electronic excitations whose relaxation results in nuclear motion, bond scission, and desorption.<sup>1,2</sup> Desorption induced by core-level excitations may involve direct or indirect electronic processes. Indirect desorption processes are initiated by the secondary electron emission, which induces valence excitations, whereas direct processes proceed through the relaxation of core holes.<sup>3,4</sup> Desorption processes stimulated by core-level electronic excitations have been studied extensively in recent years, in particular for the negatively charged desorbing ions.<sup>5–11</sup> Studies of the ion fragments produced by the core-level excitations have yielded insight into dissociation pathways.<sup>12–16</sup> Many of these studies have shown that two-hole, one-electron ( $2hle$ ) states, in which two holes are produced in valence band and one electron is excited to an antibonding level, are often responsible for ionic dissociation.<sup>16</sup>

The mechanism of stimulated desorption promoted by core-level ionization and the contribution of direct and indirect processes may be studied in some detail by comparing the ion yield and the near-edge x-ray absorption fine struc-

ture (NEXAFS) recorded by measuring the partial electron yield for selected electron-kinetic energies. In this paper, we employed this method to study desorption of hydrogen ions, stimulated by the C ( $1s$ ) core-level photoexcitation, from both hydrogenated diamond films deposited by the chemical vapor deposition (CVD) method and monocrystal diamond and from an amorphized diamond film.

The study of photon stimulated desorption (PES) of hydrogen ions from carbon surfaces is simplified by the fact that this surface has a relatively simple electronic structure, composed of one core level and the valence band. In addition, well-defined and chemically stable surfaces can be easily prepared. The interaction of hydrogen with diamond surfaces is not only important from the fundamental point of view, but also for some practical applications such as the nucleation and growth of diamond films by CVD. However, the determination of adsorbed hydrogen on diamond surfaces is a most difficult experimental problem: commonly used surface sensitive techniques, such as Auger and x-ray photoelectron spectroscopy, are not sensitive to hydrogen. From an analytical perspective, therefore, it is important to determine whether photodesorption is sensitive to the amount and chemical state of hydrogen adsorbed on diamond surfaces.

The present paper consists of an experimental section in which the sample surface preparation and characterization are recalled followed by a short description of the system where the NEXAFS and photodesorption experiments were carried out. Then, we present and discuss the photodesorption results. Here the  $H^+$  and  $H^-$  ion yields as a function of photon energy in the 280–340 eV range are compared to the NEXAFS of secondary electrons of selected energies. These measurements are complemented by the low-energy secondary electron emission measurements of well-defined and amorphized diamond and energy distribution of secondary electrons and  $H^+$  ions. Finally, we discuss the mechanism and dynamics of photodesorption of hydrogen ions from diamond surfaces and summarize our results.

## EXPERIMENT

### A. Preparation and characterization of surfaces

Polycrystalline diamond films 10  $\mu\text{m}$  thick were deposited on silicon substrates by the hot filament CVD method, using a system previously described.<sup>18</sup> The Raman spectrum measured for these films shows only the characteristic diamond line at 1333  $\text{cm}^{-1}$ . No additional lines associated with amorphous carbon or graphite were measured in the Raman spectrum. Scanning electron microscopy examination of the films indicated that these were continuous and composed of crystallites of 2–3  $\mu\text{m}$  in size.<sup>18</sup>

Auger analysis of the films shows that their surface was free of oxygen and other impurities (<0.05 at %). The electron-energy-loss spectrum and the C (*KLL*) line shape of the films were characteristic of diamond.<sup>19,20</sup> The surface of the as deposited films was terminated by atomic hydrogen. This was determined *ex situ* by temperature programmed desorption (TPD) measurements of the as deposited film.<sup>21</sup>

