AIP | Applied Physics Letters

Hydrogen bonding at grain surfaces and boundaries of nanodiamond films detected by high resolution electron energy loss spectroscopy

Sh. Michaelson, O. Ternyak, A. Hoffman, O. A. Williams, and D. M. Gruen

Citation: Applied Physics Letters **91**, 103104 (2007); doi: 10.1063/1.2779848
View online: http://dx.doi.org/10.1063/1.2779848
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/91/10?ver=pdfcov
Published by the AIP Publishing

APPLIED PHYSICS LETTERS **91**, 103104 (2007)

Hydrogen bonding at grain surfaces and boundaries of nanodiamond films detected by high resolution electron energy loss spectroscopy

Sh. Michaelson, O. Ternyak, and A. Hoffman[a]
Schulich Faculty of Chemistry, Technion, Israeli Institute of Technology, Haifa 32000, Israel

O. A. Williams
Institute for Materials Research, Hasselt University, Wetenschapspark 1, B-3590 Diepenbeek, Belgium and Division IMOMEC, IMEC, Wetenschapspark 1, B-3590 Diepenbeek, Belgium

D. M. Gruen
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439

(Received 3 May 2007; accepted 14 August 2007; published online 4 September 2007)

Hydrogenated nanodiamond films consisting of 300 and 10–30 nm grain sizes were examined by high resolution electron energy loss spectroscopy. C–H stretching modes were identified at 350, 360, and 375 meV. The mode at 375 meV was enhanced in the case of 10–30 nm grain size and it is stable up to *in situ* annealing to >800 °C. Complete hydrogen desorption occurs upon annealing to 1000 °C. Exposure of the nanodiamond film to atomic hydrogen results in a strong quenching of the 375 meV C–H mode, most likely due to preferential etching of (sp^2)-carbon-hydrogen at the surface and grain boundaries of the films. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2779848]

The properties and associated practical applications of diamond films are significantly modified by their surface structure and composition.[1] The characterization of diamond grain size (especially in nanometric scale) requires the use of quite complicated transmission electron microscopy usually combined with x-ray diffraction analysis.[2] The quest of additional complementary techniques providing information about the grain size, grain boundaries, and film surface is of high importance.

In the present letter, we apply high resolution electron energy loss spectroscopy (HR-EELS) to study the hydrogen bonding configuration on nanodiamond film surfaces. Hydrogen is the key component of the gas mixture usually used for diamond nucleation and growth by chemical vapor deposition (CVD) methods. In our recent works, we applied secondary ion mass spectroscopy and Raman spectroscopy to correlate the retention of hydrogen atoms in the films with diamond grain size.[3,4] In addition, the assignment of different HR-EELS peaks of hydrogenated diamond surface was done based on gas mixture isotopic exchange.[5] In this letter, we present HR-EELS studies of submicro- and nanocrystalline diamond films consisting of ~300 and 10–30 nm grain sizes at the film's surfaces.

The nanocrystalline diamond film was deposited by microwave (MW) CVD at a frequency of 2.45 GHz using a microwave power of 1200 W and total gas pressure of 200 Torr onto a Si substrate at 800 °C.[6] Prior to deposition, the silicon substrate was seeded mechanically in solution with diamond powder. The gas mixture composition was 1.4% CH_4, 1% H_2, and 97.6% Ar (growth rate 2.7 μm/h), resulting in a grain size in the 10–30 nm range.[6]

The microcrystalline film was grown by hot filament (HF) CVD using a methane/hydrogen ratio of 1/99, pressure of 50 Torr, and filament (Re) temperature 2000 °C onto a Si substrate at 800 °C with a primary nucleation density of $\sim 5 \times 10^{10}$ particle/cm^2. After 1 h of deposition, the average grain size at the film's surface was 300 nm.[7]

The HR-EELS chamber is equipped with a Delta 0.5 spectrometer (VSI-SPECS) consisting of a double monochromator and a single analyzer housed in an ultrahigh vacuum system with base pressure of $\sim 8 \times 10^{-10}$ Torr.[5] 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 at half maximum of 5–8 meV, up to loss energies of 800 meV.

