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High resolution electron energy loss spectroscopy of hydrogenated polycrystalline diamond: Assignment of peaks through modifications induced by isotopic exchange

Shaul Michaelson [a], Yeshayahu Lifshitz [b], Alon Hoffman [a,*]

[a] Schulich Faculty of Chemistry, Technion — Israel Institute of Technology, Haifa 32000, Israel
[b] Deptartment of Materials Engineering, Technion — Israel Institute of Technology, Haifa 32000, Israel

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Abstract

In this work we unambiguously determine the origin of the different peaks which appear in the High Resolution Electron Energy Loss Spectrum (HREELS) of hydrogenated polycrystalline diamond films for an incident electron energy of 5 eV and loss energies extending to 700 meV. High quality diamond films deposited by hot filament chemical vapor deposition from various isotopic gas mixtures: $^{12}CH_4+H_2$, $^{12}CD_4+D_2$, $^{12}CH_4+D_2$, $^{12}CD_4+D_2$, $^{13}CH_4+H_2$ were characterized. The different vibrational modes, fundamentals and overtones, were directly identified through the modifications of the HREEL spectra induced by the isotopic exchange of H by D and ^{12}C by ^{13}C Three types of peaks were identified: (1) pure C–C related peaks (a diamond optical phonon at ~155 meV and its overtones at 300, 450 and 600 meV), (2) pure C–H related peaks (C–H bend at ~150 meV and C–H stretch of sp^3 carbon at 360 meV), (3) coupling of C–H and C–C peaks (510 meV peak due to coupling of the C–H stretch at 360 meV with either the C–C stretch or the C–H bend at ~155 meV). The overtones at 300, 450 and 600 meV (associated with electron scattering at diamond optical phonons) indicate a well defined hydrogenated diamond surface since they are absent in the HREEL spectrum of low energy ion beam damaged diamond surface.

Keywords: Optical phonon; Overtones; Hydrogenated diamond surface

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1. Introduction

The properties and associated practical applications of diamond films are significantly modified by their surface structure and composition. The chemical characterization of the very surface region of diamond films is thus most important. Fully hydrogenated diamond surfaces possess negative electron affinity (NEA) and a large surface conductivity which are strongly affected by the presence of adsorbents or sp^2 carbon [1].The most common surface treatment for preparation of well defined hydrogenated diamond surfaces is exposure to hydrogen plasma (usually microwave (MW) plasma) [2]. This treatment gives rise to a number of the interrelated surface phenomena: (1) surface termination of dangling bonds by hydrogen maintaining a truncated diamond surface with sp^3 hybridization and preventing surface reconstruction; (2) appearance of surface conductivity upon incorporation of appropriate absorbents, (3) creation of negative electron affinity (NEA) and (4) surface smoothing.

Various vibrational spectroscopies have been applied to characterize the composition of diamond films in the past two decades. Raman [3] and FTIR [4] are bulk sensitive methods while high resolution electron energy loss spectroscopy (HREELS) is sensitive to the surface chemical composition and bonding. The HREELS studies of diamond surfaces [5–25] report different loss features for similar hydrogenated diamond surfaces of different authors and some vibration loss features are not yet clarified. Table 1 summarizes the assignments of the peaks of the HREEL spectra by different groups.

In the present work we directly clarify the nature of all the different peaks (C–C related or C–H related) which appear in the HREEL spectra of hydrogenated polycrystalline diamond films. We achieve it by analysis of the modifications of the

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[*] Corresponding author.
E-mail address: choffman@tx.technion.ac.il (A. Hoffman).

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Table 1

HREELS Vibrational mode position	Assignment based on literature survey	Our present assignment
Hydrogenated diamond (C-12) surface		
~155 meV	C–H bending modes [5–11]; mixed C–H bend and C–C stretch modes [12–24]	Mixed ^{12}C–H bend and ^{12}C–^{12}C stretch modes
300 meV	First overtone of C–H modes [6,8–10]; first overtone of C–C modes [7,12,13,17–22].	First overtone of ^{12}C diamond optical phonon
358–362 meV	C–H stretching mode [4–32]	^{12}C–H stretching mode
450 meV	Second overtone of C–H modes [6,8,9]; second overtone of C–C modes [17–22].	Second overtone of ^{12}C diamond optical phonon
510 meV	Coupled C–H deformation and C–H stretching modes [5]; coupled C–C stretch and C–H bend modes [22,25].	Overlapping of both ^{12}C–H bend and ^{12}C–H stretching modes and ^{12}C–^{12}C stretch and ^{12}C–H bend modes
600 meV	Third overtone of C–C modes [22].	Third overtone of diamond optical phonon
Deuterated diamond (C-12) surface		
~110 meV	C–D bending modes [7–9,12,13]	^{12}C–D bending modes
150 meV	C–C stretching modes [7,12,13,16]	^{12}C–^{12}C stretching modes
~270 meV	C–D stretching modes [7–9,12–14,16,28,29]	^{12}C–D stretching modes
300 meV	First overtone of C–C mode [7,12]	First overtone of ^{12}C diamond optical phonon
~380 meV	–	Coupling of ^{12}C–D bend and ^{12}C–D stretch modes
420 meV	–	Coupling of ^{12}C–^{12}C stretch and ^{12}C–D stretch modes
450 meV	–	Second overtone of ^{12}C diamond optical phonon
Hydrogenated diamond (C-13) surface		
148 meV	–	Mixed ^{13}C–H bend and ^{13}C–^{13}C stretch modes
290 meV	–	First overtone of ^{13}C diamond optical phonon
358 meV	–	^{13}C–H stretching mode
435 meV	–	Second overtone of ^{13}C diamond optical phonon
508 meV	–	Overlapping of both ^{13}C–H bend and stretching modes and ^{13}C–^{13}C stretch and ^{13}C–H bend modes
580 meV	–	Third overtone of ^{13}C diamond optical phonon

