Effect of Fe ion implantation on tribological properties and Raman spectra characteristics of diamond-like carbon film

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Abstract Fe ions in the fluence range of 2×10^{15} to 1×10^{17} cm^{-2} were implanted into diamond-like carbon (DLC) thin film of 100 nm thick, which were deposited on silicon substrate by plasma enhanced chemical vapor deposition. Effects of Fe ion implantation on microstructure and friction coefficient of the DLC were studied. With increasing Fe ion fluence, friction coefficient of the DLC film increased as compared with that of DLC without implantation, and then decreased. The Raman spectra characteristics also show a dependence on the Fe ion fluence. With increasing the ion fluence, the sp^2 bonding increased in the DLC film, resulting in the decrease of friction coefficient of the film after implantation. Substantial surface roughness was also measured.

Keywords DLC (diamond-like carbon film), Microstructure, Friction coefficient, Fe ion implantation

CLC numbers TL99, O571.33

1 Introduction

It is well known that DLC (diamond-like carbon) prepared by physical vapor deposition, plasma enhanced chemical vapor deposition (PECVD) and other plasma processing is an amorphous carbon material containing sp^2 and sp^3 bonded carbon atoms. DLC film possesses some interesting properties, such as high hardness and Young's modulus, chemical inertness and low friction coefficient. The property and structure of DLC film can be modified by adding some metals. Ion implantation can be used to modify many of the near-surface properties of materials.[1] In this paper, we describe the effects of Fe ion implantation on DLC film prepared by PECVD. After ion implantation, the nano-frictional properties and microstructures of the DLC films were investigated by Dynamic Friction Parameter Measure (DFPM) system and Raman spectroscopy. The effect of the ion fluence on the structures and properties of DLC is discussed.

2 Experimental

The DLC thin films with thickness of 100 nm were prepared by PECVD.[2] The base pressure was less than 6.65 mPa maintained by a turbo-molecular pump. The substrate electrode was water cooled, and coupled to a radio frequency (RF) generator (with RF excited frequency of 13.56 MHz) by an impedance-matching network and a blocking capacitor. The RF power was applied between the ground and substrate electrode which was placed at the center of the chamber. Polished Si(100) wafers with the thickness of 0.3 mm were used as substrates. Prior to deposition the substrates were sputter-cleaned in Ar glow discharge at the negative bias voltage of 400 V for 10 min. Pure methane (99.995%) was used as a feed gas for DLC film deposition. During the deposition, the methane pressure was kept at 2.66 Pa, and the negative bias voltage was kept to 200 V.

Ion implantation was performed using an ion implantation accelerator in Institute of Modern Physics, the Chinese Academy of Sciences. Fe^+ ion (beam density was 0.6 $\mu A/cm^2$, temperature of target was 500 °C or so) with energy of 100 keV were used in the experiment. And the ion beam fluence was fixed at 2×10^{15}, 5×10^{15}, 2×10^{16}, 5×10^{16} and 1×10^{17} cm^{-2}, respectively.

After ion implantation, the DLC films were characterized by Raman spectroscopy (Ar ion laser of

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514.5 nm for excitation), and friction coefficient (μ) was measured by DFPM. In the friction measurement, the ball was a stainless steel sphere with the diameter 3 mm, the applied load 0.5 N and the speed 1.5 mm/s. Three friction tests were done for each data point.

The morphological features of DLC films were observed by atomic force microscopy (AFM) using a tapping mode. The root mean square (RMS) roughness of the DLC films was evaluated by AFM measurements on a 1 μm×1 μm area.

3 Results and discussion

3.1 Tribology property

Friction coefficient of the DLC film is usually much smaller than that of Si surface. For example, μ for DLC-Si is about 0.15, and μ for Si is 0.70 in our experiment. After Fe ion implantation, μ of the DLC:Fe film initially increased, compared with that of DLC film alone. However, with increasing Fe ion implantation flux, μ of the DLC:Fe film decreased. The dependence of friction coefficient of the DLC:Fe film on Fe ion beam fluence is shown in Fig.1.