The single-crystal diamond (100) surface was hydrogenated by exposure to microwave hydrogen plasma. The hydrogen flow as 100 SCCM (SCCM denotes cubic centimeter per minute at STP), the hydrogen pressure was 50 torr and the diamond sample temperature was  $\sim 900^\circ\text{C}$ . After this cleaning treatment, the Di (100) surface was examined *ex situ* by Auger, TPD, EELS, and low-energy electron diffraction (LEED). The Auger spectrum showed a characteristic C (*KLL*) line of diamond and no evidence of oxygen impurities. The EELS spectrum measured by an incident primary electron energy of 100 eV displays only the bulk and surface plasmon characteristic of diamond at 33 and 23 eV loss energy, respectively. The LEED pattern displays a (100)- $2\times 1$  reconstructed surface. TPD measurements show a single hydrogen desorption peak at  $\sim 900^\circ\text{C}$ . These measurements suggest that after exposure to the hydrogen plasma a stable and well-defined, reconstructed and hydrogen terminated Di (100)- $2\times 1$ -H is obtained.

### B. The experimental chamber

The as-deposited film and single-crystal diamond samples were inserted into an ultrahigh vacuum (UHV) chamber connected to the SA72 line of SUPERACO at LURE, which is capable of delivering photons in the 150–600 eV range. Details of the UHV chamber have been given previously.<sup>22,23</sup> The UHV chamber is equipped with a hemispherical electron

analyzer (CLAM) for photoelectron spectroscopy and energy selected NEXAFS. Ion detection is carried out using a highly sensitivity RIBER quadruple mass spectrometer. The energy distribution of the positive ions was measured using a cylindrical mirror analyzer followed by a mass quadrupole filter for simultaneous mass and kinetic energy analysis. In addition, the chamber is equipped with gas activation set up and a gas manifold for adsorption experiments. After inserting diamond film and single crystal into the UHV chamber, the chamber was heated at  $150^\circ\text{C}$  for 48 h, which resulted in the base pressure of  $\sim 7\times 10^{-11}$  torr.

### C. Deuteration experiments

*In situ* deuteration of the films was carried out with a filament positioned  $\sim 5$  cm from the diamond surface. The filament temperature was  $\sim 1700^\circ\text{C}$ ,  $D_2$  pressure was  $10^{-6}$  Torr, and the deuteration time was 90 min. This procedure resulted in the chemisorption of atomic deuterium through exchange reactions in which thermally activated deuterium  $D^*(g)$  displaces a chemisorbed hydrogen atom H (ads) and adsorbs onto the diamond surface.<sup>28,29</sup> Under the conditions used in the present study the probability for this exchange process is  $\sim 0.05$ .<sup>28,29</sup>

## RESULTS AND DISCUSSION

### A. NEXAFS measurements of different surfaces

The NEXAFS spectra of diamond films were obtained by measuring the intensity of secondary electrons of selected kinetic energies (8 and 35 eV), using photon excitation in the 280–340 eV energy range. The NEXAFS measured with 8 eV electrons is more bulk sensitive and is similar to the total electron yield (TEY), which is proportional to the low-energy secondary electron emission. On the other hand, the NEXAFS measured with 35 eV electrons is more surface sensitive.<sup>26,27</sup>

The NEXAFS spectra taken from the CVD films are shown in Figs. 1 and 2 along with the PSD of hydrogen ions [we would like to point out here that very similar spectra were obtained from the hydrogenated Di (100) surface as well]. The NEXAFS displays a threshold at  $\sim 289$  eV followed by a very sharp peak at 289.2 eV and broader peaks at higher photon energies. The energy calibration was derived from the energy position of the dip at 302.4 eV, which is associated with the absolute second band gap of diamond.<sup>24–27</sup> In particular, the sharp peak at 289.2 eV is associated with a core exciton. It should be mentioned here that the core exciton at 289.2 eV was resolved only when best resolution conditions were applied to the incident photon beam.

