Effect of Sputtering Conditions on Transmittance and Wear Resistance of Diamond-Like Carbon Film

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Abstract. Diamond-like carbon (DLC) film was prepared by magnetron sputtering method on glass substrate. The microstructure, transmittance, and wear resistance of the diamond-like carbon film were investigated and analyzed. This study clearly showed the significance of sputtering power, Ar pressure and substrate temperature in controlling the transmittance and wear resistance of DLC film. The sp3 bond in the film had a greater impact on the transmittance and wear resistance of DLC film. The optimized deposition parameters obtained through experiments were: Ar pressure of 0.7 Pa, sputtering power of 100 W, and substrate temperature of 150 °C.

1. Introduction
Carbon-based films are formed by depositing carbon atoms on the substrate. Carbon-based films possess many merits including low coefficient of friction, high wear resistance and chemical stability, as well as good corrosion resistance and optical properties [1-2]. As one of the members of carbon-based films, the Diamond-like carbon (DLC) film has prominent advantages in optical properties, such as good infrared and visible light transmittance, high anti-ultraviolet transmittance. It can be used as anti-reflective protective film for optical instrument and infrared window, practical examples as anti-reflective film for silicon solar cell, anti-wear protective films for infrared optical lenses made by Ge, ZnS and ZnSe, etc [3]. DLC film is a metastable form of amorphous carbon containing fraction of sp3 and sp2 bonds, and the sp2 and sp3 are hybrid bonds between carbon atoms. DLC film has many of the useful properties of diamond and some properties of graphite, and has been one of the hotspots in the field of coating research.

However, there are still many shortcomings in the production of DLC film at present. For example, the higher the sp3 bond in the DLC film, the higher the hardness of the DLC film would be and the closer the film to diamond, but the optical properties of the DLC film are not necessarily good. It is still a problem to make the DLC film have good optical and mechanical properties at the same time. This paper starts with the transmittance and wear resistance of DLC film, and studies the difficult problems. The physical properties of DLC film are mainly controlled by the sp3 bond and sp2 bond, which are closely related to the method of film deposition [4], so the magnetron sputtering technology owning low sputtering temperature, high deposition rate and strong adhesion between film and substrate [5] was chosen to prepare the DLC film. The transmittance and wear resistance of DLC film were investigated by changing Ar pressure, sputtering power and substrate temperature. Optimal experimental parameters had been explored to ensure that the DLC thin film had high transmittance and good wear resistance.

2. Experimental
The DLC film was prepared using GP500 Multi-Function Ultrahigh Vacuum Magnetron Sputtering System. C (99.99% purity) was used as target for sputtering. High purity Ar (99.999% purity) was introduced as the sputtering gas. Float glass was selected as substrate. The specific
experimental scheme was shown in Table 1. The Ar pressure as 0.5Pa, 0.7Pa and 0.9Pa, respectively. The sputtering power was 80W, 100W and 120W, respectively. The substrate temperature was room temperature, 150℃ and 300℃, respectively. The sputtered time was set at 3600s and the gas flow of Ar was 25sccm.

| Sample | Pressure (Pa) | Power (W) | Temperature (℃) | Argon flow rate (sccm) | Time (s) | Thickness (nm) |
|--------|--------------|-----------|-----------------|------------------------|---------|---------------|
| C1     | 0.5          | 100       | 150             | 25                     | 3600    | 541           |
| C2     | 0.7          | 100       | 150             | 25                     | 3600    | 670           |
| C3     | 0.9          | 100       | 150             | 25                     | 3600    | 729           |
| C4     | 0.7          | 80        | 150             | 25                     | 3600    | 501           |
| C5     | 0.7          | 100       | 150             | 25                     | 3600    | 670           |
| C6     | 0.7          | 120       | 150             | 25                     | 3600    | 1086          |
| C7     | 0.7          | 100       | R.T             | 25                     | 3600    | 730           |
| C8     | 0.7          | 100       | 150             | 25                     | 3600    | 670           |
| C9     | 0.7          | 100       | 300             | 25                     | 3600    | 644           |

3. Results and discussion

3.1. Argon pressure

![Figure 1. SEM surface images of the carbon-based films under different Ar pressure.](image1)