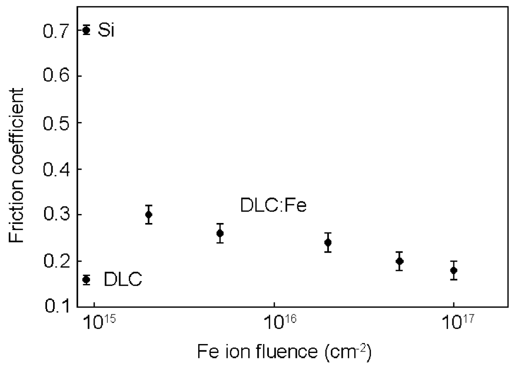


Fig.1 Dependence of friction coefficient of the DLC film on the Fe ion fluence.

3.2 Morphology

The morphological features were examined by AFM. The DLC film is smooth, as shown in Fig.2(a). After Fe ion implantation, the surface of DLC film becomes rough. Fig.2(b) shows a typical AFM image of DLC:Fe film implanted at 2×10^{16} cm^{-2} ion fluence, some nano-particles can be observed on the surface of the film. The dependence of RMS roughness of the DLC:Fe film on Fe ion fluence is shown in Fig.3. With increasing Fe ion implantation flux, the roughness of the DLC:Fe films decreased slightly.

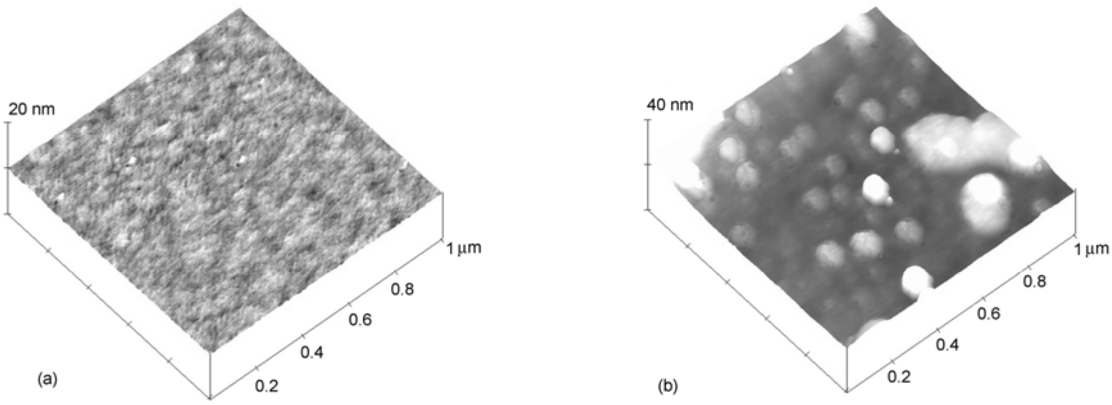


Fig.2 AFM images of the DLC films, (a) as-deposited; (b) implanted at 2×10^{16} cm^{-2}.

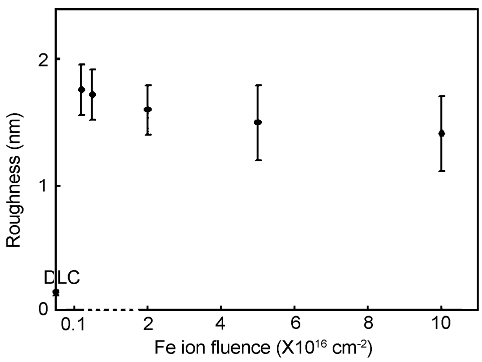
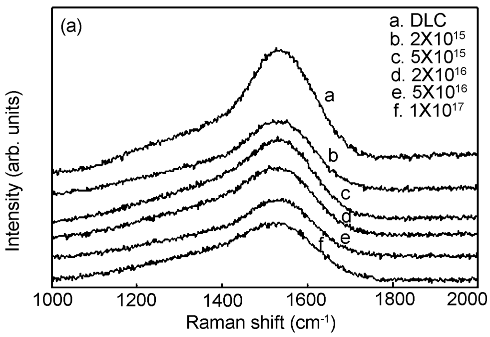


Fig.3 Dependence of RMS roughness of the DLC film on the Fe ion fluence.

