

Electron induced functionalization of diamond by small organic groups

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Abstract. In this work, we show that the interaction of low energy electrons with CH₃CN molecules condensed on hydrogenated diamond substrates induces functionalization of the diamond. The process is discussed in terms of electron dissociation mechanisms of acetonitrile molecules and interaction of the subsequent fragments with the substrate. At 2 eV incident electron energy, the dissociative electron attachment reaction is alone operative, so that it is possible to demonstrate that these electrons induce exclusively covalent attachment of about 1 ML of H₂CCN fragments on diamond through C_{diam}-C and C_{diam}-N linkages and to propose a description of the microscopic steps involved in the process.

PACS. 78.68.+m Optical properties of surfaces – 73.20.-r Electron states at surfaces and interfaces – 79.20.-m Impact phenomena (including electron spectra and sputtering)

1 Introduction

Functionalization of semi-conductor materials by small organic groups is a fast growing field, in particular due to possible applications in chemical or biological sensors and in molecular electronics [1–3]. Moreover, functionalization by small organic groups may serve as route toward further chemical modifications of semi-conductor surfaces [4].

Wet and dry chemistry methods have been developed, some of them being photon or electron initiated [5,6]. Silicon has been the most extensively studied substrate. However, in the last years, due to its good electrical, chemical, thermal and mechanical properties, and to its biocompatibility, diamond has attracted growing interest. Another interest for using diamond substrates is that thin diamond films can now be easily deposited on microelectronic compatible substrates using methane/hydrogen gas mixtures by the microwave Chemical Vapor Deposition (mw-CVD) method [7].

In the case of electron driven processes, oxidation of InP (110) [6] has been obtained as the result of electron bombardment of O₂ molecules condensed on InP surfaces. The role of O₂⁻ resonant state formation was invoked to explain the reaction. Later, fluorination and oxidation of hydrogen passivated silicon substrates have been obtained as the result of electron bombardment of CF₄ and

H₂O films respectively condensed on hydrogen-passivated Si surfaces [8,9]. In these studies, electron energy dependences of the functionalization have shown that dissociative electron attachment (DEA) process must play a role in the reaction. However, in the different studies, detailed mechanisms of the functionalization processes of InP and Si substrates are not fully understood.

In this paper, we demonstrate in particular that the interaction of 2 eV energy electrons with condensed CH₃CN on hydrogen passivated polycrystalline diamond induces exclusively covalent attachment of H₂CCN fragments on diamond through C_{diam}-C and C_{diam}-N linkages. This reaction is initiated by DEA on CH₃CN, leading to H[•] + [H₂CCN]⁻ fragments. This DEA reaction is then followed by depassivation of the diamond surface via recombinative abstraction of H atoms giving H₂ desorption and the simultaneous bonding of H₂CCN fragments to the created dangling bond of diamond and electron ejection to vacuum.

2 Experiments

The experiments were performed in a UHV system (base pressure below 5×10^{-11} Torr) with a HREEL spectrometer (IB500 by OMICRON). All the spectra presented were obtained in the specular geometry with an incident direction of 55 degrees from the surface normal, at an incident

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energy of $E_0 = 5$ eV and with an overall resolution of ~ 5 meV, measured as the full width at half maximum (FWHM) of the elastic peak.

The samples, polycrystalline diamond films, are fitted to the end of the He flow cryostat, and were deposited on *p*-type doped silicon substrates by a standard mw-CVD using conditions described elsewhere [7]. The thickness of the as grown films was 5–10 μm with crystallite size of 1–2 μm . These CVD conditions result in fully hydrogen-terminated surfaces. The surface composition and phase purity of the films were examined ex-situ by various spectroscopic methods and photodesorption. Before performing the measurements these ex-situ hydrogenated samples were annealed to 400 °C in the UHV to desorb all species possibly physisorbed on its surface like water or hydrocarbons.

Bare diamond films surfaces were prepared in-situ by several annealing cycles to 1000 °C. In-situ hydrogenated diamond surfaces were prepared by exposure of the bare diamond to activated hydrogen during of 1–1.5 h. This was achieved by molecular gas flow over a hot (1850 °C) tungsten filament positioned 3 cm away from the sample surface. The surface temperature during this process was only few tens of degrees above room temperature, and the pressure of hydrogen was kept at 1×10^{-6} Torr by leaking hydrogen into the system and continuously pumping with a turbomolecular pump to maintain high-purity conditions.

In the present experiment, the condensed CH_3CN films were prepared by dosing 99.995% purity CH_3CN at 35 K with typical coverage of 1–2 monolayers. The hydrogenated diamond surfaces are known to be chemically very stable and we have checked that condensation of CH_3CN followed by desorption up to 400 K restore the HREEL spectrum of hydrogenated diamond.