![Figure 2. AMF 3D morphologies of the carbon-based films under different Ar pressure.](image2)

Fig. 1 and Fig. 2 show the SEM surface images and AMF 3D morphologies of carbon-based films under different Ar pressure, respectively. As can be seen from Fig. 1, the surface structure of the film deposited at 0.7 Pa is more dense, and the particles on the surface of the film are more uniform. In combination with the film 3D morphology of Figure 2, it can be seen that the 0.7Pa film surface is less fluctuating and more uniform than the 0.5Pa and 0.9Pa deposited films. When the Ar pressure was 0.5Pa, the Ar plasma density was low. The low Ar plasma density would result in less carbon particles and a lower deposition rate of carbon. The non-uniform distribution of carbon particles and more defects on the film surface would be caused. When the Ar pressure was increased to 0.7Pa, the density of Ar plasma, the number of carbon particles sputtered and the deposition rate of carbon particles were all increased, so there had enough carbon particles on substrate to construct a smooth and compact film. However, when the Ar pressure was increased to 0.9Pa, the Ar plasma density was too high, thus the collision frequencies between carbon particles and gas molecules were increased, which would
weaken the energy of carbon particles. When carbon particles did not have enough energy to migrate on substrate, the defects of thin film were generated.

Figure 3 shows the XRD diagram of carbon-based films under different Ar pressure. There was only a broad peak near 30 degrees. The change of diffraction peaks in carbon-based films were not apparent with the increasing of Ar pressure, which indicated that the film mainly existed in the form of amorphous.

![Figure 3. XRD patterns of the films under different Ar pressure.](image1)

**Figure 3.** XRD patterns of the films under different Ar pressure.

![Figure 4. Raman spectra of the films under different Ar pressure.](image2)

**Figure 4.** Raman spectra of the films under different Ar pressure.

![Figure 5. Transmittance spectra of the films under different Ar pressure.](image3)

**Figure 5.** Transmittance spectra of the films under different Ar pressure.

### Table 2. The parameters of the C Raman spectra in DLC films

| Sputtering conditions | FWHM (G) (cm\(^{-1}\)) | FWHM (D) (cm\(^{-1}\)) | R (I\(_{G}/I_{D}\)) |
|----------------------|------------------------|------------------------|---------------------|
| 0.5Pa                | 130.14                 | 191.32                 | 2.89                |
| 0.7Pa                | 135.18                 | 182.83                 | 3.36                |
| 0.9Pa                | 142.94                 | 172.70                 | 3.40                |
| 80W                  | 132.15                 | 201.78                 | 4.10                |
| 100W                 | 135.18                 | 182.83                 | 3.36                |
| 120W                 | 121.88                 | 349.30                 | 2.67                |
| R.T                  | 148.99                 | 142.67                 | 5.80                |
| 150°C                | 135.18                 | 182.83                 | 3.36                |
| 300°C                | 99.11                  | 126.56                 | 1.19                |

Fig. 4 displays the Raman spectra of carbon-based films under different Ar pressure. The main feature in the Raman spectra was the G peaks appearing at approximately 1554 cm\(^{-1}\), and a weak D peak at near 1366 cm\(^{-1}\), which accounted for the large amounts of amorphous domain in DLC film. The G peak is due to the bond stretching of all pairs of sp\(^2\) atoms in both rings and chains. The G band corresponds to the symmetric E\(_{2g}\) vibrational mode in graphite-like materials. The D peak is due to the breathing modes of sp\(^2\) atoms in rings caused by A\(_{1g}\) non-active vibrations mode [6]. The G and D peaks were fitted with Lorentzian by fitting the data in Table 2. The R = I\(_{G}/I_{D}\) can reflect the degree of carbon graphitization. The higher R in thin film will lead to more the diamond-like properties, the lower R in thin film will lead to more the graphite-like properties.

As the pressure of Ar increased, the G peak shifted slightly to the high wave number, the G peak was more asymmetrical, and the D peak was less obvious. As can be seen from Table 2, R increased as the Ar pressure increased. Therefore, the sp\(^3\) bond fraction in the carbon-based film increased as the Ar pressure increased, and the film structure tended to be diamond-like.

