Influence of Heat Treatment on Mechanical Properties of DLC Deposited by FIB-CVD*

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The influence of heat treatment on the mechanical properties of DLC deposited by FIB-CVD was examined. To evaluate the mechanical properties, Young's modulus and Vickers hardness were measured by the nano indentation tester. For the characterization of DLC structure, Raman scattering was used. The microstructures of samples were characterized by HRTEM equipped with EELS. From results of the indentation experiments, it was found that Young's modulus and Vickers hardness decreased with increasing heat treatment temperature. Analysis of Raman and EELS spectra indicated that the decrease of Young's modulus and hardness was caused by the decrease of sp^3 fraction.

Key Words: Diamond-Like Carbon, Focused Ion Beam, Chemical Vapor Deposition, Heat Treatments, Mechanical Properties, Raman Spectroscopy, High-Resolution Transmission Electron Microscopy

1. Introduction

Diamond-like carbon (DLC) is of great interest due to superior properties as a coating material, e.g., high hardness, high wear resistant, very low roughness, chemical stability and high transparency. In many area of engineering applications, DLC have found as coatings for cutting tools, hard disks, metal molds and optical windows^{(1),(2)}. Therefore, production of DLC has been investigated by a number of different methods such as vacuum evaporation⁽³⁾, laser ablation^{(4),(5)}, magnetron sputtering^{(6)–(8)}, chemical vapor deposition methods^{(9)–(11)}.

Recently, focused ion beam assisted CVD (FIB-CVD) method is developed as a new technique for producing of micro- and/or nano- DLC structures. In this method, scanning of focused ion beam leads to deposition of DLC at arbitrary nano-scale area. This technique realizes fabrication of three dimensional structures, which formed complex shape with overhung, hollow and bridging structures⁽¹²⁾. Therefore, the FIB-CVD is expected to be useful method for application to micro- and/or nano-electromechanical system and other fields. Actually, R.

Kometani et al. reported fabricating nanomanipulator and actuator⁽¹³⁾, and T. Hoshino et al. demonstrated performance of FIB-CVD method by fabricating a moth's eye-like structure and a morpho butterfly-like structure with using this method⁽¹⁴⁾.

In view of practical application of the technology, it is important to understand influence of heat treatment on the mechanical properties and microstructures of DLC deposited by FIB-CVD. The influence, however, is not clear adequately. In this study, therefore, influence of the heat treatment was examined in detail. Furthermore, a relationship between the mechanical properties and microstructures was investigated.

2. Experiments

2.1 Production and heat treatment of DLC

The DLC was deposited by the FIB system (JEOL JFIB-2300) with an irradiation apparatus of a Ga^+ ion beam operating with 30 kV. For Ga^+ ion beam irradiation, extraction bias, emitter current, filament heat power and diameter of aperture were fixed 5.5 kV, 1.35 μA , 1 W and 0.5 mm, respectively. Under this condition, ion beam current was 0.6–0.8 μA . The FIB-CVD was carried out by using phenanthrene ($C_{14}H_{10}$) powder heated at 348 K as the source gas. The DLC was deposited on Si(100) substrate without heating. Produced DLC samples were heat treated in the range from 373 to 1573 K in Ar gas atmosphere. For the heat treatment experiments, heating and

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cooling rate were 0.05 K/s and samples were kept at given temperatures for 1.2×10^3 s.

2.2 Evaluation of mechanical properties

To evaluate the mechanical properties, Young's modulus and Vickers hardness were measured by a nano indentation tester (CMS Instruments Nano hardness tester). A Berkovich diamond pyramid was used as the indenter. Measurements were made by increasing the loading force with a load rate of 4 mN/min, to a maximum force of 2 mN, followed by decreasing the loading force with the same rate.

2.3 Characterization of structure by Raman spectroscopy

Various characterization methods have been used to determine the structural parameter. Raman scattering is a very popular tool for the structural characterization of DLC. For the study of the heat treatment influence on the structural properties of the DLC samples, Raman spectroscopy has been performed. The measurements were carried out using RAMANNOR-T64000 JOBIN YVON with Ar⁺ laser. The laser output of 0.6 W was used.

2.4 Analysis of microstructure and sp^3 fraction

The microstructures of the DLC samples were characterized by high-resolution transmission electron microscopy (HRTEM; FEI Tecnai 30 S-Twin) operated at 300 kV. Cross-sectional HRTEM samples were prepared by using environmental scanning electron microscopy (ESEM; FEI Quanta 3D) or focused ion beam system (Hitachi FB-2100) equipped with micro-sampling systems. To investigate crystallographic structure of the DLC, HRTEM images were observed and convergent electron beam diffraction images were obtained. Moreover, electron energy loss spectroscopy (EELS) spectra were measured in order to estimate sp^3 fraction in the DLC^{(15)–(17)}.

3. Results and Discussion

3.1 The influence of heat treatment on mechanical properties

Figure 1 shows load-displacement curves for the as-deposited and heat treated DLC samples at 673, 773 and 1573 K. These samples show similar curve, while the displacement tends to increase with increasing heat treatment temperature. In addition, it is found that the slope of curve decreases with heat treatment temperature.

