Local Structure Analysis of Carbon-Implanted Silicon Prepared with Plasma-Based Ion Implantation

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Abstract

The local structure of carbon-implanted silicon was analyzed by soft X-ray spectroscopy and TEM observation to ascertain the mechanism for high adhesion of diamond-like carbon film. The carbon-implanted silicon samples were prepared with the plasma-based ion implantation technique using methane plasma. The cross-sectional TEM observation indicated that the carbon ion implantation led to the deformation in crystalline structure of silicon substrate. The soft X-ray emission and absorption spectra in the C K region of carbon-implanted silicon were measured with using highly brilliant synchrotron radiation, showing the formation of chemical bonding between implanted carbon and silicon substrate.

Keywords: Diamond-like carbon (DLC), Soft X-ray spectroscopy, Chemical bonding, TEM observation, High adhesion, Plasma-based ion implantation (PBIID)

1. Introduction

In recent years, diamond-like carbon (DLC) films have attracted a great deal of interest because of their excellent tribological properties such as high wear resistance, super-high hardness, and low friction coefficient. However, poor adhesion of DLC films is an important problem for practical uses. High-adhesion DLC films were prepared on metal substrates by a hybrid process of plasma-based ion implantation and deposition (PBIID) using hydrocarbon gas. The ion implantation during deposition relaxed residual stress in DLC film to almost 0 and produced an interface graded in carbon component. Besides, at the time of ion implantation, the ion-implanted region should be increased up to enough temperature to induce the chemical bonding between implanted carbon and elements of substrate component. These ion implantation effects resulted in the improvement in adhesion strength of DLC films above the epoxy resin glue strength. However, the existence of chemical bonding is not experimentally confirmed yet.

In this paper, we study on the local structure of carbon-implanted silicon by soft X-ray spectroscopy and also TEM observation to ascertain the mechanism for high adhesion of DLC film prepared with PBIID process.

2. Experimental

The carbon-implanted silicon (C-Si) sample for soft X-ray spectroscopy was prepared by the plasma-based ion implantation (PBIID) technique using methane plasma. Figure 1 shows a schematic diagram of the PBIID system using superimposed RF and negative high-voltage pulses. In this system, the RF pulse for initial plasma generation was supplied to the substrate together with a negative high-voltage pulse for ion implantation through a single electrical feed-through using a joint matching circuit for both pulses. The RF pulse had the peak power of 300 W, the pulse duration of 50 µs, the frequency of 13.56 MHz, and the repetition rate of 1 kHz. A negative high-voltage pulse for ion implantation with the voltage of \( V_p = -5 \sim -20 \) kV, the duration of 5 µs, and the same repetition rate as the RF pulse was applied to the substrate at the time of 50 µs later after each RF pulse. The methane plasma was used for ion implantation to the silicon substrate and the toluene plasma for DLC preparation. The precursor gas pressure was held at 0.5 Pa. Silicon substrates were cleaned by ultrasonic cleaning in acetone and set on a hexagonal sample holder (dimension of each face: 6 cm in width and 17 cm in height) in the center of vacuum chamber.

The carbon film (C film/Si), highly oriented

![Fig.1 Schematic diagram of plasma-based ion implantation system using superimposed RF and negative high-voltage pulses.](image-url)
pyrolytic graphite (HOPG), and SiC film were used for the reference. Soft X-ray spectral measurements using synchrotron radiation in the carbon (C) K region were performed at the Advanced Light Source (ALS) of Lawrence Berkeley National Laboratory (LBNL). X-ray emission spectra (XES) were measured using a grating X-ray spectrometer installed in the undulator beamline, BL-8.0.1. X-ray absorption spectra (XAS) were measured in the bending-magnet beamline, BL-6.3.2 with a total-electron-yield method. The C-Si sample for TEM observation was prepared as follows: At first, carbon ions were implanted by PBII technique from the methane plasma and then DLC film was deposited using the toluene plasma. The DLC film on Silicon substrate (DLC/Si) was prepared without carbon-ion implantation using the methane plasma. The microstructure of C-Si and DLC/Si samples was analyzed in detail by HR-TEM (JEM-4000EX, JEOL) and STEM (JEM-3000F, JEOL) observations in combination with energy dispersive X-ray spectroscopy. The samples for TEM observation was prepared using focused ion beam (FIB, FB2100, HITACHI). The depth profile of carbon in the silicon substrate was measured with Auger Electron Spectroscopy (AES, Model 255, PII).