In the surface sensitive mode (using 35 eV secondary electrons), a structure centered at 287.5 eV is observed. This peak has been previously assigned to a C ( $1s$ ) $\rightarrow\sigma^*(\text{C-H})$  resonance.<sup>17</sup> This assignment is supported by NEXAFS measurements reported by Comelli *et al.*<sup>25</sup> who observed a peak at 287.5 eV for cyclohexane molecules and associated it to the C ( $1s$ ) $\rightarrow\sigma^*$  transition [compared to the C ( $1s$ ) $\rightarrow\pi^*$  transition at 285.5 eV for graphite]. Therefore, the appearance of the 287.5-eV peak in the surface sensitive mode may be associated with the presence of C-H species on the dia-

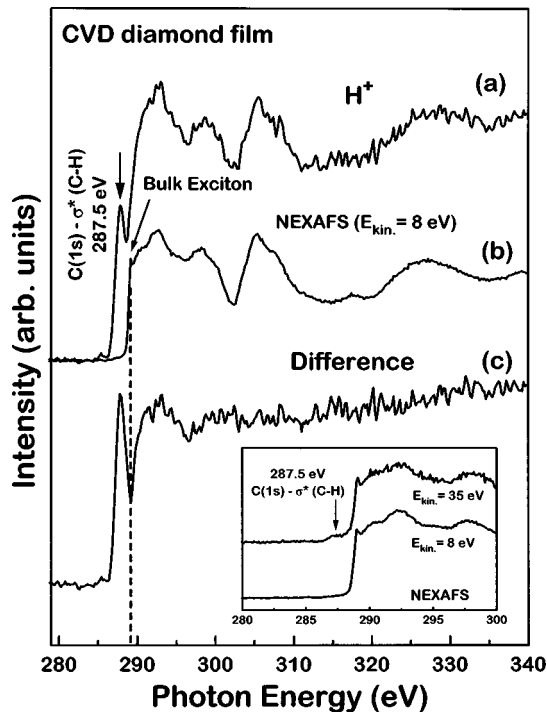


FIG. 1.  $H^+$  desorption yield from the CVD diamond film as a function of incident photon energy (curve *a*) compared to the NEXAFS spectrum recorded using 8 eV secondary electrons (curve *b*). Curve *c* is the difference between the  $H^+$  yield and the normalized NEXAFS spectrum. In the inset the NEXAFS spectrum measured by 8 and 35 eV secondary electrons (bulk and surface sensitive modes, respectively) are shown in the 280–300 eV photon energy range.

mond surface and not to disordered carbon or  $sp^2$  bonded carbon. A comparison between the near-edge structure of the NEXAFS measured for 8 and 35 eV electrons is shown in the inset of Fig. 1.

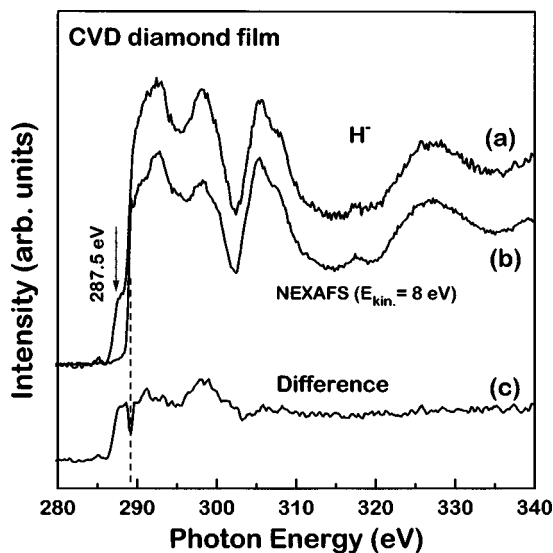


FIG. 2.  $H^-$  desorption yield from the CVD diamond film as a function of incident photon energy (curve *a*) compared to the NEXAFS spectrum measured using 8 eV secondary electrons (curve *b*). Curve *c* is the difference between the  $H^-$  yield and the normalized NEXAFS spectrum.

The NEXAFS spectrum measured after 2 keV Ar ion beam irradiation of the diamond film surface shows a threshold at 283 eV and a well-defined peak at 285.5 eV. The peak at 285.5 eV is associated with a  $C(1s) \rightarrow \pi^*$  transition in the amorphized carbon structure. This result confirms that the ion beam irradiated surface contains carbon atoms predominantly bonded in a  $sp^2$  hybridization, in agreement with our EELS measurements and other published work.<sup>20</sup>

### B. Photodesorption of positive and negative hydrogen ions from CVD diamond films

The PSD of positive hydrogen ions from the CVD diamond film was measured using photons in the 280–340 eV energy range. The results of these measurements are shown in Fig. 1(a) along with the NEXAFS spectrum of 8 eV secondary electrons. The  $H^+$  desorption yield displays features similar to those of the NEXAFS (although they seem to be superimposed on a monotonically increasing background) except a sharp structure at 287.5 eV, 2 eV lower than the threshold of the NEXAFS spectrum.