Young's modulus and Vickers hardness calculated from the load-displacement curves are shown in Fig. 2. With increasing heat treatment temperature, Young's modulus first decreases gradually, and decreases rapidly near 673 K, then decreases gradually again. On the other hand, the variation of Vickers hardness against to heat treatment temperature is slightly different to Young's modulus. The hardness remains fairly constant until 673 K. Over 673 K, Vickers hardness decreases with increasing heat treatment

Fig. 1 Typical load-displacement curves for the as-deposited DLC sample and three heat treated DLC samples at 673, 773 and 1573 K

Fig. 2 Variations of Young's modulus (open circle) and Vickers hardness (open triangle) as a function of heat treatment temperature

temperature as well as Young's modulus. For the heat treated DLC produced by FIB-CVD, therefore, it was obvious that the heat treatment increased the displacement, while decreased Young's modulus and Vickers hardness.

3.2 The variation of Raman spectroscopy due to heat treatment

The visible Raman spectra of the DLC exhibit two broad peaks^{(3),(18),(19)}. The first peak, commonly labeled G (graphite), is located at around 1580 cm^{-1} due to in-plane vibration of the graphite-like rings. The second peak, labeled D (disorder), is located around 1330 cm^{-1} which results from the formation of ordered sp^2 cluster. Thus, the G-peak occurs in crystalline graphite, while D-peak occurs in many disordered graphitic materials. The Raman spectra are shown in Fig. 3 for all DLC samples. These spectra imply that a structural change occurs with heat treatment.

To determine the position and intensity of the G- and D-peaks, the Raman spectra were fitted two Gaussian distribution, centered at ~ 1580 and $\sim 1330\text{ cm}^{-1}$. The G-peak position and the $I(D)/I(G)$ ratio obtained from these Raman spectra are shown in Fig. 4, where $I(D)$ and $I(G)$ were intensity of D- and G-peak, respectively. The behav-

Fig. 3 Raman spectra of the DLC samples obtained at different heat treatment temperature

Fig. 4 (a) Position of Raman G-peak, and (b) intensity ratio of the $I(D)/I(G)$ as a function of heat treatment temperature

iors of the G-peak position and the $I(D)/I(G)$ ratio give information on the chemical bonding of the DLC. Ferrari et al.⁽¹⁹⁾ reported that Raman spectra of all disordered car-

Fig. 5 HRTEM and convergent diffraction images for (a) as-deposited, heat treated samples at (b) 673 K, (c) 873 K and (d) 1573 K

bon were classified into three-stage by disordering process of carbon network. In one of the stages corresponding to disordering of a nano-crystalline graphite and loss of aromatic bonding, G-peak position shifts lower wave number and $I(D)/I(G)$ ratio decreases owing to reduction of cluster size of the sp^2 -C rings and the number of clusters. In Fig. 4, the G-peak position shifts higher wave number and the $I(D)/I(G)$ ratio increases with increasing heat treatment temperature. This behavior seems to be caused by increases of cluster size and the number of sp^2 fractions.

3.3 Microstructures and sp^3 fraction

Figure 5 (a)–(c) and (d) show HRTEM and convergent diffraction images for as-deposited and heat treated samples at 673 K, 873 K and 1573 K, respectively. For the DLC samples heat treated below 873 K (Fig. 5 (b) and (c)), HRTEM images and convergence electron diffraction images reveal that the DLC has amorphous structures as as-deposited sample (Fig. 5 (a)). Thus, there is no difference in the microstructure due to heat treatment below 873 K. By contrast, in Fig. 5 (d), a lattice images and spot diffraction pattern were observed. So it was found that the DLC was crystallized by heat treatment at 1573 K. However it was impossible to explain of decreases of Young's modulus and Vickers hardness by these results.

Accordingly, sp^3 fractions were calculated from EELS spectra. Figure 6 is comparison of carbon K-edge EELS spectra from as-deposited, heat treated DLS samples and graphite. The background model used was a standard power law, AE^{-r} , where E is energy loss and A and r are fitting parameters. The spectrum of graphite was obtained from graphite powder (Nippon graphite CPB-S)

Fig. 6 Comparison of carbon K-edge EELS spectra for as-deposited and heat treated DLC samples. Graphite reference spectrum are also shown.

Fig. 7 Change of sp^3 fraction as a function of heat treatment temperature

with 99.99% purity. Common features include a peak at about 285 eV and a broader peak at about 296 eV. The first peak is commonly corresponds to transmissions from $1s$ to π^* antibonding states, while the second is attributed to transmissions from $1s$ to σ antibonding states. As shown in Fig. 6, EELS spectra tend to vary similarly from spectrum of as-deposited to that of graphite with increasing heat treatment temperature.

By integrating the π^* peak intensity relative to the σ^* peak, the fraction of sp^3 bonds is quantified^{(8), (16), (17)}. Figure 7 shows the change of the sp^3 fraction as a function of heat treatment temperature. From Fig. 7, it is found that the sp^3 fraction decreased with increasing heat treatment temperature. This result is consistent with Raman spectra analysis, which suggests increase of the sp^2 fraction. Therefore, it was indicated that the fraction of sp^3 corre-

lated with the mechanical properties of the DLC. Consequently, the decrease of sp^3 fraction is one of the most influential factors, which decreases Young's modulus and Vickers hardness.

4. Conclusion

The influence of heat treatment on the mechanical and structural properties of DLC deposited by FIB-CVD was investigated. Young's modulus and Vickers hardness decreased with increasing heat treatment temperature. Analysis of Raman and EELS spectra indicated that the fraction of sp^3 decreased with increasing temperature. Therefore, it was shown that the fraction of sp^3 correlated with the mechanical properties of the DLC, and found that the decrease of sp^3 fraction was one of the factors, which decreases Young's modulus and Vickers hardness.

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