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High resolution electron energy loss spectroscopy surface studies of hydrogenated detonation nano-diamond spray-deposited films

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ABSTRACT

Nano-diamond films composed of 3–5 nm grains prepared by the detonation method and spray deposited onto silicon substrates were examined by high resolution electron energy loss spectroscopy (HR-EELS), Raman spectroscopy and transmission electron microscopy. The HR-EEL spectrum of the annealed and hydrogenated films displays dominant C–H losses at 360–365 meV; the diamond optical phonon and its overtones. These results suggest that the films reveal well defined hydrogenated diamond surfaces on the nanometric scale. Detailed analysis of the diamond optical phonon overtone revealed a red-shift of the basic C–C vibration by 5 meV. We attribute this shift to a phonon quantum confinement effect detected by HR-EELS spectroscopy.

1. Introduction

Nano-diamond particles formed by detonation methods form a most interesting state of carbon, with size distributions in the nm regime.[1] The physical properties of diamond surface are strongly affected and determined by adsorbed species and their bonding configuration, surface impurities and morphology.[2] Commercially available nano-diamond powders are also treated in order to define and control the diamond particle size and the powder impurity concentration. The surface chemical properties of nano-diamond particles are expected therefore to depend on the source of the powder and their chemical processing history, and an experimental technique is required to investigate the extent and role of the non-sp^3 carbon shell of each nano-diamond.[3] Among the large number of surface sensitive methods used to investigate carbon surfaces high resolution electron energy loss spectroscopy (HR-EELS) has the distinguished advantage to render surface information of the surface hydrogen bonding configuration.[4] This is most important as the chemical, physical and electronic properties of such surfaces are readily determined by hydrogen bonding.[5] While the HR-EEL spectrum of single crystal diamond surfaces and polycrystalline diamond surface consisting of diamond grains in the micron to nano-size range deposited by chemical vapor deposition (CVD) methods had been extensively investigated by us and others[6–18]; the HR-EELS of detonation nano-diamond powder, to the best of the authors knowledge, has not been reported.

In the present study we report on a HR-EELS study of the chemical surface properties of hydrogenated nano-diamond particles produced by detonation processes obtained from a commercial source and spray deposited by us onto a silicon substrate to form a continuous film. The films were produced using a commercial nano-diamond powder purchased from Nanostructured and Amorphous Materials Inc. with a size range of 3–5 nm, spherical-like isometric shaped particles and purity of >97%.[19] The HR-EELS experiments were carried out using incident electron energies in the 5–10 eV range with a resolution of 5–6 meV. The as deposited films were first examined by Raman and transmission electron microscopy (TEM) to ensure their quality in terms of their phase composition and grain size. An indication of the surface versus sub-surface phase composition was obtained from conventional electron energy loss (EELS) experiments carried out using 500 and 1000 eV incident electron energies to vary the elastic mean free path and thus control the surface versus sub-surface sensitivity of the measurement. The hydrogen bonding to the films were studied following annealing to 400, 600, 700 and 800 °C in ultra high vacuum (UHV) followed by exposure to thermally activated hydrogen after each annealing temperature.

Our surface studies reveal a red-shift in the diamond optical phonon as detected by HR-EEL spectroscopy. We attribute this effect to a phonon confinement phenomenon in nano-diamond, previously detected by Raman spectroscopy.[20–27] This effect is reflected in the observed red-shift of the diamond optical phonon mode measured by Raman spectroscopy of nano-diamond particles reaching ~8 cm^{-1} for few nm sized grains. Recently, a red-shift of the diamond Raman peak due to the quantum confinement effect was reported for single nano-diamond particles as large as 90 nm in size.[24]

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2. Experimental

Films were produced using a commercial nano-diamond powder purchased from Nanostructured and Amorphous Materials Inc. with a stated size range of 3–5 nm, spherical-like isometric shaped particles and purity of >97%.[19] A solution of this nano-diamond powder was produced by mixing 0.1 g in 20 mL methanol, followed by ultra-sonification for 1 h. A film was then deposited onto a silicon substrate using a nitrogen spray system to a thickness of >1 μm. The transmission electron microscopy (TEM) measurements were carried on as deposited films and after annealing to 800 °C using a TEM operated at 200 keV. The Raman spectrum was measured using a commercial Ranishow spectrometer using a 514.5 nm incident photon excitation. The HR-EELS measurements were performed using a Delta 0.5 spectrometer (VSI-SPECS) consisting of a double monochromator and a single analyzer housed in the ultra high vacuum (UHV) system, operated with base pressure of 8×10^{-10} Torr. All spectra were recorded in specular mode with an incident angle of 55° from the surface normal, incident energies of 5–10 eV, full width half maximum (FWHM) of 5–6 meV and up to loss energies of 650 meV. The high energy EELS measurements were carried out using 1000 and 500 eV incident electrons in a backscattering geometry. In-situ hydrogenation was performed using a hydrogen thermal cracker (EPI-AHS 7884) housed in the ultra high vacuum system. The hydrogenation experiments, vacuum annealing, HR-EELS and EELS measurements were carried out sequentially without exposure of the sample to ambient conditions. The hydrogenation experiments were carried out for 30 min with a 10^{-7} Torr hydrogen partial pressure.