As similar features are observed in PSD and NEXAFS, we subtracted the normalized NEXAFS spectrum from the normalized  $H^+$  yield. The energy scale and the intensity of each spectrum was normalized to the intensity and position of the second band gap of diamond at 302.4 eV. From the subtracted spectrum we concluded that the  $H^+$  yield consists of a signal proportional to the TEY and with a threshold at  $\sim 289$  eV, superimposed to a resonance at 287.5 eV and a signal that varies monotonically with the excitation energy.

It appears from that result that the  $H^+$  desorption involves two distinct processes: the first  $H^+$  desorption process is generated by the bulk excitations, i.e., by the large flow of secondary electrons from the relaxation of  $C(1s)$  core holes from the bulk carbon atoms. The second process, quite distinct from the first one, is characterized by the resonance at 287.5 eV and does not show the features of the TEY. This may be an indication that the second process is generated by some surface excitations on the diamond film.

Figure 2(a) shows the negative hydrogen ions desorption yield measured in the 280–340 eV range from the CVD diamond film. The  $H^-$  yield is much more intense than the  $H^+$  desorption yield. However, an absolute comparison between the  $H^+$  and  $H^-$  ion yield intensities is not possible, as the relative sensitivity of the mass spectrometer to the positive and negative hydrogen ions is not known.

Following the same procedure as that used for the  $H^+$  ion yield, we determined the difference between the normalized  $H^-$  yield and the NEXAFS spectrum [see Fig. 1(b)]. To the great extent the  $H^-$  yield is proportional to the TEY, which means that the  $H^-$  photodesorption process is predominantly an indirect process. However, an additional five times less intensive contribution is also observed. It includes the same resonance at 287.5 eV as the  $H^+$  yield, followed by a rather monotonous signal and a broad resonance at  $\sim 298$  eV, which does not appear in the  $H^+$  yield.

### C. Photodesorption of positive and negative hydrogen ions from the hydrogenated Di (100)

The PSD of  $H^+$  and  $H^-$  ions from CVD diamond films has been compared in Fig. 3 to that from the hydrogenated D

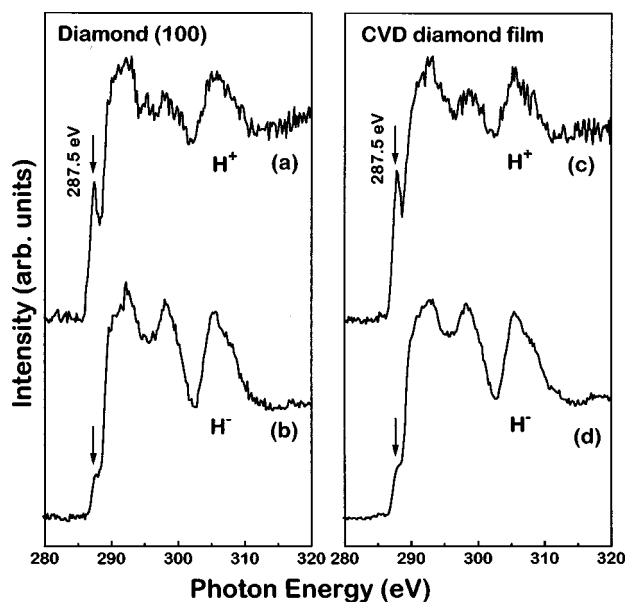


FIG. 3.  $H^+$  and  $H^-$  yields as a function of the photon energy for diamond (100) (curves *a* and *b*) and the CVD diamond film (curves *c* and *d*).

