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RAMAN AND EELS STUDIES ON NANOCRYSTALLINE DIAMOND PREPARED IN A LOW PRESSURE INDUCTIVELY COUPLED PLASMA

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ABSTRACT

Nanocrystalline diamonds with several hundred nm in diameter have been prepared in a 13.56 MHz low pressure inductively coupled CH_4/H_2 or $CH_4/CO/H_2$ plasma. The bonding structures were investigated by Raman spectroscopy and electron energy loss spectroscopy (EELS). Visible (514 nm) and UV (325, 244 nm) excited Raman spectra with CO additive exhibit peaks at ~1150 cm^{-1} assigned to sp3 bonding and at 1332 cm^{-1} due to zone center optical phonon mode of diamond, respectively. It indicates that the UV excitations are possibly sufficient to excite the σ state of both sp2- and sp3-bonded carbon. The high resolution EELS (HREELS) spectra with CO additive show peaks at ~1100 cm^{-1} assigned to C-C stretching vibration of sp3 bonding and at ~700 cm^{-1} corresponding to the bending vibration of sp3 bonding. It is qualitatively agreement with the Raman spectra. Furthermore the EELS spectrum without CO additive exhibits two peaks at 284 eV and at 292 eV corresponding to π^* states and σ^* states, respectively, and is similar to that of graphite rather than that of sp^2-rich amorphous carbon. The EELS spectrum with CO additive, on the other hand, shows a peak at 292 eV due to σ^* states and is similar to that of diamond. A slight peak appears at ~285 eV corresponding to π^* states. It consequently implies that the particles almost consist of sp^3 bondings and that the small amount of sp^2 bondings are considered to exist in grain boundaries. The EESL spectra are consistent with the results of Raman scattering and HREELS.

INTRODUCTION

Amorphous and nanostructured carbon materials have attracted considerable attention in the last twenty years since the chemical vapor deposition of diamond was developed, followed by fullerenes and carbon nanotubes. From applied perspectives, they are being extensively studied for electron-emitting elements, cold-cathode sources, and ultrahard tribological coatings, etc. From fundamental perspectives, on the other hand, the structure of these materials contains both three-fold coordinated (sp^2-bonded) and four-fold coordinated (sp^3-bonded) carbon atoms. The phonon density of state (PDOS) and the fraction of sp^3 bondings were quantitatively measured by Raman spectroscopy[1,2] and electron energy loss spectroscopy (EELS).[3]

Nanocrystalline diamond films also have drawn remarkable attention[4] because they have a low coefficient of friction and low electron emission threshold voltage. The small grain size (approximately 5-100 nm) gives films with valuable tribology and field-emission properties,[5] being compared with those of conventional polycrystalline diamond films. We have tried to prepare diamond films in a 13.56 MHz low pressure inductively coupled plasma (ICP).[6] The resultant deposits were found to be nanocrystalline diamond and diamond-like carbon (DLC) films as characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM). The CO additive to a CH_4/H_2 plasma brought about the morphological change from a platelet deposit to a particle one. The diameter of particles were 200-500 nm. The vibrational studies of the nanocrystalline diamond were performed with Raman spectroscopy[7] and high resolution EELS (HREELS).[8] The qualitative analysis of the bonding structures has been carried out.

EELS in TEM has been demonstrated as powerful techniques for performing microanalysis and studying the electronic structure of materials. The energy loss near edge structure (ELNES) is sensitive to the crystal structure. The C-K edge of diamond and graphite are typical example. For trigonal sp^2-bonded carbon, the spectrum within the first 30 eV of the edge can be separated into two broad features, corresponding to the π^* states between 282 and 288 eV and the σ^* states between 290 and 320 eV, whilst for tetrahedral sp^3-bonded carbon only the σ^* peak is observed between 289 and 320 eV.[9] Bruley's two-window technique by integrating intensities of the π^* and σ^* peaks has demonstrated the quantitative analysis of the sp^2 content in the samples.[3] In this paper, we first review the previous Raman and HREELS results, then report the high resolution TEM (HRTEM) observations and the EELS measurements of the nanocrystalline diamond.

