

Diamond surface modification following thermal etching of Si supported hydrogenated diamond films by DBr

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Abstract

In this work, we study the modification of hydrogenated diamond films deposited on silicon resulting from its exposure to DBr followed by an annealing above 600 K, using high resolution electron energy loss spectroscopy (HREELS). This procedure results in silicon carbide SiC formation within the diamond film, as evidenced by the observation of a loss peak at 117 meV and its first harmonic at 233 meV in HREEL spectra. This diamond surface modification is interpreted as resulting from the reaction of products of the silicon support thermally activated etching with hydrogenated diamond.

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1. Introduction

Thin diamond films can now be easily deposited on microelectronic compatible substrates like silicon using methane/H₂ gas mixtures by microwave chemical vapor deposition (MW-CVD) method. Further exposition of these films to MW H₂ plasma leads to fully hydrogenated diamond films [1]. These hydrogenated diamond films have been extensively studied because of their many possible applications: (i) in microelectronics with a special interest in the hydrogen surface adsorption and hydrogen incorporation into grown films, since these parameters influence strongly their remarkable electronic properties like surface conductivity and negative electron affinity [2–4], or (ii) as a support for chemical and biological sensors [5–8] since it has been shown that these surfaces which are known to be chemically very stable can be functionalized by wet and dry methods, some of them being photon or electron

induced. In the context of functionalization by dry methods, the films are exposed to gases containing the interesting chemical groups to be attached to diamond. However, because silicon is spontaneously etched by different molecules, in particular those containing halogen atoms [9–13], unwanted reactions at diamond surfaces may be initiated by the released etched products in the case of silicon supported films.

In this paper, we report on reactions at diamond surfaces resulting from exposure to 8 L of DBr of polycrystalline hydrogenated diamond films deposited on silicon and from a subsequent heating. These reactions lead to the formation of silicon carbide SiC within the diamond film, as evidenced in high resolution electron energy loss (HREEL) studies by the presence of an energy loss peak at 117 meV. The results are interpreted in terms of reactions of Si etched products SiBr_{x=1–4} with hydrogenated diamond surface.

2. Experiment

The experiments were performed with a HREEL spectrometer consisting of a double monochromator and a

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single analyzer (model IB500 by OMICRON), housed in an ultra-high vacuum (UHV) system whose base pressure is kept below 5×10^{-11} Torr. All the spectra presented were obtained at room temperature, in the specular geometry with an incident angle of 55° from the surface normal and an overall resolution of ~ 5 – 6 meV, measured as the full width at half maximum of the elastic peak.

The samples, polycrystalline diamond films, were deposited on p-doped silicon substrates by microwave chemical vapor deposition (MW-CVD) using conditions described elsewhere [14]. The grown diamond film is 5–10 μm thick and contains crystallites having a size of 1–2 μm . After deposition the diamond films are further exposed to a MW H_2 plasma leading to fully hydrogen terminated films, whose surface composition and phase purity were examined ex situ by various spectroscopic methods and by photodesorption. Using this procedure, one face of our samples is made of silicon and the other one of hydrogenated diamond. Due to the holding system used to maintain the samples on the manipulator, the silicon back face of the studied substrates cannot be probed.

The ex situ grown films and plasma hydrogenated samples were transferred in air to be implemented in our experimental set up. Before performing experiments, the samples were annealed to 670 K in UHV to desorb all species possibly physisorbed on its surface like water or hydrocarbons. Bare diamond surfaces were prepared in situ by several annealing cycles to 1300 K, before being in situ hydrogenated by dosing atomic hydrogen. H_2 was thus flowed over a hot (2120 K) tungsten filament positioned 3 cm away from the sample surface for 1.5 h, while the chamber pressure was kept at 1×10^{-6} Torr. During this process the surface temperature was only a few tens of degrees above room temperature.

DBr (99% D atoms) was supplied by CEA (Saclay). Exposures are performed at room temperature and at a typical pressure of 2×10^{-8} Torr (without correction for ion gauge sensitivity) and are given in Langmuir (L).