(100) single-crystal sample. From this figure the same features appear in the PSD of  $H^-$  and  $H^+$  from both surfaces, but with somewhat different relative intensities. The relative contribution of the direct process is higher in the case of the CVD diamond films than in the case of Di (100) [i.e., the relative intensity of the peak at 287.5 eV of  $H^+$  yield is higher for the diamond film than for the hydrogenated Di (100) surface]. These small differences may reflect the higher concentration of hydrogen atoms in the boundary region of the CVD diamond films. However, other effects may be responsible for this small difference, for example, the angular distribution of the desorbed ions from the Di (100) surface should peak along bond directions and perhaps the mass spectrometer samples certain directions more efficiently than others. In any case, our results suggest that photodesorption may be used as a probe for detection of hydrogen on the diamond surface, although it seems to be insensitive to the bonding configuration of hydrogen.

#### D. Photodesorption of positive hydrogen ions from amorphized diamond films

In Fig. 4 the  $H^+$  ion yield from the ion beam amorphized diamond surface is shown along with the NEXAFS measured from the same surface for 8 eV electrons. From this figure the NEXAFS of the amorphized surface displays a well-defined peak at 285.5 eV associated, as described above, with carbon atoms bonded in a  $sp^2$  configuration. In contrast, the  $H^+$  yield is completely smeared out and does not show any structure characteristic to the NEXAFS spectrum from the same surface.

This large difference between the  $H^+$  photodesorption and NEXAFS measured for the amorphized diamond surface suggests that, in this case, the photodesorption process is mostly dominated by direct surface excitations rather than by bulk excitations (secondary electrons). This can be understood considering that hydrogen bonded in a disordered car-

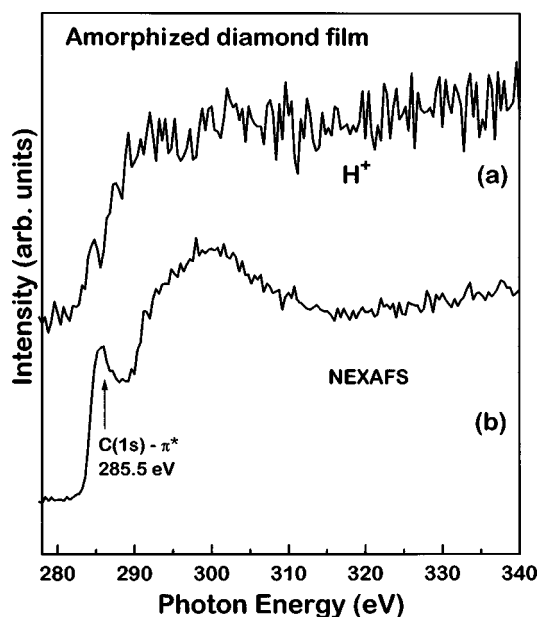


FIG. 4.  $H^+$  desorption yield as function of incident photon energy from the amorphized diamond film (curve *a*) compared to NEXAFS spectrum recorded using 8 eV secondary electrons (curve *b*).

bon network results in a destabilization of carbon  $sp^2$  bonding in favor of  $sp^3$  bonding and from a comparison of the secondary electron emission yield measured for the well and amorphized diamond surfaces described in the next section.

We were not able to measure the  $H^-$  yield from the amorphized diamond surface as it dropped below the sensitivity level of our mass spectrometer. This result clearly shows a great difference in the  $H^-$  yield from a polycrystalline diamond surface and an amorphous carbon structure. This effect is most probably due to a reduction of the secondary electron yield for the amorphized surface (see below).

#### E. Secondary electron emission distribution and yield from the well-defined and amorphized diamond surfaces

The reduced yield of the photon-stimulated  $H^-$  desorption for the amorphous surface may be associated with the re-

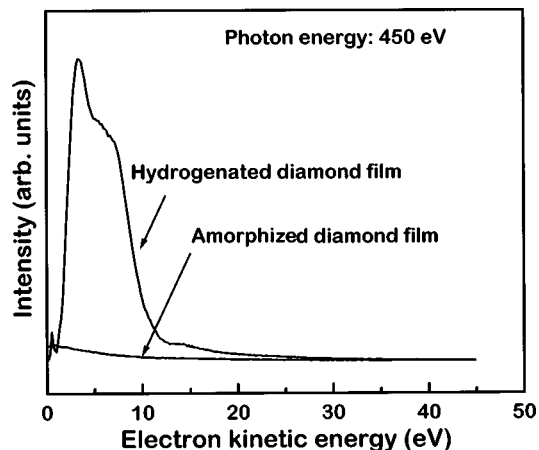


FIG. 5. Secondary electron emission spectrum of the diamond film (curve *a*) and the amorphized diamond surface (curve *b*) excited by a 450 eV photon beam.