The low energy electrons used to irradiate were produced by a tungsten filament (energy resolution approximately 350 meV) and the energies were changed by adjusting the bias voltage between the filament and the sample. Electron exposures of typically 10^{16} electrons/ mm^2 were used for the irradiation.

3 Results and discussions

Figure 1 shows, respectively, HREEL spectra of hydrogenated diamond (Fig. 1a), of 2 ML of CH_3CN condensed on hydrogenated diamond substrate before (Fig. 1b) and after (Fig. 1c) electron irradiation at 2 eV energy, and after evaporation of the condensed or physisorbed species by heating the irradiated film to about 400 K (Fig. 1d).

The spectrum of Figure 1a is quite well understood [10,11]. It is characterized mainly by a strong structure around 150 meV attributed to the mixing of lattice C–C vibrations with hydrogen termination bending modes, and its overtones around 300 and 450 meV, and by a loss feature at 362 meV attributed to C–H stretching modes. It contains in addition a loss at 180 meV generally associated with C–H bending vibration.

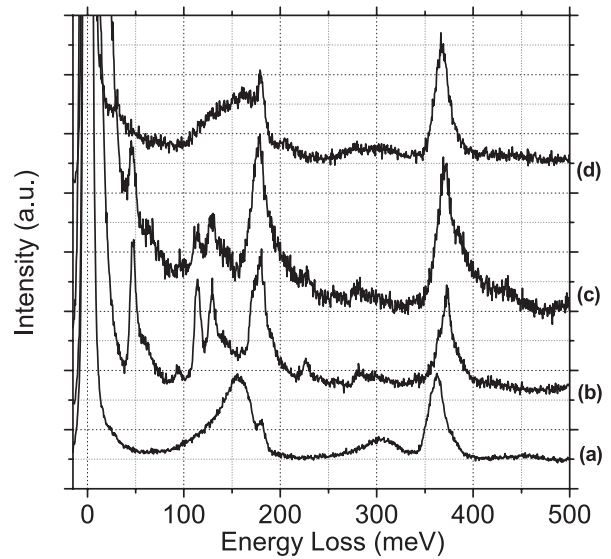


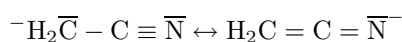
Fig. 1. HREEL spectra of hydrogenated diamond (a), of 2 ML of CH_3CN condensed on hydrogenated diamond substrate before (b) and after (c) electron irradiation at 2 eV, and after evaporation of the condensed or physisorbed species by heating the irradiated film to about 400 K (d).

The HREEL spectrum of condensed CH_3CN (Fig. 1b) is in general agreement with those obtained in previous studies [12,13]. Only the striking features are described in this paper, and we refer to previous publications for exhaustive discussion of this spectrum. This spectrum is mainly characterized by peaks associated to $\delta(\text{C–CN})$ bending modes around 48 meV, C–C stretching and methyl rock vibrations, respectively, at 117 and 129 meV, methyl bending mode at 180 meV, the $\text{C}\equiv\text{N}$ stretching mode at 280 meV and finally C–H stretching vibrations at 370 meV. This spectrum is only slightly modified upon irradiation by 2 eV electrons (Fig. 1c), essentially we observe a change in the relative intensities of the loss peaks.

After evaporation to 400 K of the irradiated film, which drives away all the physisorbed species, the HREEL spectrum shown in Figure 1d is observed. This spectrum, which corresponds to chemisorbed species on diamond, presents major differences with those of hydrogenated diamond and of condensed CH_3CN . Peaks at 50, 117, 129 meV are no more observed, whereas the $\text{C}\equiv\text{N}$ stretching vibration at 280 meV is still present, and new peaks show up at 32 and 200 meV, this last peak being associated with $\nu(\text{C=N})$ and/or $\nu(\text{C=C})$ vibrations. These results mean that species containing C=N and or C=C and species containing $\text{C}\equiv\text{N}$ bonds are chemisorbed on the diamond substrate. Also compared to the spectrum of the hydrogenated diamond we see that the 180 meV loss is more pronounced, that the C–H stretching vibration is shifted to higher energies, and finally that the 450 meV overtone of the C–C stretching vibration is no more observed which means that the vibrational signatures of hydrogenated diamond are no more observed in spectrum of Figure 1d. These transformations must be initiated by and

associated with electron dissociation processes in CH_3CN condensed layer on hydrogenated diamond since (i) hydrogenated diamond surfaces are known to be chemically very stable, and we have checked that condensation of few ML of CH_3CN on this surface followed by desorption at 400 K restore the original HREEL spectrum of the hydrogenated diamond, and since (ii) the interaction of 2 eV electrons on the hydrogenated diamond leads only to vibrational excitation, H^- desorption being observed only above 4.5 eV [7].