3. Results and Discussion

3.1 Depth profile of implanted carbon

At first we will examine the depth profile of carbon deposited by the PBII technique in the silicon substrate. Figure 2 shows the AES depth profiles of carbon, silicon, and oxygen at the surface region of silicon substrate for various implantation voltages, where the oxygen was resulted from the oxide layer on the top surface of silicon substrate before implantation. As seen in Fig.2, carbons are observed in the silicon substrate beyond the oxide layer even for the implantation voltage of -5 kV. With increasing implantation voltage carbons are deposited deeper into the silicon substrate and the number of carbon deposited is also increased. These results indicate carbons are implanted into the silicon substrate by PBII technique. On the other hand, as the peak position of the oxygen corresponds to the surface of substrate, a little deposition of carbon on the substrate is observed in Fig.2.

3.2 TEM observation of carbon-implanted silicon

The cross-sectional HR-TEM images of (a) DLC/Si and (b) C-Si(10kV) samples are shown in Fig.3, where the carbon implantation voltage for C-Si sample was -10 kV. As seen in Fig.3(a), the lattice lines of silicon substrate are in order, showing no deformation of crystalline structure except the top surface (about 5 nm from the surface). On the other hand, it is found in Fig.3(b) that irregular color patterns in several nm size are observed in the microscopic appearance of the substrate surface region, suggesting the deformation of crystalline structure. Furthermore, some parts of lattice lines are in disorder. The width of deformed layer is about 21 nm that is slightly less than the carbon-ion range (34 nm) of 10 keV. These results indicate that carbon-ion implantation led to the deformation of crystalline structure of silicon substrate. However, the evidence of chemical bonding between carbon and silicon is not confirmed by the TEM observation. A distinct oxide layer is not observed in Fig.3, indicating the destruction of oxide by carbon ion implantation.

3.3 Soft X-ray spectroscopy

Figure 4 shows the soft X-ray emission spectra in the C K region of carbon-implanted silicon, where the
excitation energy was tuned at 320 eV. Integrated X-ray signal intensity dependent on the implantation voltage is shown in the inset. Since the larger signals from the carbon-implanted silicon are observed than that from the non-implanted silicon as shown in Fig.4, the observed signal should be due to the carbons implanted into the silicon substrate. The intensity of

![Image](image-url)

Fig.4 Soft X-ray emission spectra in the C K region of C-implanted Si. Excitation energy was tuned at 320 eV. Integrated X-ray signal intensity dependent on the implantation voltage is shown in the inset.

![Image](image-url)

Fig.5 Soft X-ray emission spectra in the C K region of C-Si, C film/Si, HOPG, and SiC.

Fig.3 Cross-sectional HR-TEM images of (a) DLC/Si and (b) C-Si(-10kV) samples, where the implantation voltage for C-Si sample was -10 kV, showing the deformation of crystalline structure by carbon-ion implantation.
X-ray signal increases with increasing the implantation voltage, indicating the increase in the concentration of implanted carbon. This fact is in agreement qualitatively with the results in Fig.2. Figure 5 shows the C K X-ray emission spectra of the C-Si sample prepared with the implantation voltages of -5, -10, and -20 kV and those of HOPG, C film, and SiC as a reference. As seen in Fig.5, the shape of emission spectrum of C-Si(-5kV) is a triangle with a peak at 278.2 eV that is similar to the C film with a peak at 277.7 eV, but not agreement with those of HOPG and SiC. With increasing of ion implantation voltage, the peak position of emission spectrum of C-Si sample is shifted to the higher-energy side. Besides, the shape of emission spectrum of C-Si(-20kV) resembles that of SiC. Figure 6 shows the X-ray absorption spectra near the C K absorption edge of the same samples as those in Fig.5. The absorption spectrum of C-Si sample is shifted from C film to SiC with increasing carbon implantation energy. These results of soft X-ray spectroscopy suggest the formation of chemical bonding between implanted carbon and silicon substrate.

4. Conclusion

The cross-sectional TEM observation indicated that the carbon-ion implantation by plasma-based ion implantation technique resulted in the deformation in crystalline structure of silicon substrate. Using highly brilliant synchrotron, we measured the soft X-ray emission and absorption in the C K region of carbon-implanted silicon prepared with the plasma-based ion implantation technique. The results of soft X-ray spectroscopy suggest the formation of chemical bonding between implanted carbon and silicon substrate.

References

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