HREEL spectra induced by the isotopic exchange of H by D and ^{12}C by ^{13}C. This exchange was performed by using an appropriate gas mixture for the CVD growth of the films: (1) complete exchange of D by H (using CD_4+D_2) or partial exchange (using CH_4+D_2 or CH_4+D_2) instead of (CH_4+H_2) as well (2) replacement of ^{12}C atoms ^{13}C (using $^{13}CH_4+H_2$ instead of $^{12}CH_4+H_2$). The completely exchanged samples were exposed to ex-situ MW-H (MW-D) plasma to ensure their H termination. (CH_4+H_2) deposited films were also bombarded by low energy argon ions for comparison between crystalline and amorphized surfaces. All samples were characterized by HREEL, XPS and electronic EELS (plasmon scattering). Our assignments of diamond-related HREELS peaks are summarized in Table 1.

2. Experimental

Hot filament (HF) chemical vapor deposited polycrystalline diamond films were grown using: methane/hydrogen ratio 1/99, pressure 50 Torr, filament (Re) temperature 2000 °C and silicon substrate temperature 800 °C [26]. The films were grown from gas mixtures of the following composition: $^{12}CH_4+H_2$, $^{12}CD_4+H_2$, $^{12}CH_4+D_2$, $^{12}CD_4+D_2$, $^{13}CH_4+H_2$. Hydrogenation was done ex-situ in a commercial Astex CVD microwave reactor (Astex model AX5010) at sample temperature of 800 °C and hydrogen pressure of 50 Torr.

The HREELS chamber is equipped with a Delta 0.5 spectrometer (VSI-SPECS) consisting of a double monochromator and a single analyzer housed in an ultra-high vacuum (UHV) system with base pressure of $\sim 8\times10^{-10}$ Torr. All spectra were recorded at room temperature in the specular geometry with an incident angle of 55° from the surface normal, incident energy of 5 eV and full width half maximum (FWHM) of 5–8 meV and up to loss energies of 700 meV. The HREELS chamber is attached to a second UHV system equipped with various surface analytical techniques allowing in-situ surface modification and characterization. The surface phase composition (plasmon losses) was analyzed in the second analytical chamber by electronic EELS with a primary electron energy of $E_p=500$ eV and FWHM of 0.7 eV. The hydrogenated diamond surface was ion beam damaged by sputtering with 500 eV Ar ions. The chemical composition of the surface was monitored by X-ray photoelectron spectroscopy (XPS, not shown).

3. Results

The HREEL spectra of the films deposited from the different gas mixtures are given in Fig. 1. The $^{12}CH_4+H_2$ ($^{12}CD_4+D_2$) film was exposed ex-situ to MW-H (MW-D) plasma for 20 min. The two other (partially exchanged samples) were measured as-grown. Prior to the HREELS measurements the samples were annealed at 450 °C under UHV conditions. The different vibrational modes are enumerated on top of Fig. 1 for clarity. Modes #2, #4, #6 are present in all spectra indicating they are associated with C–C vibrations. Peaks #1 and #3 appear only in spectra 1C and 1D of the CH_4+D_2 and CD_4+D_2, films, while peaks #5 and #7 appear only in spectra 1A and 1B of the $^{12}CH_4+H_2$ and $^{12}CD_4+H_2$ films. We attribute this appearance/disappearance of peaks to isotopic shifts related to the change of the reduced mass of the C–H mode by replacement of H by D. A full assignment of all peaks is given in the discussion section. Note that substitution of H by D via methane only (i.e. use of a gas mixture of $^{12}CD_4+H_2$ instead of $^{12}CH_4+H_2$) does not modify the HREEL spectrum while substitution through hydrogen only (i.e. use of a gas mixture of $^{12}CH_4+D_2$ instead of