Figure 1 shows the HR-EELS of the microcrystalline diamond film as a function of annealing temperature. The shape of the spectrum [Fig. 1(a)] is dominated by five main peaks positioned at 155, 300, ~360, 450, and ~510 meV ($1\ \text{meV} = 8.066\ \text{cm}^{-1}$). These modes were extensively investigated in our previous work[5] and here, we give a short description of these peaks for convenience. Mode 1 at ~155 meV is a superposition of a C–C stretch and a C–H bending vibration (the latter shifts to 108 meV upon replacement of H by D). Modes 2 and 4 (300 and 450 meV energy loss) are pure C–C vibrations, most likely the first and second overtones of the diamond optical phonon positioned at 150 meV.[5] Peak 3 (359 meV energy loss) is attributed to C–H stretching mode and will be discussed in detail below. Peak 5 at ~510 mV is a coupled C–H stretch mode positioned at ~360 and ~155 meV bands. As may be seen in Fig. 1(a), the general shape of the spectra is nearly unaffected up to annealing to 800 °C, while annealing to 1000 °C results in elimination of hydrogen associated features (360 and 510 meV peaks) and a new peak appears near 90 meV. This mode was associated with C=C dimer positioned on bare hydrogen surface.[8]

The detailed peak fitting procedure of the C–H stretching HR-EELS mode [Fig. 1(b)] reveals at least three different contributions at ~350, ~360, and ~375 meV. The first two are most likely associated with diamond (111) and (100) surfaces,[9] while the last one may be attributed to sp^2 hybridized carbon (symmetric olefinic or aromatic sp^2 CH stretch).[10,11] Upon annealing to 800 °C, the maximum peak

---

[a] Author to whom correspondence should be addressed; electronic mail: choffman@tx.technion.ac.il

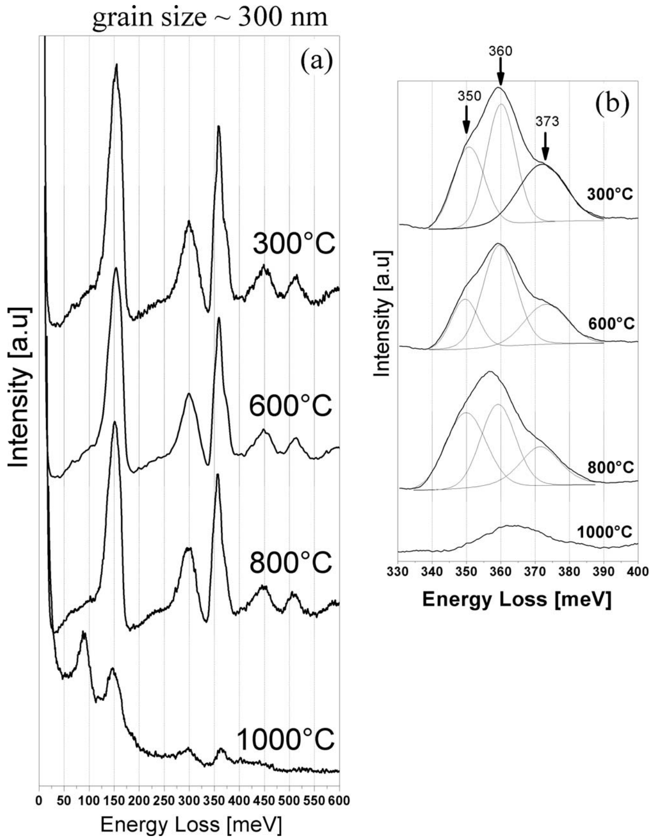

FIG. 1. (a) HR-EEL spectra of as-deposited HF CVD films as a function of annealing temperature. The primary electron energy was 5 eV and FWHM of 7–8 meV. The shape of the spectrum is nearly unchanged up to $T_A = 800$ °C. The $T_A = 1000$ °C results in complete hydrogen desorption (the absence of ~360 meV peak) alongside with appearance of C═C dimer mode at 92 meV. (b) Detailed analysis of HR-EELS C–H stretching mode of as-deposited HF CVD diamond film. Peak fitting procedure reveals three different contributions at ~350, ~360, and ~375 meV energy loss.