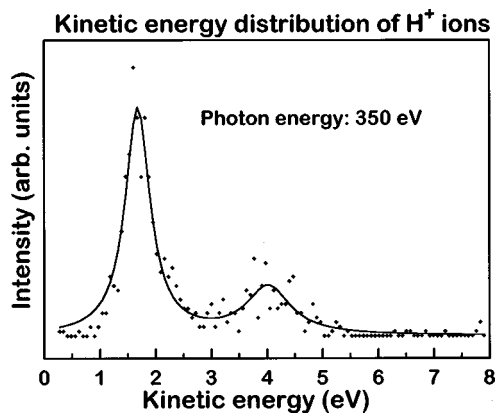


FIG. 6. Kinetic energy distribution of  $H^+$  photodesorbed ions from the diamond film for a photon excitation energy of 350 eV.

duced secondary electron emission yield from the amorphous carbon. To further investigate this possibility, we compare in Fig. 5 the secondary electron emission spectra of the well-defined and amorphized diamond surface measured as a response to 450 eV photon irradiation. The secondary electron emission distribution was carried out in the 0–50 electron kinetic energy as most of the secondary electrons are emitted in this range.

As observed from Fig. 5, the low-energy secondary electron emission yield is severely reduced for the amorphized surface. The fact that the intensity of low-energy secondary electrons is much lower in the case of the amorphized surface as compared to the hydrogenated diamond surface may have several reasons. First, the mean-free path of electrons is reduced in the disordered amorphous region. Second, the negative electron affinity of the hydrogenated diamond surface is known to increase the yield of ejected electrons from it surface.

This reduction in intensity is in full agreement with our conjecture that  $H^-$  desorption is mainly a consequence of indirect processes involving secondary electrons. Furthermore, as described above, for the amorphized surface the  $H^+$  photodesorption yield does not show the well-defined peak measured in the NEXAFS at 285.5 eV. The channel for photodesorption through indirect processes (by valence excitations induced by secondary electrons) is strongly reduced as compared to the case for the well-defined surface, direct processes are dominant, thus giving a stronger weight to surface localized processes. Considering now that hydrogen ‘‘opens’’ double bonds when bonded to carbon in a disordered carbon matrix, photodesorption processes promoted mainly by a direct process should not reflect the  $sp^2$  signature (peak at 285.5 eV), which is due to bonding between carbon atoms only, as ended found (Fig. 4).

#### F. Energy distribution of $H^+$ photodesorbed ions

In order to gain some more insight in the photodesorption process, we have also recorded the kinetic-energy distribution of  $H^+$  ions. These measurements involve extremely low counting rates and, therefore, require long measuring times and very intense photon beam. The kinetic-energy distribution of photodesorbed  $H^+$  ions from the diamond film was measured for incident photon energies of 290 and 350 eV. A

similar distribution was obtained for both photon energies and it is shown in Fig. 6 for the case that the diamond surface was irradiated by 350 eV photons.

As seen from Fig. 6, the kinetic-energy distribution of  $H^+$  consists of two peaks at 1.7 and 4.0 eV. It may be suggested that the sources of the two peaks in the  $H^+$  energy distribution may be the direct and indirect electronic processes responsible for the photodesorption. The existence of low (1.7 eV) and rapid (4.0 eV) desorbing  $H^+$  ions may be ascribed to one or several of the following effects: First, one could argue that the direct process gives rise to rapid desorbing ions whereas the indirect one gives rise to slow ions. Indeed, the direct process involved a C (*1s*) hole formation followed by an Auger relaxation. This is expected to result in highly ionized species, which may release a high amount of kinetic energy for desorbing ions. On the contrary, the indirect process involves only valence electronic excitation, which is expected to release less kinetic energy. Second, one could argue that slow and rapid  $H^+$  ions originate from different adsorption sites. Third, one cannot exclude that for a given H adsorption site and given desorption process (for example the direct process), both slow and rapid  $H^+$  ions can be desorbed due to electronic relaxation of the initially excited state towards two separate repulsive curves. From our measurements it is difficult to distinguish between these effects and further experimental work is planned to establish the nature of these two peaks.