3. Results and discussion

Fig. 1 shows respectively HREEL spectra of in situ hydrogenated Diamond (a), of this surface after being exposed to 8 L of DBr and heated first to 650 K (b) and then to 900 K (c). The spectrum 1(a) is quite well understood [15,16]. It is characterized mainly by a strong loss 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 feature centered at 362 meV and attributed to C–H stretching vibrations. It contains in addition a loss process at 180 meV generally associated by C–H bending vibration. This spectrum is not modified after exposure of the sample to DBr at room temperature. However if, afterwards, this exposed sample is heated we see clearly that a new loss peak is observed at 117 meV, together with its overtone at 233 meV (spectra 1(b) and 1(c)). Their

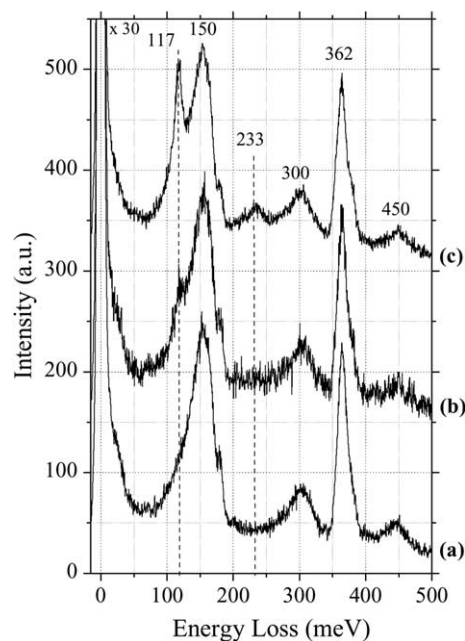


Fig. 1. HREEL spectra of in situ hydrogenated diamond (a), of the hydrogenated diamond after exposure to 8 L of DBr and heating to 650 K (b) and 900 K (c). The spectra were recorded at an incident electron energy $E_0 = 5$ eV, and normalized by setting the elastic peak intensity to 200.

intensities are increasing when the heating temperature is raised.

As explained in the experimental part, bare diamond surfaces are prepared in situ by several annealing cycles to 1300 K of a hydrogenated sample. The HREEL spectrum of bare diamond, shown in Fig. 2(a), is mainly characterized by a strong loss peak located around 154 meV engendered by C–C lattice vibrations and by a peak at 92 meV, which is attributed to a vibration mode of the car-

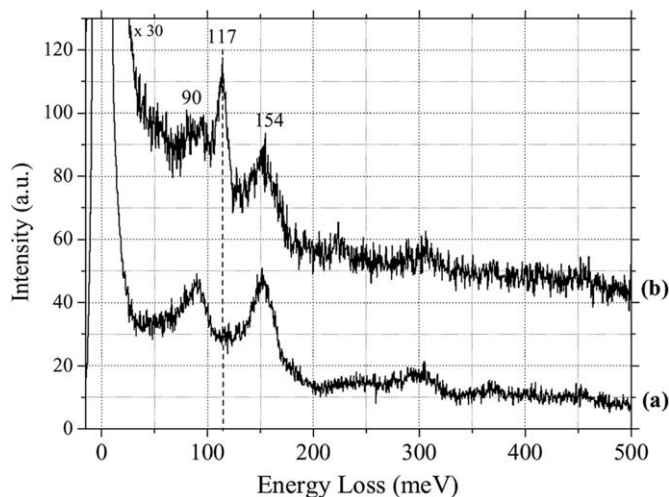


Fig. 2. HREEL spectrum of the bare diamond surface obtained by heating hydrogenated diamond substrate up to 1300 K (a). The spectrum (b) is associated to the modified surface, which results from the exposure of hydrogenated diamond to 8 L of DBr followed by heating to 1300 K. $E_0 = 5$ eV and $I_{\text{elastic}} = 200$ a.u.

bon dimers formed upon closing the surface dangling bonds (surface reconstruction) [16,17]. However once the hydrogenated sample has been exposed to DBr and heated up to 1300 K, the HREEL spectrum of bare diamond is no more observed as shown in Fig. 2(b). The peak at 117 meV is still present in the loss spectrum after such a thermal treatment, which leads in particular to the complete decomposition of hydrogenated species and results in the dehydrogenation of the surface. This demonstrates that the peak at 117 meV originates from the vibrational excitation of an atom or a hydrogen free chemical group, which is chemisorbed or even inserted in the upper layers of diamond lattice. This species was produced by a surface reaction involving hydrogenated diamond.

The 117 meV peak is in fact characteristic, in HREEL studies of silicon, of the presence of silicon carbide SiC formed with remaining carbon contaminant during the heating process [18]. In contrast it has been shown in HREELS studies of alkylsilane $C_xH_ySi_nH_b$ adsorption and alkyl group chemisorption on silicon surface, that the stretching frequency of C–Si bonds belonging to hydrogenated species is expected in the energy region 80–90 meV [19]. In Fig. 3 HREEL spectra of contaminated hydrogenated Si(111) ((a) and (b)) are compared with spectra of the modified diamond surface ((c) and (d)), resulting from DBr exposure and heating to 900 K, at two different incident electron energies. The contamination by carbon of the silicon surface occurred during the thermal treatment of a substrate polluted by residual vacuum hydrocarbons, as clearly identified in situ by Auger electron spectroscopy (AES). The loss at 117 meV is observed in spectra recorded