DEA is the only known electron dissociation mechanism in CH_3CN at energies below 4 eV. This process has been studied in the gas phase [14], and it has been shown that CN^- ions are observed around 2 eV, CHCN^- and CH_2CN^- around 3.2 eV. Since in the condensed phase, resonances are observed at energies about 0.8 eV lower than in the gas phase, and considering that the cross-section for CH_2CN^- formation is about $4 \times 10^{-23} \text{ m}^2$, i.e., two orders of magnitude higher than for HCCN^- or CN^- formation, we will consequently discuss the spectrum of Figure 1d exclusively in terms of interaction of CH_2CN^- and H^\bullet fragments with the hydrogenated diamond substrate. If we take into account (i) the fact that two mesomeric forms can be written for CH_2CN^- ions:



so that the negative charge in these ions is probably distributed around N and C atoms and (ii), that the 32, 180, 200 meV losses can be associated respectively with diamond- (CH_2CN) stretching, CH_2 scissor and $\nu(\text{C}=\text{C})$ and/or $\nu(\text{C}=\text{N})$ vibrational modes i.e., consistent with vibrational signatures of chemisorbed CH_2CN fragments through $\text{C}_{\text{diam}}-\text{C}$ and $\text{C}_{\text{diam}}-\text{N}$ covalent linkage on diamond, the overall mechanism for the functionalization reaction of diamond can then be described as follow:

1. DEA process: $e^-(2 \text{ eV}) + \text{CH}_3\text{CN} \rightarrow (\text{CH}_3\text{CN}^-)^* \rightarrow [\text{CH}_2\text{CN}]^- + \text{H}^\bullet$;
2. depassivation of the hydrogenated diamond surface via recombinative abstraction of H atoms by H^\bullet radicals [15];
3. simultaneous bonding of H_2CCN fragments through C or N linkage to the dangling bond of diamond and electron ejection in vacuum.

We have studied the functionalization of diamond at higher energies using the same procedure as at 2 eV. The results are shown in Figure 2, which represents in particular HREEL spectra obtained after bombardment of 1–2 ML of condensed CH_3CN on hydrogenated diamond, respectively, at 8 and 13 eV followed by evaporation of the condensed molecules at about 400 K. We see very clearly that species containing groups characterized by $\nu(\text{C}\equiv\text{N})$, $\nu(\text{C}=\text{N})$ and/or $\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{H})$ vibrations have been chemisorbed on the diamond substrate. However, because it is still possible to distinguish loss peaks associated to hydrogenated diamond, in particular around 150 and 360 meV, we may conclude that the substrate is only partially functionalized although it was submitted to the same electron exposure as at 2 eV incident energy.

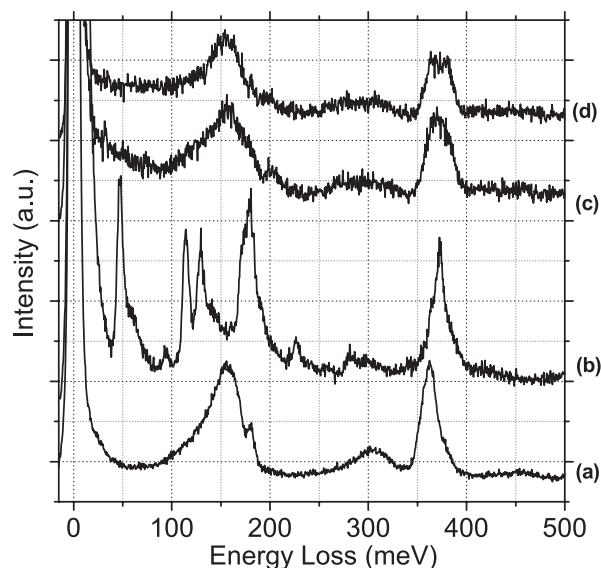


Fig. 2. HREEL spectra of hydrogenated diamond (a), of 2 ML of CH_3CN condensed on hydrogenated diamond substrate (b) and after electron irradiation at 8 and 13 eV respectively followed by evaporation of the condensed or physisorbed species by heating the irradiated film to about 400 K (c) and (d).

Concerning the mechanisms involved, they are not easy to establish since several DEA and dissociative processes into neutral fragments in CH_3CN molecules exist at these energies (including H^- formation [16]) and since electron stimulated desorption of H atoms and H^- ions from the passivated substrate is also possible [7].

4 Conclusions

We have demonstrated that the interaction of low energy electrons with 1–2 ML of condensed CH_3CN on hydrogenated substrates induces functionalization of the diamond by different organic groups contained in CH_3CN .

At 2 eV, the selectivity and characteristics of DEA process in CH_3CN allow efficient covalent attachment of CH_2CN groups to diamond substrate and the understanding of the microscopic steps involved in the process, namely, DEA leading to the formation of CH_2CN^- ions and H^\bullet fragments, depassivation of hydrogenated diamond via recombinative abstraction of H atoms by H^\bullet radicals and, finally, simultaneous bonding of H_2CCN fragments through C or N linkage to the dangling bond of diamond and electron ejection in vacuum.

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