#### G. Photodesorption from deuterated diamond film surfaces

It is known that the diamond CVD surface is fully saturated by chemisorbed hydrogen, while the bulk hydrogen concentration is estimated to  $<1$  at.%.<sup>16</sup> In order to verify that the measured  $H^+$  and  $H^-$  photon-stimulated desorption reflects a surface process, *in situ* deuteration of the surface was performed and the  $D^+$  and  $D^-$  photon-stimulated desorption was measured. Following the deuteration process a  $D^+$  (and  $D^-$ ) signal could be measured when the diamond surface was subjected to photon irradiation showing that the exchange reaction took place (Fig. 7). The  $D^+$  ( $D^-$ ) yield, as a function of photon energy, was similar to that obtained for  $H^+$  ( $H^-$ ), although with much lower intensity. The similarity between the  $H^+$  ( $H^-$ ) and  $D^+$  ( $D^-$ ) yields and photon energy indicates that the photon-stimulated  $H^+$  and  $H^-$  desorption yields as a function of photon energy represent a surface process.

#### H. Mechanism of photodesorption: evidence for direct and indirect processes

The present study reveals two distinct processes for the  $H^+$  and  $H^-$  photodesorption: the first one results from the bulk excitations and the second one from the surface excitations. The first process is considered to be of an indirect nature whereas the second is a direct one.

The first process implies the role of secondary electrons from the bulk of diamond, i.e., *indirect processes*, for nearly all the  $H^-$  yield and some of the  $H^+$  yield. In this case, two photodesorption mechanisms may be assumed. The first one involves valence excitations of the hydrogenated surface induced by secondary electrons. Considering that the minimum energy to desorb an  $H^+$  ion may be estimated by the sum of

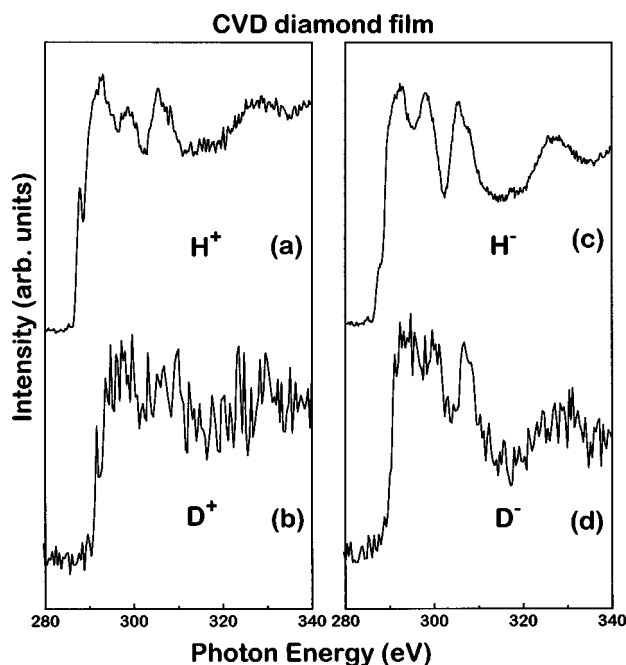


FIG. 7.  $H^+$  and  $H^-$  desorption yields as a function of incident photon energy (curves *a* and *b*) from the hydrogenated CVD diamond film.  $D^+$  and  $D^-$  desorption yields (curves *c* and *d*) from a deuterated diamond surface as a function of incident photon energy.

the C-H bond energy ( $\sim 4.3$  eV), plus the ionization energy of H (13.6 eV), minus the electron affinity of the hydrogenated diamond surface ( $-0.5$  to  $-1$  eV), this makes a minimum energy to desorb  $H^+$ , which should be around 18–19 eV. Clearly a single valence-band excitation is not likely to be energetic enough to produce ion desorption. As we proposed in our paper Ref. 23, the excitation to desorb  $H^+$  should involve a multielectron valence excitation, for example ionic satellite state excitations. Secondary electrons with such high kinetic energies (19–50 eV) do exist as can be seen from the NEXAFS spectrum with electrons having kinetic energies of 35 eV (Fig. 1). However, these secondary electrons are coming from the top layers of the diamond sample rather than from the bulk.