EXPERIMENT

The detailed description of the low pressure ICP system and the deposition procedure was previously reported elsewhere.[6] The nanocrystalline diamond and DLC were grown in an ICP at 1 kW, 900 ℃ of the substrate (silicon wafer) temperature, 2 hours of the deposition duration, in a CH_4/H_2 or $CH_4/CO/H_2$ plasma at 45 to 50 mTorr.

The procedures of the Raman measurements with three different excitation wavelength (514, 325, 244 nm) and the HREELS measurements were described previously.[7,8] The EELS measurements were carried out by using a Hitachi HF-3000 dedicated HRTEM fitted with a GATAN-GIF parallel acquisition electron energy loss spectrometer (PEELS) operating at 300 keV. The microscope vacuum was less than 1.2×10^{-6} Pa. The typical energy resolution of the instrument was approximately 0.7 eV. To acquire EELS, the typical CCD readout times were 5 sec.

RESULTS AND DISCUSSION

As we have reported previously,[6] the CO additive to a CH_4/H_2 plasma brought about the morphological change from a platelet deposit to a particle one. The diameter of particles were 200-500 nm. Besides, the number of encountered particles was increased with increasing CO concentration. Figure 1 shows the 514 nm excited Raman spectra with different [CO]. The Raman spectrum without CO additive [Fig. 1(a)] exhibits two peaks at ~1355 cm^{-1} (*D* peak) and at ~1580 cm^{-1} (*G* peak) assigned to sp^2 bonding. New peaks appear at ~1150 cm^{-1} and at ~1480 cm^{-1} with CO additive [Fig. 1(b)]. The former peak is derived from sp^3 bonding[10] although it was recently proposed[11] that the peak is attributed to sp^2 bonding of *trans*-polyacetylene oligomer. Both *D* and *G* peaks become relatively small compared with those of Fig. 1(a). With increasing [CO] as shown in Fig. 1(c), the intensity of the peak at ~1150 cm^{-1}

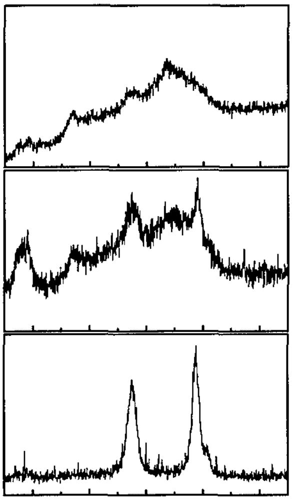

Figure 1. 514 nm excited Raman spectra with different gas mixture: (a) $[CH_4]/[CO]=4.5/0$ sccm, (b) $[CH_4]/[CO]=4.5/1.0$ sccm, and (c) $[CH_4]/[CO]=4.5/10$ sccm, respectively.

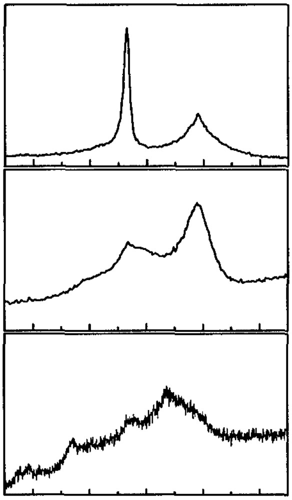

Figure 2. Raman spectra of Sample C ($[CH_4]/[CO]=4.5/10$ sccm) with different excitation wavelength: (a) 514 nm, (b) 325 nm, and (c) 244 nm, respectively.

