Characterization of $sp^3$ content in amorphous carbon films

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Q-carbon (quenched carbon) is a newly discovered amorphous phase of carbon [1], and shows extraordinary physical properties such as room-temperature ferromagnetism and high-temperature superconductivity by boron doping [2]. Despite much interest, the research of Q-carbon is limited because of the difficulty in preparation of Q-carbon using rapid nonequilibrium laser processing. In this study, we prepared Q-carbon by adjusting the $sp^3$ content in diamond-like carbon (DLC) films and the laser energy density of pulsed laser annealing (PLA).

The amorphous DLC films are fabricated on sapphire $Al_2O_3(0001)$ substrates using a pulsed laser deposition technique with a KrF excimer laser ($\lambda = 248$ nm). The $sp^3$ content in the films varied between 20% and 42% by changing the laser energy density. To determine the $sp^3$ content in the films, X-ray photoemission spectroscopy (XPS) measurements were carried out on the beamline BL-5, at the Hiroshima Synchrotron Radiation Center in Hiroshima University with non-monochromatic $Mg$ $K\alpha$ X-ray source ($h\nu = 1253.6$ eV). C 1$s$ core-level spectra were measured under an ultrahigh vacuum of $\sim 10^{-7}$ Pa using a VSW hemispherical analyzer. The total energy resolution was about 1.8 eV. The binding energy of the films was corrected using the peak position of molybdenum spectra. Before measurements, the films were annealed at 100 °C under ultrahigh vacuum ($\sim 10^{-6}$ Pa) for 1 h to clean the film surface. PLA was performed on the DLC films using the KrF excimer laser with energy densities between 0.5 and 1.2 J/cm$^2$ at ambient atmosphere and temperature.

Figure 1 shows the XPS spectra of the C 1$s$ core-level for the as-grown DLC films. A peak at the binding energy of $\sim 284$ eV was observed in the spectra for all the films. The peak position of the films moved towards higher binding energy, with slight broadening, as the laser energy density increased. Results of the spectral fitting are also shown in Fig. 1. After subtraction of a Shirley background, the C 1$s$ spectra of the films were fitted using a Gaussian-Lorentzian mixed function. Lorentzian linewidth was set to 0.095 eV [3]. In this fitting process, for simplicity, symmetric line shapes were assumed, and one component for each $sp^3$ and $sp^2$ bond was considered. Full-width-half-maximum (FWHM) of peaks was set to the same value in each film. The experimental results were well reproduced by the three components with peak positions of 283.9, 284.9, and 286.5 eV. The peaks of $\sim 284$ and $\sim 285$ eV corresponded to $sp^2$ carbon atoms and $sp^3$ C-C bond, respectively [4]. The feature at 286.5 eV was assigned to C-O contamination formed on the film surface due to air exposure [5]. Gaussian linewidth was estimated from FWHM of peaks to be 1.7, 1.5, 1.8 eV for the films with laser energy densities of 0.4, 0.8, and 1.3 J/cm$^2$, respectively.

The $sp^3$ content in the films was determined from the ratio of the corresponding $sp^3$ peak area over the sum of $sp^3$ and $sp^2$ peak areas to be 20%, 35% and 42% for the laser energy density of 0.4, 0.8, and 1.3 J/cm$^2$, respectively. The $sp^3$ content in the films increased with increasing the laser energy density. This indicated that the $sp^3$ content in the DLC films was successfully varied by changing the laser energy density during deposition. These results are qualitatively in good agreement with the result recently reported by Joshi [6].

Since DLC films with different $sp^3$ content were obtained, PLA was performed on the DLC films. Consequently, for the combination of 20% $sp^3$ content and laser density of 1.0 J/cm$^2$, as well as 42% $sp^3$ and 0.5 J/cm$^2$, the films showed characteristic features of Q-carbon: filamentary nanostructures, the presence of a $\Gamma$ peak in the Raman spectrum, room-temperature ferromagnetic behavior (Fig. 2), and $\sim 80% sp^3$ content. The results indicate that Q-carbon can be obtained by using a proper combination of $sp^3$ content in DLC films and an appropriate PLA energy density [7].
**FIGURE 1.** XPS spectra of C 1s core-level for the as-grown DLC films prepared with the laser energy density of (left) 0.4, (middle) 0.8, and (right) 1.3 J/cm². The results of spectral fitting are also shown. Open circles are experimental data, red lines are the fitting result, black lines are the Shirly background, blue lines are the component used for the fittings.

**FIGURE 2.** Field dependence of magnetization ($M$-$H$ curve) for the 20-sp³ and 1.0-PLA film, measured at 300 K.

**REFERENCES**