3. Results and discussion

The bulk properties of the as deposited films were examined with Raman spectroscopy in the 1000–1800 cm^{-1} range and it is shown in Fig. 1. A typical Raman spectrum of the as deposited films displays an intense and clear diamond line at 1330 cm^{-1} along with broad peaks centered at ~1580 and 1628 cm^{-1}. The downshifting of this Raman line for the nano-diamond, as compared to the reference single crystal diamond at 1332.2 cm^{-1}, has been associated with a phonon quantum confinement effect within the nano-diamond particles and it was previously discussed in the literature.[20–26] The Raman spectrum of the as deposited films does not display the 1140 cm^{-1} peak, associated with hydrogen bonding in nano-diamond films, in contrast to the films deposited by chemical vapor deposition (CVD) methods.[28–31] The inset in Fig. 1 shows a typical TEM micrograph of the spray-deposited detonation type nano-diamond film, used to verify the microstructure and particle size of the as deposited film. A similar electron micrograph was obtained for films annealed to 800 °C in vacuum. The TEM sample was prepared by lifting a portion of the deposited film with a micromanipulator and positioning it onto a TEM grid. This procedure avoids sample preparation artifacts, ensuring that the measured material reflects the structure of the original agglomerated film. As can be seen from this figure the diamond particle sizes range from 3 to 5 nm with an apparent non-diamond shell <0.5 nm thick. As seen in this figure the diamond particle cores display very clear crystallinity. These results are in agreement with previous TEM pictures taken from similar films as supplied by the manufacturer thus showing that the spray deposition method does not affect the structure of the nano-diamond particles.

To compare the bulk with the surface carbon phase composition, electronic EEL spectroscopy was utilized at two incident electron energies, 500 eV and 1000 eV. Fig. 2 displays the EEL spectra recorded from the nano-diamond films after annealing to 400 °C. Both spectra display two peaks centered at ~34 and ~23 eV, associated with the bulk diamond plasmon and either the diamond surface plasmon or an amorphous carbon plasmon, respectively.[32] The EELS measured at 1000 eV also shows a clear shoulder at ~18 eV. The nature of this peak is not clear but it is possibly associated with a plasmon localized at the boundary between two adjacent nano-diamond particles within agglomerate.[33,34] As can be seen from Fig. 2 the relative intensity ratio of the 34 to the 23 eV peaks is larger in the EELS measured at

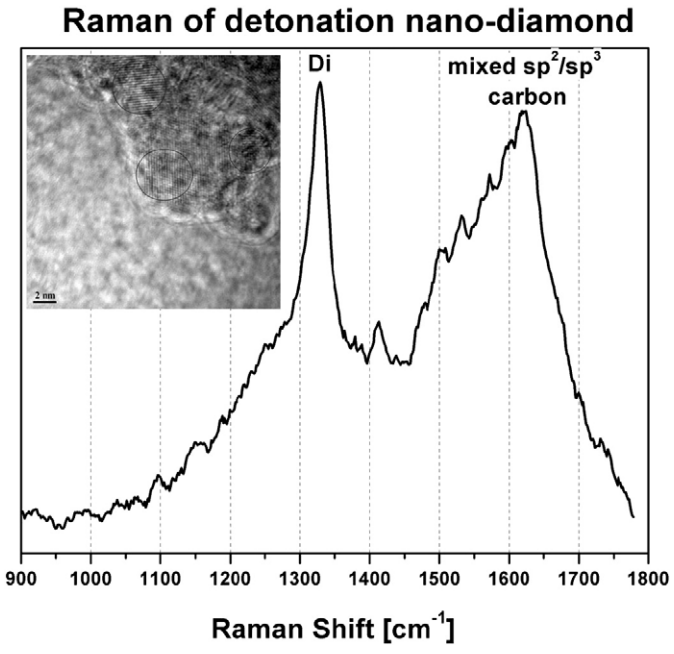

Fig. 1. Raman spectrum of a spray-deposited nano-diamond film. The spectrum displays the diamond optical phonon line at 1330 cm^{-1} and sp^2 related peak at ~1580 and 1628 cm^{-1}. Note the absence of hydrocarbon related peaks at 1140 and 1480 cm^{-1}. In the inset high resolution TEM picture of the nano-diamond film carried out at 200 keV is shown. Similar electron micrographs were observed for the as deposited films and after annealing to 800 °C. As can be seen from this figure the particle size is in the 3–5 nm range.

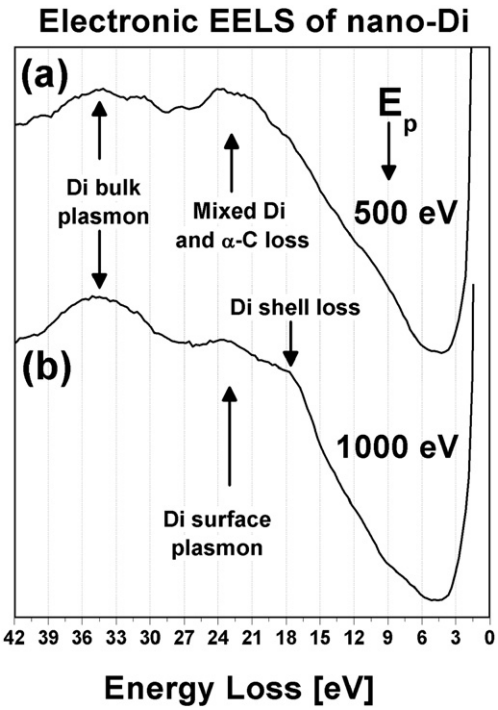

Fig. 2. Electronic EEL spectra (plasmon losses) of detonation nano-diamond film annealed at 400 °C and measured using incident electron energy of (a) 500 eV and (b) 1000 eV. Note the distinguished diamond bulk (~33 eV) and surface (~23 eV) plasmon losses.