Influence of compressive load on microstructure of micro-scaled DLC structures produced by FIB-CVD

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Abstract. Influence of compressive load on microstructure of micro-scaled diamond-like carbon (DLC) structures was investigated by high-resolution electron transmission microscopy (HRTEM) analyses. The micro-scaled structures were produced by the focused ion-beam chemical vapor deposition method. The compressive loads were applied by a dynamic ultra micro hardness tester equipped with a flat-tip diamond indenter. Microgrid images in HRTEM observation and selected area diffraction patterns were varied by the compressive loads. The variations revealed that constituent atoms arranged disorderly in DLC were clustered by compressive loads. Electron energy loss spectroscopy measurements indicated that sp³ fraction in DLC was decreased by the compressive load. Consequently, it was suggested that graphitic clusters were formed in the microstructure of DLC by the compressive loads.

1. Introduction

A focused ion-beam chemical vapor deposition (FIB-CVD) method has attracted strong interests as one of the promising technologies for production of three-dimensional micro-/nano-scaled structures [1]. The FIB-CVD method has made the production process more simple, and has realized production of complex-shaped structure. Diamond-like carbon (DLC) can be deposited by the FIB-CVD from accessible hydrocarbons, and has superior properties such as high hardness, high elastic modulus and high wear resistance. Micro-/nano-scaled DLC structures produced by the FIB-CVD method are, therefore, expected to apply for future micro/nano-electromechanical systems (MEMS/NEMS) and other nanotechnology fields. As a matter of fact, production of nanodevices has been attempted utilizing a combination of the FIB-CVD and DLC [2].

In view of practical applications for MEMS/NEMS, it should be took into account that the micro-/nano-scaled DLC structures will be subjected to various mechanical loads, and they must cause considerable influence on DLC microstructures that contribute to properties of DLC. While influence of internal compressive stress on microstructures of amorphous carbon films has been investigated [3], the influence of direct mechanical loads on microstructures of micro-scaled DLC structures is not yet fully studied. In this study, therefore, micro-scaled DLC rectangular column specimens produced by the FIB-CVD method were loaded by uniaxial compressive loads, and their influence on microstructures of the micro-scaled DLC specimens were investigated by high-resolution transmission electron microscopy (HRTEM) in detail.
2. Experiments

2.1. Production of specimens and compressive loading

DLC rectangular columns were produced on tungsten carbide blocks by a FIB system (JEOL FB-2300) with 30 kV Ga\(^+\) ion-beam under an optimized condition in our previous study [4]. Source gas was supplied by heating phenanthrene (C\(_{14}\)H\(_{10}\)) powder at 348 K. The dimension of the column was 3.0 \(\mu\)m \(\times\) 3.0 \(\mu\)m \(\times\) 3.4 \(\mu\)m as shown in Figure 1 (a).

Compressive loads were applied by a dynamic ultra micro hardness tester (SHIMADZU DUH-W201) with a flat-tip diamond indenter. The diameter of the tip was 20 \(\mu\)m. In this study, load/unload rates were set to 2.65 mN/s and the maximum load was varied 50-180 mN. The compressive loads were applied in a direction perpendicular to the top face of the column. The load of 180 mN was the limit of loading without fracture in the DLC/WC specimens. To enhance the effect of compressive load, the DLC-column/DLC-film/Si-substrate specimens were also prepared to avoid fracture up to 300 mN as shown Figure 1 (b).

![Figure 1](image-url)  
**Figure 1.** Schematic illustrations of (a)DLC-column/WC and DLC-column/DLC-film/Si specimens.

2.2. Microstructure analysis

Microstructures of the DLC specimens before and after compression were analyzed by HRTEM (FEI Tecnai 30 S-Twin) operating with 300 kV. For the HRTEM analysis, cross-sectional specimens were prepared by a FIB system (Hitachi High-Technologies Co. FB-2100) with "micro-sampling" which can in-situ extract a thin plate from specific site of interest in the specimen. Bright field and HRTEM images of the cross-sectional specimens were observed, and selected area diffraction patterns were obtained. In addition, to evaluate chemical bonding state of carbon atoms, electron energy loss spectroscopy (EELS) spectra were measured and \(sp^3\) fraction in the DLC was estimated from the spectra [5-7]. The \(sp^3\) fraction was quantified by an integrated intensity ratio of \(\pi^*\) peak to \(\sigma^*\) peak \(I_{\pi^*}/I_{\sigma^*}(dE)\), i.e.,

\[
sp^3\text{ fraction} = 1 - \frac{I_{\pi^*}}{I_{\sigma^*}} \frac{I_g(dE)}{I_{\pi^*}(dE)}
\]

where \(I_{\pi^*}\) and \(I_{\sigma^*}(dE)\) are appropriate integrals for reference graphite (\(sp^3\) fraction = 0 %).