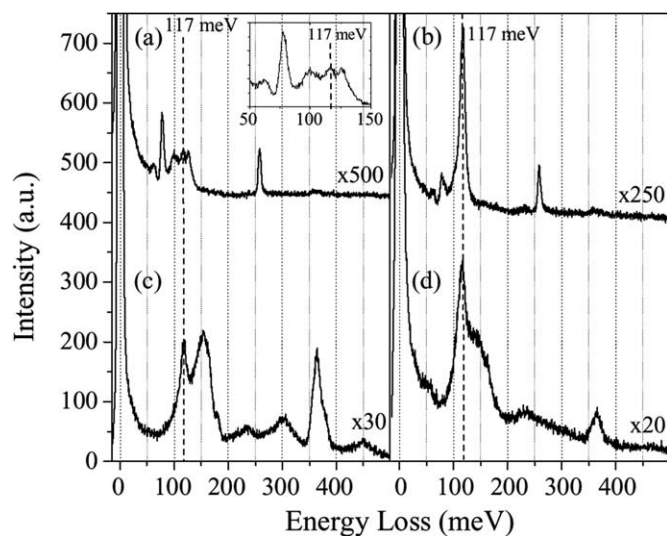


Fig. 3. HREEL spectra of hydrogenated Si(111) contaminated with carbon at $E_0 = 4$ eV (a) and 12 eV (b), compared with spectra of hydrogenated diamond after exposure to DBr and heating to 900 K at $E_0 = 5$ eV (c) (same spectrum as in Fig. 1(c)) and 12 eV (d). In the top left inset an expanded representation of the spectrum (a) is given for the 50–150 meV energy loss region. The hydrogen termination modes $\delta(\text{Si}-\text{H})$ and $\nu(\text{Si}-\text{H})$ are observed at 77 meV and 258 meV, respectively. For all spectra $I_{\text{elastic}} = 200$ a.u.

for both carbon contaminated silicon and modified hydrogenated diamond. Moreover, in both cases, the intensity of the considered loss increases as the incident electron energy used to record HREEL spectrum is increased from 4–5 eV to 12 eV. Nevertheless, such a comparison on energy loss intensities should be considered with caution, since the measured intensities for losses of a HREEL spectrum depends in particular on the substrate electron reflectivity, the crystalline characteristics, the stoichiometry.

As mentioned above, DBr interaction alone with our sample, i.e. at room temperature, does not modify the observed HREEL spectrum of the hydrogenated diamond surface. The sample needs to be heated. Then in order to explain the formation of $C_{\text{diam}}-\text{Si}$ bond, we must consider the thermally activated etching reaction by DBr of the silicon substrate, on which diamond film has been deposited. Etching of silicon by halogen containing molecules (plasma and temperature assisted) have been extensively studied. The etching reactions involve the formation of volatile silicon halide products which desorb in the gas phase. It has been shown in the particular that SiCl_2 is the main etching product observed from thermal desorption studies following HCl interaction with Si [9]. In the case of Br_2 adsorption, $\text{Si}-\text{Br}_{x=1-4}$ desorption products have been observed around 500 and 770 K [10].

Although there are no similar studies for DBr or HBr, we can assume that the results should be similar in nature. Then our observations must be understood as follows:

1. DBr interaction (chemisorption) with the silicon substrate.
2. Temperature induced desorption of SiBr_x .
3. Reaction of SiBr_x with the hot hydrogenated diamond surface which leads to the formation of $C_{\text{diam}}-\text{Si}$ bond(s) and presumably HBr molecules. The detailed mechanism of these last reactions being not easy to established. In the case of SiBr etched product, the reaction $C_{\text{diam}}-\text{H} + \text{SiBr} \rightarrow C_{\text{diam}}-\text{Si} + \text{HBr}$ is exothermic by 0.24 eV [20]. We believe that the silicon atoms are inserted in the diamond lattice, since the loss observed here at 117 meV has an energy very close from the loss attributed to the Fuchs–Kliwer phonon of SiC semiconductor surface [21].

4. Conclusion

We have studied DBr interaction with polycrystalline hydrogenated diamond films grown on silicon support using HREEL spectroscopy. We have shown that exposure of these samples at room temperature to 8 L of DBr does not modify the hydrogenated diamond surface. However, when the exposed samples are heated above 600 K, silicon carbide SiC is formed within the diamond film, since the characteristic loss peak at 117 meV is observed in the HREEL spectra. These results are interpreted in terms of thermally activated silicon etching products reaction with

the hydrogenated diamond surface. More generally, this work shows that when working with silicon supported grown films and with etching gases, this type of reaction should be taken into account.

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