The second mechanism may involve the electron attachment to the hydrogen atoms ejected by a direct process at the surface. For the present study we were not able to measure the yield of atomic hydrogen as a function of the incident photon energy in order to prove that assumption. However, it is known from the literature that desorbing H atoms or positive ions may efficiently capture electrons when leaving the surface, giving rise to  $H^-$  photodesorbed ions. The negative electron affinity of diamond,<sup>30</sup> which results in the photoemission of electrons with very low kinetic energy, will certainly enhance the probability of electron attachment process.

Turning now to the *direct process* in the PSD, we note that this process has been observed mainly in the  $H^+$  photodesorption yield but also, with the reduced probability, in the  $H^-$  yield. It is characterized by a resonance at 287.5 eV, which is 2.0 eV lower than the threshold of the TEY. The energy position of that resonance is the same as the resonance in the surface sensitive NEXAFS where it was associated with a  $C(1s) \rightarrow \sigma^*(C-H)$  transition.<sup>25</sup> Therefore, the resonance at 287.5 eV may be associated to the  $H^+$  photo-

desorption following the core-level excitation of surface carbon atoms bonded to hydrogen atoms, H (ads). We suggest the following mechanism for this process. After the ionization of the  $C(1s)$  level, relaxation of the core hole occurs on a time scale of  $10^{-16}$ – $10^{-17}$  s, characteristic to the electronic processes (Ref. 3 and references therein). This electronic relaxation is much faster than any nuclear motion, responsible for desorption of  $H^+$  that occurs on a time scale of  $10^{-13}$ – $10^{-12}$  s.<sup>3</sup> Obviously, the relaxation of the  $C(1s)$  core hole takes place through a downward electronic transition involving the local valence band. It may result in a radiative (emission of x-ray) or a nonradiative transition, involving the emission of a third electron (Auger electron) as a mean to relax the excess electron energy. For the low  $Z$  elements, such as carbon, a nonradiative or Auger type relaxation process is preferred with a probability of nearly 1. Therefore, the most probable relaxation process of the  $C(1s)$  core hole is through an Auger transition leading to the emission of a  $C(KLL)$  Auger electron with  $\sim 270$  eV kinetic energy and formation of two localized valence-band holes. When the ionization occurs in a carbon atom bonded to a hydrogen atom, the localized two hole states in the C-H(ads) bond may cause the bond breaking and the emission of  $H^+$  through the charge separation as the most likely way to relax the large hole-hole repulsive interaction. This process may explain desorption of  $H^+$  ions, but cannot account for desorption of negative species, such as  $H^-$ .

The contribution of the resonance at 287.5 eV to the photodesorption of  $H^-$  ions is about five times less intensive than the contribution from the secondary electron processes. We speculate that this small resonance-driven contribution may be induced by some valence excitations of surface molecular species by electron impact or, alternatively, by the electron attachment from the diamond surface to an H atom or positive ion whose desorption was stimulated by a direct process.

## SUMMARY

The photodesorption of  $H^+$  and  $H^-$  ions has been studied in detail from various diamond surfaces. For each surface, two photodesorption processes were identified. The first one is an indirect process generated by the electron impact of secondary electrons from the bulk. In this case, the photodesorption of  $H^+$  and  $H^-$  ions may originate from the valence excitation of C-H bonds on the surface induced by the secondary electron emission. In addition, the photodesorption of  $H^-$  ions may also proceed through an electron attachment process involving photodesorbed H atoms and/or  $H^+$  ions. The second photodesorption process is a direct process characterized by a resonance at 287.5 eV, which is 2.0 eV lower than the threshold of the total electron yield. This process involves the ionization of the  $1s$  levels of carbon atoms, which are bonded to hydrogen adatoms at the surface.

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