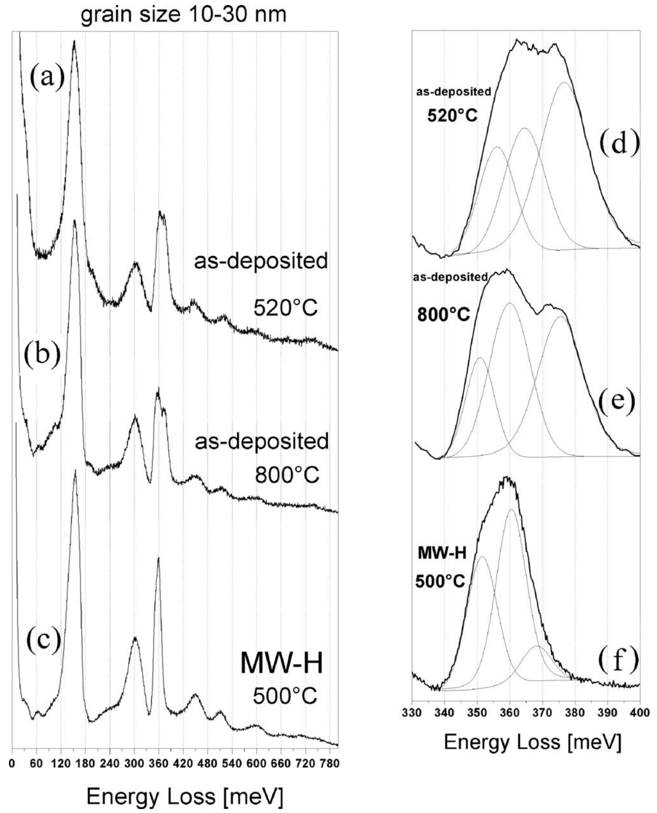

FIG. 2. HR-EEL spectra of MW CVD deposited nanodiamond films with 10–30 nm grain size. (a) As-deposited sample *in situ* annealed to 520 °C. (b) As-deposited sample followed subsequent *in situ* annealing to 800 °C. (c) As-deposited sample followed *ex situ* MW hydrogenation for 10 min and consequent *in situ* annealing to 500 °C. [(d)–(f)] Detailed analysis of HR-EELS C–H stretching mode [data originated from spectra (a)–(c) correspondingly]. Note the splitting of C–H stretching mode of as-deposited nanodiamond sample due to strong contribution of 375 meV mode. The last mode disappears following *ex situ* MW-H treatment [spectra (c) and (f)].

position is slightly shifted to smaller loss energies (from 359 to 357 meV), while the sp^2 associated mode at ~375 meV is still prominent. Based on the peak fitting procedure, the ratio of 375 meV mode area to the total C–H stretching area is 0.255 (in the case of 800 °C annealing). According to thermal stability studies of different kinds of hydrogenated carbon matrixes,[12–16] annealing to a temperature of ~600 °C results in desorption of hydrogen atoms alongside with hydrocarbon species independently of the method used for amorphous carbon film preparation. This allows us to attribute the ~375 meV HR-EELS mode to hydrogen bonded to sp^2 hybridized carbon positioned at diamond grain surface and boundary, which may be stable up to these high temperatures. This suggestion may be confirmed by HR-EELS studies of the nanodiamond film discussed below.

Figures 2(a)–2(c) show the HR-EEL spectra of the nanodiamond film (grain size of 10–30 nm). Detailed analysis of C–H stretching mode is shown in Figs. 2(d)–2(f). Figure 2(a) corresponds to the *as-deposited* sample followed by *in situ* annealing to 520 °C. It is dominated by mixed C–C stretching and C–H bending mode at 155 meV, the overtones of diamond optical phonon at 300 and 450 meV, C–H stretching vibration at 360–375 meV, and mixed C–H associated mode at ~515 meV. Note the strong splitting of the C–H stretching mode in this spectrum: the two maxima are positioned at ~360 and ~375 meV, reflecting hydrogen bonding to sp^3 and sp^2 carbon correspondingly [Fig. 2(d)]. Subsequent annealing to 800 °C does not change the general shape of the spectrum [Fig. 2(b)], while the relative intensity of two different C–H stretching modes is somewhat changed [Fig. 2(e)]. This change may be associated with thermal induced desorption of hydrocarbon species as well as to $sp^2 \rightarrow sp^3$ carbon transformation.[13] Based on the peak fitting procedure, the ratio of 375 meV mode area to the total C–H stretching area is 0.431 [Fig. 2(e)].