3. Results

Figure 2 shows the HRTEM images for (a) as-produced specimen, and compressed ones at (b) 140 mN, (c) 180 mN. Although each specimen shows a microgrid image indicating that the specimen has an amorphous structure, higher contrast and granularity are observed in the specimen with increasing the compressive load. This result suggests that disordered constituent atoms in DLC are clustered by compressive load [8].

In order to confirm the crystallographic variations more certainly, selected area diffraction patterns were obtained from DLC-column regions with about \(\phi 2 \mu m\). The diffraction patterns are showed in Figure 3. The diffraction pattern of as-produced specimen shown in Figure 3 (a) exhibits typical halo
which is observed in amorphous materials. In Figure 3 (b), although the pattern of compressed specimen at 140 mN also shows halo, a ring-like pattern is found around the halo. For the diffraction pattern of the specimen applied higher compressive load i.e. 180 mN, a ring-like pattern was evidently observed. An appearance of the ring-like pattern in halo indicates clustering constituent atoms in amorphous materials [8]. Therefore, not only HRTEM image observation but these diffraction patterns suggests that the constituent atoms in DLC were clustered by the compressive load.

![Figure 2. HRTEM images for (a) as-produced, and compressed DLC/WC specimens at (b) 140 mN and (c) 180 mN.](image1)

![Figure 3. Selected area diffraction patterns for (a) as-produced, and compressed DLC/WC specimens at (b) 140 mN and (c) 180 mN.](image2)

To demonstrate the clustering more clearly, it is effective to apply higher compressive loads to the specimens. The DLC-column/WC specimens were, however, fractured by a load of more than 180 mN. Hence, the DLC-column/DLC-film/Si-substrate specimens were produced in order to avoid the fracture. For the DLC/DLC/Si specimens, loads of 300 mN were applied without fracture. A bright-field image obtained from the compressed specimen is shown in Figure 4 (a). In this bright field image, regions of the DLC-column, film and the Si substrate are obviously distinguished by their contrasts. Figure 4 (b) shows a selected area diffraction pattern of the DLC-column from the region indicated by a circle in Figure 4 (a). It is found that the bright center region in the halo pattern is inconsiderably elliptical, which suggests that amorphous matrix is slightly ordered [8]. In addition, it was confirmed that the ordering was induced in extremely microscopic regions, since spotty pattern was observed in an extended halo pattern as shown in Figure 4(c) [9]. It is, therefore, revealed that disordered constituent atoms in DLC were slightly crystallized, i.e. clustered by the compressive load.

4. Discussion
For more correct understanding of the clustering phenomena in the amorphous structures, it is important to investigate chemical bonding of constituent carbon atoms. Thus EELS spectra measurements were carried out to estimate chemical bonding states of as-produced and compressed DLC/DLC/Si specimens with compressive loads of 80, 150 and 300 mN. Figure 5 shows carbon K-
edge EELS spectra obtained from the DLC-column region in the specimens. These spectra give common features of a peak at around 285 eV and a broader one at around 296 eV. The former is commonly considered to correspond to $1s \rightarrow \pi^*$ transmission, while the latter is attributed to $1s \rightarrow \sigma^*$ transmission [6,10]. Although line-shapes of the spectra are similar each other, ratios of $\pi^*$ peak intensity to $\sigma^*$ one were different between uncompressed and compressed specimens. While as-produced specimen shows 0.54 of the ratio, the compressed specimens indicate higher values of 0.58-0.60. This results suggest decrease in the $sp^3$ fraction by the compression loads.

To verify the change in the microstructure quantitatively, $sp^3$ fractions were estimated from equation (1) [5-7,10,11]. Figure 6 shows variation of the $sp^3$ fraction with the compressive load. While the $sp^3$ fraction is in the range of 29.6-33.4 % for the as-produced specimens, the 80 mN loaded specimens shows about 24.6 % of the fraction. By higher compressive load than 80 mN, the fraction is decreased further to 21-23 %. Consequently, it was suggested that the constituent atoms were arranged to form graphitic clusters by the uniaxial compressive loading.

Figure 4. (a) Bright filed image of the compressed DLC-column/DLC-film/Si specimen at 300 mN. (b) Selected area diffraction pattern at a region indicated by a circle in (a). (c) extended diffraction pattern at a region indicated by a rectangle in (b).

Figure 5. EELS spectra for the as-produced DLC/WC and the compressed DLC/DLC/Si specimens. The compressive load was 80, 150 and 300 mN.

Figure 6. Variation of $sp^3$ fraction as a function of the compressive load in the as-produced DLC/WC and the compressed DLC/DLC/Si specimens.
5. Conclusion

The micro-scaled DLC structures were produced by the FIB-CVD method, and the influence of the compressive load on the microstructure of the DLC specimens was investigated by HRTEM. HRTEM images and selected area diffraction patterns were revealed that disordered constituent atoms in DLC were clustered by the compressive load. EELS measurements indicated that the $sp^3$ fraction in DLC was decreased with compressive load. Therefore, it was suggested that graphitic clusters were formed in the microstructure by the compressive loads.

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