3.3 Raman spectra

Fig.4(a) shows the Raman spectra of the DLC films at various Fe-ion beam fluence. The data can be fitted by two peaks with Gaussian-Lorentzian mixture line shape. From the fitting parameters, the peak position, peak width and integrated intensity ratio of the two peaks were obtained from the DLC films deposited under different ion beam fluences. All spectra can be decomposed into two features at about 1360 cm^{-1} (disordered, *D* band) and 1540 cm^{-1} (graph-



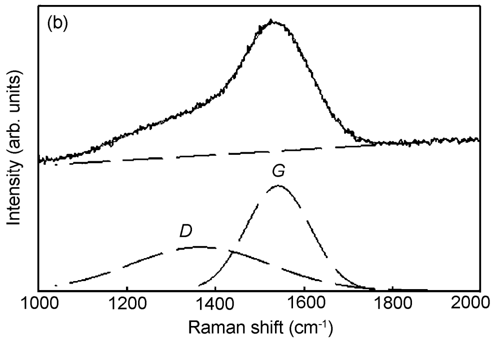


Fig.4 Raman spectra of the DLC films implanted at various Fe ion fluences (a) and the typical peak fitting of a Raman spectrum (b).

itic, *G* band). The typical peak fitting of a Raman spectrum is shown in Fig.4(b).

Spectra of DLC:Fe films are similar to the spectrum of the original DLC film, however, some Raman changes can be observed after ion implantation, indicating that small changes in microstructures in the DLC films occurred after Fe ion implantation. The Raman characteristics of the DLC films implanted at various ion fluences are shown in Fig.5. By peaking fitting, the *D* and *G* peak position, peak width and peak intensity ratio, $I(D)/I(G)$, were obtained.

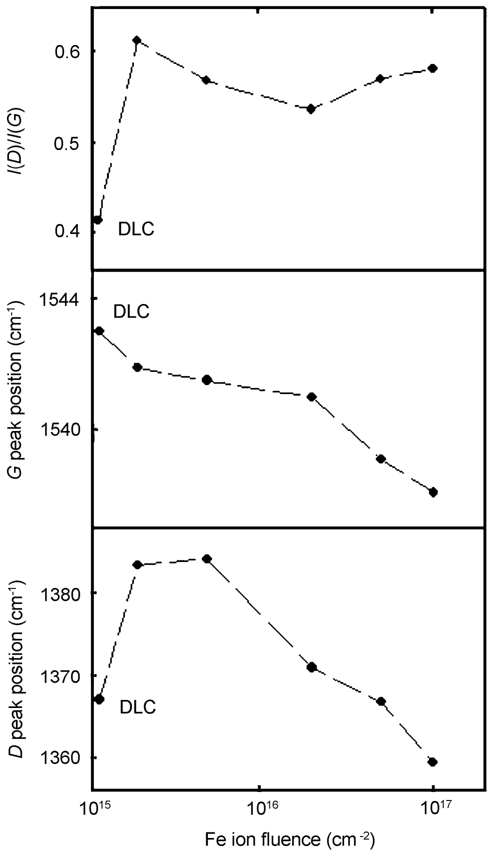


Fig.5 The Raman characteristics of the DLC films implanted at various Fe ion fluences.

After Fe ion implantation, the intensity ratio $I(D)/I(G)$ in the Raman spectra of DLC:Fe films increased , as shown in Fig.5. With increasing the ion fluence from 2×10^{15} to $5\times10^{15}\,\mathrm{cm}^{-2}$, the $I(D)/I(G)$ ratio decreased slightly, then increased when the ion fluence increased from 2×10^{15} to $1\times10^{17}\,\mathrm{cm}^{-2}$.

With increasing ion fluence, the *G* peak position (in cm^{-1}) decreased. The *D* peak position increased first, then decreased when the ion fluence is above $5\times10^{15}\,\mathrm{cm}^{-2}$, as shown in Fig.5. The $I(D)/I(G)$ ratio vs. Fe ion fluence is also presented.