The as-deposited nanodiamond film was exposed *ex situ* to MW activated hydrogen plasma (MW-H) for 10 min. This treatment is known to increase the surface smoothing[17] alongside with preferential etching of sp^2 carbon. The HR-EEL spectrum of *ex situ* MW-H treated and *in situ* annealed to 500 °C nanodiamond sample is shown in Fig. 2(c). The splitting of C–H stretching vibrations disappears and now, this mode is centered at 360 meV [Fig. 2(f)] and the 375 meV mode's intensity is strongly reduced. Exposure to MW activated hydrogen results in preferential etching of sp^2 hybridized carbon resulting in a relative increase of the sp^3 hybridized carbon on the film's surface.

Now, we compare the HR-EELS analysis of as-deposited MW CVD nanodiamond (Fig. 2) with previously discussed as-deposited HF CVD submicron crystalline samples (Fig. 1). As can be seen in Fig. 1(b), the HR-EEL spectrum of as-deposited HF CVD films with ~300 nm grains also display contributions at ~350, ~360, and ~375 meV within the C–H stretching modes which are stable up to 800 °C. Obviously, the ratio of grain boundaries in the case of nanodiamond films (10–30 nm grains) exceeds that of submicron crystallites (~300 nm grains). Since the contribution of the ~375 meV mode is much more prominent in the case of nanometric grains, this mode may be associated with hydrogen bonded to sp^2 the hybridized carbon positioned on the *surface* and *grain boundary* of the nanodiamond film. This is a very exciting feature. In our studies of hydrogen adsorption on ion irradiated diamond surfaces,[18] we concluded that nearly all kinds of hydrogenated carbon decompose near ~600 °C. This is in complete agreement with the other studies of thermal stability of diamondlike carbon which undergoes erosion/destabilization at temperature about 600 °C independently of deposition process.[12–16] The present results show that sp^2 hybridized carbon is stable up to temperatures above 800 °C. This finding allows one to distinguish the hydrogenated sp^2 hybridized carbon bonded to diamond grains from chemisorbed (or physisorbed) molecules on polycrystalline diamond surface by simple annealing procedure.

It is very interesting to note at this stage the possible correlation between the ~375 meV HR-EELS mode and the well-known Raman 1140 cm^{-1} peak of nanodiamond. It was shown in the works of many authors,[19–21] including us,[4] that the 1140 cm^{-1} Raman peak is attributed to C–H bending mode of sp^2 carbon and positioned most likely in the diamond grain boundary. Both peaks (Raman 1140 cm^{-1} and HR-EELS ~375 meV mode) are attributed to (sp^2)-carbon-hydrogen vibration. Both peaks are stable up to elevated temperatures[22] where hydrogen bonded to amorphous carbon undergoes desorption. Both peaks are strongly enhanced in the case of nanodiamond grains.[23] Therefore, our results strongly suggest that the ~375 meV mode can be attributed to the stretching of the same C–H vibration, which contributes to the 1140 cm^{-1} Raman peak (currently attributed to ν_1 mode of *t*-PA; the bending of sp^2-C–H). Both peaks may serve as indication of nanocrystalline character of diamond films. However, due to different probing depths of Raman and HR-EEL spectroscopies (tens or hundreds of nanometers in the case of Raman and 1–2 nm in the case of HR-EELS) quantitative comparison of these two peaks is impossible. It should be stressed that this assignment of the 375 meV peak is circumstantial; a computational study of this mode is in progress in our laboratory.