Fig. 5 shows the infrared transmittance of carbon-based films at different Ar pressure. It was clear that the transmittance of the films increased as the pressure of Ar increases. When the Ar pressure was raised from 0.5Pa to 0.7Pa, the maximum transmittance in the film was increased from 56.5% to 57.0%. The increased transmittance was related to the increasing of sp\(^3\) bond in the film. In addition, combined with the surface morphology of the film, it can be inferred that the increasing transmittance in the film was related to the surface morphology of the film. Deposited at 0.7Pa, the less defects and roughness of the films reflected that the scattering on the film surface were reduced.
and the transmittance of the film was increased. When the Ar pressure was risen to 0.9Pa, the maximum transmittance reached 60.5%. The increase of the transmittance of the film was mainly related to the increasing of sp3 bond in the film [7-8]. Since the surface morphology of the film deposited at 0.9Pa was rougher than the surface morphology of the film deposited at 0.7Pa, this impaired the transmittance of the film. In Table 1, as the pressure of Ar increased, the increase in thickness of the film was inversely proportional to the transmittance of the film. In the face of adversity, the transmittance of the film still increased with the increase of Ar pressure, which indicated that the sp3 bond in the film had a greater influence on the transmittance.

**Figure 6.** Metallographic microscopic images of the worn carbon-based films under different Ar pressure.

Fig. 6 shows that there was a significant difference between the metallographic microscopic images of the worn carbon-based film at different Ar pressures. When the Ar pressure was 0.5 Pa and 0.9 Pa, respectively, the edge of the worn film peeled off significantly, indicating that the adhesion between the film and the substrate was weak, and the wear resistance was weak. When the pressure was 0.7 Pa, the edges of the worn film were smoother and less debris. In order to maintain good wear resistance and optical properties of the DLC film, an optimum Ar pressure of 0.7 Pa was selected.

3.2. Sputtering power

Fig. 7 and Fig. 8 show the SEM surface topography and AFM 3D topography of carbon-based films at sputtering power of 80W, 100W and 120W, respectively. It can be found that the film surface was tightly bonded and fluctuated uniformly, and the size of the particles on film surface was uniform at 100W. While the surfaces of films deposited at 80W and 120W had some protrusions, and the size of the particles on films surface were not uniform, especially when the sputtering power was 120W.

**Figure 7.** SEM surface images of the carbon-based films under different sputtering power.

**Figure 8.** AMF 3D morphologies of the carbon-based films under different sputtering power.
The change of the film structure can be explained as follows: at a sputtering power of 80 W, the sputtering cavity having a low Ar plasma density caused a small amount of sputtering C particles and low energy, which made that the C particles deposited on the substrate did not have enough quantity and energy to migrate, thus creating holes and undulations on the surface of the film. When the sputtering power was risen to 100W, the density and energy of Ar plasma reached a suitable value, which not only improved the deposition rate of C particles, but also gave the C particles enough energy to migrate along the substrate surface. Therefore, the distribution of C particles on the film surface was more uniform, and the film surface was smoother and more compact. When the sputtering power was increased to 120 W, the density and energy of the Ar plasma were so high that some of the C particles on the surface of the substrate had excessive energy, which would collide with the surface of the substrate multiple times and break the film structure before stopping. After the appearance of holes and projections on the surface of the film, it was revealed that the structure of the film was destroyed.

Figure 9 shows the XRD patterns of carbon-based films at different sputtering power. It can be seen from the graphs that the diffraction peaks of the films did not change significantly with the increasing sputtering power, and the diffraction peaks were very broad. The broad diffraction peaks indicated that the carbon-based films existed mainly in amorphous forms under the selected sputtering powers.

Fig. 10 shows the Raman spectra of C-based films at different sputtering power. It was worth noting that the G peak was near 1558 cm$^{-1}$ and the weak D peak was near 1384 cm$^{-1}$. As the sputtering power increased, the G peak shifted slightly to a lower wave number. Table 2 shows that R decreased with increasing sputtering power, indicating that the degree of graphitization of the film increased as the sp3 bond decreased.

