Changes of chemical bonding of diamond-like carbon films by atomic-hydrogen exposure

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Introduction

In our previous study, we have annealed diamond-like carbon (DLC) films under an atomic-hydrogen exposure, and found that the structural ordering (graphitization) of the films occurred during annealing at a substrate temperature of 400°C [1]. In this study, unhydrogenated DLC films deposited by pulsed laser deposition (PLD) have been annealed under an atomic-hydrogen exposure in an ultrahigh vacuum chamber. We carried out in-situ observation of the chemical bonding of the film surfaces using SR-PES after atomic-hydrogen exposure. We also investigated the structure of the films exposed to atomic hydrogen by visible Raman spectroscopy.

Experimental

A KrF excimer laser with a wavelength of 248 nm was used for ablation of the graphite target. The graphite target (99.99%) was 25 mm in diameter. The substrate used was a Si(100) wafer. Annealing under an atomic hydrogen exposure was performed in an ultrahigh vacuum chamber, whose base pressure was of the order of 10^-8 Pa. The deposited films were exposed to atomic hydrogen generated by a hot tungsten filament in a hydrogen atmosphere. The pressure of hydrogen gas was set at 0.01 Pa.

Results and Discussion

Fig. 1 shows the photoelectron spectrum of C 1s core level of an as-deposited DLC film with 310 eV photons by SR. The escaping depth of photoelectrons from the surface was estimated to be several angstroms. The best fits to the C 1s core level spectra of our samples needed two main components. We identified one of the main components with the higher binding energy of 285.3 eV with the sp³ hybrids or C-H bonds, according to the higher binding energy of the C 1s core level in diamond than graphite. Another component with the lower binding energy of 284.5 eV was identified with the sp² hybrids. Furthermore, small contents of C-O bonds were detected at 286.6 eV, which is attributed to some residual contaminations formed on the surfaces of the samples due to air exposure.

Fig. 2 shows the photoelectron spectra of C 1s core level of a DLC film exposed to atomic hydrogen at (a) 400°C and (b) 700°C for 3 min at a detection angle of 60° to the surface normal.

![Fig. 1: Photoelectron spectrum of C 1s core level of a DLC film at a detection angle of 60° to the surface normal.](image1.png)

![Fig. 2: Photoelectron spectra of C 1s core level of a DLC film exposed to atomic hydrogen at (a) 400°C and (b) 700°C for 3 min at a detection angle of 60° to the surface normal.](image2.png)

Fig. 1 shows the photoelectron spectrum of C 1s core level of an as-deposited DLC film with 310 eV photons by SR. The escaping depth of photoelectrons from the surface was estimated to be several angstroms. The best fits to the C 1s core level spectra of our samples needed two main components. We identified one of the main components with the higher binding energy of 285.3 eV with the sp³ hybrids or C-H bonds, according to the higher binding energy of the C 1s core level in diamond than graphite. Another component with the lower binding energy of 284.5 eV was identified with the sp² hybrids. Furthermore, small contents of C-O bonds were detected at 286.6 eV, which is attributed to some residual contaminations formed on the surfaces of the samples due to air exposure.

Fig. 2 shows the photoelectron spectra of C 1s core level of a DLC film exposed to atomic hydrogen at (a) 400°C and (b) 700°C for 3 min with 310 eV photons by SR. In Figs. 1 and 2, the sp³ component centered at 285.3 eV is increased in its intensity by atomic-hydrogen exposure at 400°C. On the other hand, the sp³ component decreases with increasing exposure time of atomic hydrogen at 700°C. It is found that the change in chemical bonding by atomic hydrogen exposure at 700°C contrasts sharply with that at 400°C. We also found that the sp³ fraction was higher at the film surfaces than the subsurfaces.

Similarly, the intensity of π states in the valence-band spectra decreased at 400°C with increasing exposure time, whereas it increased at 700°C as the exposure time increased. The Raman spectrum for the film exposed to atomic hydrogen at 400°C showed that the clustering of sp³ carbon atoms progressed inside the film near the surface even at such a low temperature as 400°C.

References


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