We conclude, therefore, that hydrogen bonding to surfaces and grain boundaries of nanodiamond films display a clear contribution to the HR-EELS at 375 meV which differs from bonding to the microcrystalline diamond surfaces whose main contribution is centered around 360 meV. The ~375 meV mode is stable up to elevated temperatures of ~800 °C where all kinds of hydrogenated amorphous carbon are decomposed. The intensity of this mode is drastically decreased following *ex situ* treatment in MW activated hydrogen plasma, most likely due to preferential etching of sp^2 carbon bonded to diamond grain surfaces and boundaries.

This research project was carried out with the financial support of the Israeli Academy of Science and the Technion Fund for promotion of research.

[1] P. Reichart, G. Datzmann, A. Hauptner, R. Hertenberger, C. Wild, and G. Dollingeer, Science **306**, 1537 (2004).

[2] Y. Lifshitz, X. M. Meng, S. T. Lee, R. Akhveldiany, and A. Hoffman, Phys. Rev. Lett. **93**, 056101 (2004).

[3] Sh. Michaelson, O. Ternyak, Y. Lifshitz, and A. Hoffman, Appl. Phys. Lett. **90**, 031914 (2007).

[4] Sh. Michaelson, Y. Lifshitz, O. Ternyak, and A. Hoffman, Appl. Phys. Lett. **89**, 131918 (2006).

[5] Sh. Michaelson, Y. Lifshitz, and A. Hoffman, Appl. Phys. Lett. **89**, 223112 (2006).

[6] D. Zhou, D. M. Gruen, L. C. Qin, T. G. McCauley, and A. R. Krauss, J. Appl. Phys. **84**, 1981 (1998).

[7] R. Akhvlediani, I. Lior, Sh. Michaelson, and A. Hoffman, Diamond Relat. Mater. **11**, 545 (2002).

[8] A. Lafosse, A. Hoffman, M. Bertin, D. Teillet-Billy, and R. Azria, Phys. Rev. B **73**, 195308 (2006).

[9] T. Aizawa, T. Ando, K. Yamamoto, M. Kamo, and Y. Sato, Diamond Relat. Mater. **4**, 600 (1995).

[10] S. T. Lee and G. Apai, Phys. Rev. B **48**, 2684 (1993).

[11] J. Ristein, R. T. Stief, L. Ley, and W. Beyer, J. Appl. Phys. **84**, 3836 (1998).

[12] M. Benlahsen, B. Racine, K. Zellama, and G. Turban, J. Non-Cryst. Solids **283**, 47 (2001).

[13] R. Kalish, Y. Lifshitz, K. Nugent, and S. Prawer, Appl. Phys. Lett. **74**, 2936 (1999).

[14] Ch. Wild and P. Koidl, Appl. Phys. Lett. **51**, 1506 (1987).

[15] J. K. Walters, J. S. Rigden, R. J. Newport, S. F. Parker, and W. S. Howells, Phys. Scr., T **57**, 142 (1995).

[16] M. Lejeune, M. Benlahsen, and R. Bouzerar, Appl. Phys. Lett. **84**, 344 (2004).

[17] B. D. Thoms and J. E. Butler, Phys. Rev. B **50**, 17450 (1994).

[18] M. Bertin, A. Lafosse, R. Azria, Sh. Michaelson, O. Ternyak, and A. Hoffman, Appl. Phys. Lett. **90**, 061918 (2007).

[19] A. C. Ferrari and J. Robertson, Philos. Trans. R. Soc. London, Ser. A **362**, 2477 (2004).

[20] H. Kuzmany, R. Pfeiffer, N. Salk, and B. Günther, Carbon **42**, 911 (2004).

[21] T. Lopez-Rios, D. Mendoza, F. J. Garcia-Vidal, J. Sanchez-Dehesa, and B. Pannetier, Phys. Rev. Lett. **81** 665 (1998).

[22] Sh. Michaelson and A. Hoffman, Diamond Relat. Mater. **15**, 486 (2006).

[23] Raman spectra of these two kinds of diamond films were recently accepted to publication: Sh. Michaelson, O. Ternyak, R. Akhvlediani, O. A. Williams, D. Gruen, and A. Hoffman, Phys. Status Solidi A **204**, 2860 (2007) [see Figs. 2(b) and 2(d)].