becomes strong, while the *G* peak turns into a shoulder and the *D* peak becomes small. Figure 2 shows a sequence of Raman spectra of [CO]=10 sccm with different excitation wavelength. Compared with the spectrum of 514 nm excitation, the 325 nm excited Raman spectrum exhibits a clear peak at 1332 cm^{-1} and the remarkable enhancement of the peak at ~1580 cm^{-1}, while the peak at ~1150 cm^{-1} turns into a shoulder. In 244 nm excited Raman spectrum, the peak at 1332 cm^{-1} is only enhanced whereas the peak at ~1580 cm^{-1} is weakened. Neither peak nor shoulder can be recognized at ~1150 cm^{-1}. The 514 nm excited Raman spectra do not exhibit a clear diamond peak at 1332 cm^{-1}, though the peak due to sp^3-bonded carbon network appears at ~1150 cm^{-1}. This is explained by the resonance enhancement in the Raman cross section in the sp^2-bonded carbon network.[12] The enhancement of the peaks at both 1332 cm^{-1} and ~1580 cm^{-1} in the 325 nm excitation suggests that the resonance enhancement of Raman cross section due to sp^2-bonded carbon still remains and that the σ - σ * transition in both sp^2- and sp^3-bonded carbon is possibly induced. The remarkable enhancement of the peak at 1332 cm^{-1} and the diminution of the peak at ~1580 cm^{-1} in the 244 nm excitation reveals that the resonance Raman effect due to sp^2-bonded carbon is suppressed and that the σ - σ * transition in both sp^2- and sp^3-bonded carbon is probably dominant.[1,2]

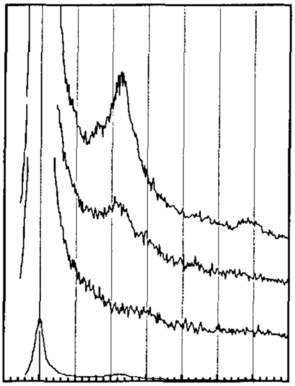

Figure 3. HREELS spectra with various $[CH_4]/[CO]$: (a) $[CH_4]/[CO]=3.0/0$, (b) $[CH_4]/[CO]=4.5/8.0$, and (c) $[CH_4]/[CO]=4.5/10$, in sccm, respectively. The elastic peak for (c), reduced by a factor of 25, is shown in comparison.

Figure 3 presents the HREELS spectra with different [CO]. In Fig. 3(a) without CO additive, the spectrum has a faint peak at ~1500 cm^{-1} derived from C=C stretching mode of three-fold bonded carbon atoms.[13] The whole spectrum is similar to that of a single crystal graphite (0001) surface.[14] With CO additive as shown in Fig. 3(b), one can see a peak at ~1100 cm^{-1}, which is assignable to C-C stretching mode of four-fold bonded carbon atoms.[13] The peak at ~1500 cm^{-1} disappeared. With increasing [CO] as shown in Fig. 3(c), the intensity of the peak at ~1100 cm^{-1} became strong. In addition, a shoulder centered at ~700 cm^{-1} appeared. These features of the vibrational DOS are consistent with the theoretical results for random network models of t-aC.

Figure 4 shows the HRTEM image of platelet deposit without CO additive. Fig.4(b) corresponds to the high magnification image of the bottom left-hand side of Fig. 4(a). The lattice image is clearly shown in Fig. 4(b). The interplanar spacing is 0.203 nm, which is agreement with the *d* value of graphite (110). The EELS spectrum corresponding to Fig. 4(a) is shown in Figure 5. It exhibits two peaks at 284 eV and at 292 eV corresponding to π * states and σ * states, respectively, and is similar to that of graphite rather than that of sp^2-rich amorphous carbon.[3] In case of anisotropic materials like this platelet deposit, it is difficult to estimate accurately the fraction of sp^2/sp^3 by using Bruley's two-window technique. In graphite the π * transition requires a transfer of momentum parallel to the *c*-axis, while the momentum transfer of the σ * transition is perpendicular to the *c*-axis.[15]

Figure 6 shows the HRTEM image of a part of particle deposit with [CO]=10 sccm. Fig.6(b) corresponds to the high magnification image of the bottom left-hand side of Fig. 6(a). The careful observation reveals that the particle consists of small particles of approximately several tens of nanometers in diameter. The lattice image is clearly shown in Fig. 6(b). The

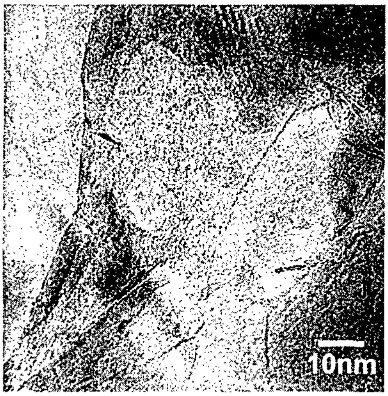

Figure 4(a). HRTEM image of the deposit with $[CH_4]/[CO]=4.5/0$ in sccm.