4 Discussion

Changes of $I(D)/I(G)$ ratio, peak position and width in the Raman spectra are related to the microstructure, such as carbon cluster size, defects, crystallinity, sp^2/sp^3 ratio, and changing of DLC films.[3] After ion implantation, the increase of the intensity ratio $I(D)/I(G)$ of DLC films may be related to the decrease of carbon cluster size of the films.[4]

When the ion fluence increased to above $2\times10^{16}\,\mathrm{cm}^{-2}$, the increase of the $I(D)/I(G)$ ratio may be attributed to increasing number of graphitic clusters in the films.[2, 5]

The *D* peak position shifts from $1367\,\mathrm{cm}^{-1}$ to $1385\,\mathrm{cm}^{-1}$ when the ion fluence is in the range of 2×10^{15} to $5\times10^{15}\,\mathrm{cm}^{-2}$, which may be related to the increasing sp^2 bondings or a loss of hydrogen due to energy transfer from implanted Fe ions.[1, 6]

The *D* and *G* peaks downshift simultaneously with Fe ion fluence increasing from 1×10^{16} to $1\times10^{17}\,\mathrm{cm}^{-2}$. This trend may be caused by the Fe induced stress release or by the high Fe content.[7]

The shift of *G* peak position to a lower frequency can be partly related to the reduction of compressive stress as Fe is implanted into the films. Fe has much higher atomic weight than C. The vibrational modes of Fe-C will tend to occur at much lower frequencies than those of C-C bonds.

The shift of *D* peak position to lower frequency may be due to the further increase of the degree of disorder of the sp^2 bonded clusters. The bond angles of bonds in the clusters also become further distorted and the bond lengths increase, which weakens the bond strength. This gives rise to the lowering of *D* peak position.[5]

The DLC film deposited by PECVD in our experiment is an amorphous hydrocarbon network consisting of sp^3/sp^2 bonding. High energy (100 keV) Fe ions implanted into DLC films caused both the film morphology and the structure to change. Because the DLC film is a hydrogenated carbon film, high energy Fe ion bombardment may result in decreasing hydrogen content of the film, and make the film more graphite-like. Another effect may come from phase transformation from sp^3 to sp^2 bonding during the Fe ion implantation, because normally Fe can be regarded as a catalyst for graphite growth.

The friction coefficient of all DLC:Fe films increased as compared with that of the DLC film without implantation. This may be attributed to significantly increased surface roughness after ion implantation. From our experiment, many nanoparticles or nano-flakes on the DLC films were observed after implantation, and the surface roughness increased greatly. With increasing ion fluence, the friction coefficient of the DLC:Fe films decreased, which may be related to both surface roughness and microstructure of the films. It was also found that at first surface roughness increased monotonically with the ion implantation fluence, but when ion fluence reached a certain value, surface roughness decreased monotonically with ion implantation fluence.[1, 3] In our experiment, when the Fe ion fluence increased from 2×10^{15} to 1×10^{17} cm^{-2}, the surface roughness of the films decreased from 2.95 nm to 1.42 nm, which may result in the decrease of the friction coefficient. In addition, after Fe ion implantation, the DLC film became a more graphite-like material which normally showed a low friction coefficient.[8, 9] With increasing the ion fluence, the sp^2 bonding in the DLC films increased, thus the friction coefficient of the DLC:Fe films decreased.

5 Conclusion

Fe ion implantation was performed for the DLC thin films deposited by PECVD, and the influences of Fe ion implantation on morphology, microstructure and friction coefficient of the DLC films were studied. With Fe ion implantation, friction coefficient of the DLC film increased as compared with that of DLC without implantation, which may be due to the increase of surface roughness and due to some nanoparticles created by ion implatation. But with increasing Fe ion fluence from 2×10^{15} to 1×10^{17} cm^{-2}, friction coefficient decreased from 0.3 to 0.18. The Raman spectra characteristics also show a dependence of the Fe ion flux: sp^2 bonding increased in the DLC film with increasing the ion fluence, resulting in decreasing the friction coefficient of the film after implantation.

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