

## XPS study on DCL films with various film thickness

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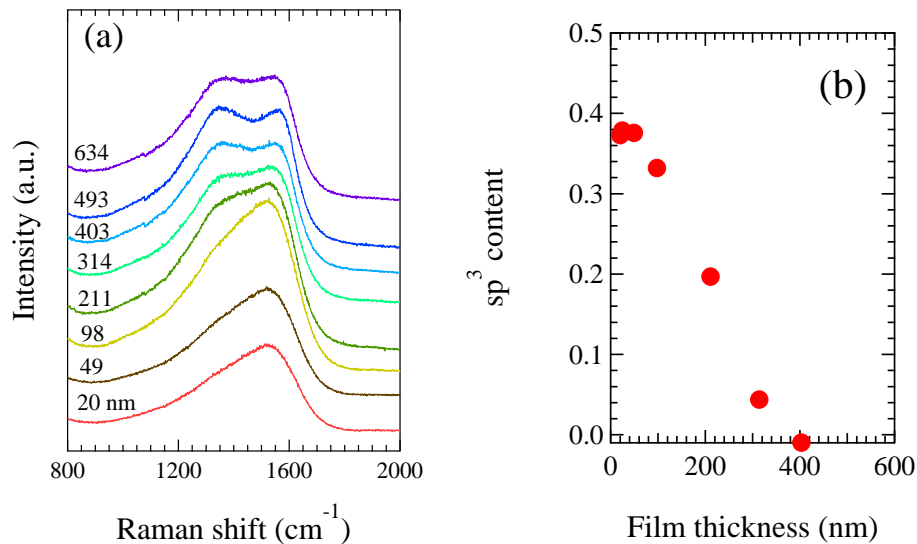
Diamond-like carbon (DLC) is a metastable form of amorphous carbon containing a significant  $sp^3$  content. It shows a high mechanical hardness, chemical inertness and optical transparency [1], depending on the  $sp^3$  content. Thus, the  $sp^3$  content is an important parameter that determines the properties of DLC. X-ray photoemission spectroscopy (XPS) and Raman spectroscopy techniques are widely used to determine the  $sp^3$  contents in DLC films, while XPS is relatively surface sensitive and Raman spectroscopy is more bulk sensitive. There are a number of studies on the  $sp^3$  content in DLC films with film thickness ranging from nanometer to several tens of micrometer order. However, only few studies for the thickness dependence of  $sp^3$  content in DLC films have been shown so far. It is beneficial to know how the  $sp^3$  content changes with the film thickness of DLC films from both viewpoints of fundamental science and applications. In this study, we prepared DLC films with various film thickness and examined the film thickness dependence of  $sp^3$  content in DLC films by means of XPS and Raman spectroscopy.

The amorphous DLC films were fabricated on sapphire  $Al_2O_3(0001)$  substrates using a pulsed laser deposition technique with a KrF excimer laser ( $\lambda = 248$  nm). Before film deposition, the substrates were heated at 573 K for 1.5 h in a vacuum of  $4 \times 10^{-7}$  Pa for the surface cleaning. Film deposition was performed at 300 K in a vacuum of  $4 \times 10^{-7}$  Pa. Laser fluence was 1.1 J/cm<sup>2</sup> and deposition rate was  $\sim 6$  nm/min. The films thickness was controlled by changing the deposition time and was varied from 20 to 634 nm. Raman spectroscopy measurements of DLC films were performed using a micro-Raman spectrometer with a 532-nm laser (JASCO NRS-5100). 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 1s 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 373 K under ultrahigh vacuum ( $\sim 10^{-6}$  Pa) for 1 h to clean the film surface.

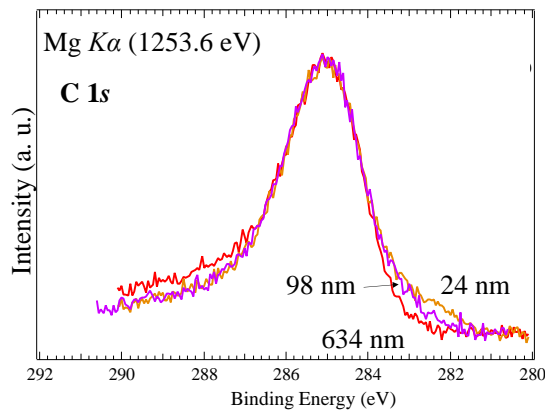
Figure 1(a) shows the Raman spectra of the DLC films. A peak at  $\sim 1550$  cm<sup>-1</sup> and shoulder structure at around 1350 cm<sup>-1</sup> were observed in the spectrum for 24-nm-thick film. The shoulder structure at  $\sim 1350$  cm<sup>-1</sup> developed to become a peak as the film thickness increased. For the obtained spectra, spectral fitting was performed using a Gaussian function. The experimental data was correctly fitted with three peaks. The three components had peak positions of 1140-1170,  $\sim 1400$ , and  $\sim 1560$  cm<sup>-1</sup>. The peak of 1140-1170 cm<sup>-1</sup> was assigned to nanocrystalline diamond [2,3]. The peaks of  $\sim 1400$  and  $\sim 1560$  cm<sup>-1</sup> correspond to the so-called D and G peaks, respectively. The  $sp^3$  content in the DLC films was estimated from full-width-half-maximum, FWHM of G peaks [4]. The results are shown Fig. 1(b). The  $sp^3$  content in the DLC films decreased as the film thickness increased; the  $sp^3$  content reduced from approximately 37 % at 24 nm to 0% over 400 nm. In order to check the film thickness dependence of the  $sp^3$  content in the DLC films, XPS measurements of the films were also conducted.

Figure 2 shows the XPS spectra of the C 1s core-level for the DLC films with film thickness of 24, 98 and 634 nm. A peak at the binding energy of  $\sim 285$  eV was observed in the spectra for all the films. The peaks of  $\sim 285$  eV corresponded to  $sp^3$  C-C bond [5]. The peak position of the films did not move and always located at  $\sim 285$  eV regardless of film thickness. The results of XPS measurements are inconsistent with those of Raman spectroscopy. The thickness dependence of  $sp^3$  content in DLC was observed in Raman spectroscopy measurements, but it was not in XPS measurements. A possible reason is the difference in the probing depth between the two methods. Raman spectroscopy is a bulk sensitive method and the probing

depth is more than thousands of nm. By Raman spectroscopy measurements, the  $sp^3$  content in the entire film can be evaluated. On the other hand, XPS is a relatively surface sensitive method and the probing depth is estimated to be a few nm near the surface in this study. By XPS measurements, the  $sp^3$  content near the film surface can be examined. If the surface of the DLC films is modified or/and is covered with contaminations which are not easy to remove our cleaning procedure, the XPS spectra for all of the films should be identical regardless of film thickness of DLC. More bulk sensitive XPS measurements help examine this consideration.



**FIGURE 1.** (a) Raman spectra for the DLC films with various film thickness. (b)  $sp^3$  content in the DLC films as a function of film thickness.



**FIGURE 2.** C 1s core-level spectra for the DLC films with the film thickness of 24, 98, 634 nm.

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