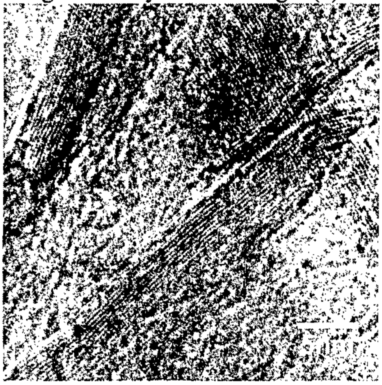

Figure 4(b). The high magnification image of the bottom left-hand side of Fig. 4(a).

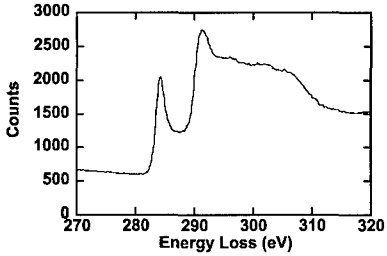

Figure 5. EELS spectrum corresponding to Fig. 4(a)

interplanar spacing is 0.206 nm, which is agreement with the *d* value of diamond (111). The EELS spectrum corresponding to Fig. 6(a) is shown in Figure 6. It shows a peak at 292 eV due to σ * states and is similar to that of diamond rather than sp^3-rich tetrahedral amorphous carbon.[3] A slight peak appears at ∼285 eV corresponding to π * states. The small amount of sp^2 bondings are considered to exist in grain boundaries between small grains of several ten nm in diameter.

CONCLUSIONS

The bonding structures of nanocrystalline diamonds prepared in a 13.56 MHz low pressure inductively coupled CH_4/H_2 or $CH_4/CO/H_2$ plasma were investigated by Raman spectroscopy, HREELS, and EELS. The EELS spectrum without CO additive exhibits two peaks at 284 eV and at 292 eV corresponding to π * states and σ * states, respectively, and is similar to that of graphite rather than that of sp^2-rich amorphous carbon. The EELS spectrum with CO additive, on the other hand, shows a peak at 292 eV due to σ * states and is similar to that of diamond. It consequently implies that the particles almost consist of sp^3 bondings and that the small amount of sp^2 bondings are considered to exist in grain boundaries. The EESL spectra are consistent with the results of Raman scattering and HREELS.

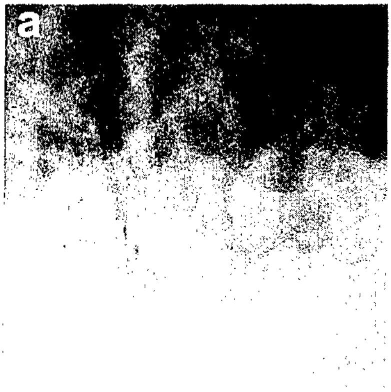

Figure 6(a). HRTEM image of the deposit with [CH_4]/[CO]=4.5/10 in sccm.

Figure 6(b). The high magnification image of the bottom left-hand side of Fig. 6(a).

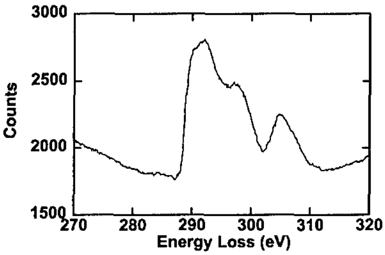

Figure 7. EELS spectrum corresponding to Fig. 6(a)

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