Fig. 11 shows the wave number dependence of the infrared transmittance of C-based films under different sputtering power. It can be seen that as the sputtering power increased, the maximum infrared transmittance of the film decreased from 60.0% to 57.0% and then dropped to 54.7%. The film showed that the red shift for the absorption edge of the films was moved to the low wave number. The result intimated that the sp3 bond in the film was decreased, which was consistent with the previous Raman spectroscopic analysis. The content of sp3 bond was lower, and the transmittance was decreased more[9]. In addition, increasing power would increase the deposition rate of C particles and the thickness of the film (Table 1). Excessive thickness would weaken the transmittance and lead to the decreasing of the film infrared transmittance [10]. When the sputtering power was reached at 120W, the surface roughness of the film was larger, which can enhance the scattering effect of the film and would affect the film transmittance.
Fig. 12 shows metallographic microscopic images of the worn films at different sputtering power. When the sputtering power was 80W and 120W, the carbon-based film at the edge of the wear trace had obvious peeling phenomenon, indicating that the wear resistance of the carbon-based film was poor under the two sputtering powers. While the sputtering power was 100W, the film on the edge of the wear mark was smooth, and the film was tightly bonded to the underlying substrate. The optimum sputtering power was selected to be 100 W in consideration of the abrasion resistance and optical properties of the C-based film.

3.3. Substrate temperature

Fig. 13 and 14 show the SEM and AMF 3D morphologies of carbon-based films at room temperature, 150℃ and 300℃, respectively. When the substrate temperature was raised from room temperature to 150℃, the film structure was improved, the fluctuation of film surface became smaller and the particles in film became more uniform. When the substrate temperature reached 300℃, the particles on film surface became smaller, but there were some large clusters and bulges on the film surface. When the energy of C particles arriving at the substrate was constant, substrate temperature was an important factor determining the film morphology [11].

With the temperature rising from room temperature to 150℃, the kinetic energy of C particles deposited on substrate was increased, and the migration ability of C particles along the substrate surface was improved, thus the film defects were reduced and the film surface became smooth and dense. When the substrate temperature rose to 300℃, the kinetic energy of C particles on substrate was large, which would cause the C particles on the substrate to move in a non-directional direction,
and did not be easily adsorbed and condensed by the substrate. Some C particles would escape and return to the sputtering chamber, which would destroy the film structure, increase the defects and roughness of the film.

Fig. 15 shows the XRD patterns of C-based films at different substrate temperatures. It can be found that the diffraction peaks of C-based films were increased slightly with the increasing temperature, indicating that the high substrate temperature could promote the crystallization of the films. However, the broad peaks suggested that the films still existed mainly in amorphous form.

Fig. 16 shows the Raman spectra of C-based films at different substrate temperatures. It can be seen that there were obvious G peaks near 1552 cm⁻¹ and weak D peaks near 1353 cm⁻¹ from the spectra. With the increasing of temperature, the half-width and wave-peak of G-peak were decreased, and the G-peak shifted slightly to the direction of the low wave number. It indicated that the sp3 bond fraction in the films decreased and the sp2 bond fraction increased, which was proved in Table 2 too by the decrease of R with the increasing of substrate temperatures. It can be speculated that the film structure was being transformed to graphite-like structure, but that R was always greater than 1 in table 2 proved that the film was still the DLC thin film.

Fig. 17 shows that the wave number dependence of the infrared transmittance of film under the different substrate temperatures. It can be seen from the graph that the maximum transmittance of the film was increased from 56.5% to 57.0% when the substrate temperature was raised from room temperature to 150°C, which was in contradiction with the Raman test results. The Raman test result showed that the sp3 bond fraction in the film was decreased with the increasing of the substrate temperature, so the transmittance of the film should be decreased. As the substrate temperature increased, the vibration of C particles on the substrate became more intense, the energy dissipation would slow down, and the relaxation time would increase, so the degree of crystallization of films would be improved. The film transitioning from disorder-to-order would lead that the metastable sp3 bond would be turned into the lower binding energy sp2 bond [10,12]. If the inverse relationship between the transmittance and thickness of film was considered, this abnormal behaviour could be explained. Table 1 showed that as the temperature increased, the film thickness decreased, so that the transmittance of the film deposited at 150 °C can be improved. When the temperature was raised to 300 °C, the transmittance of the film was lowered to 54.7%, which indicates that the reduced transmittance was caused not only by the decrease of the sp3 bond in the film but also by the irregularity of the surface morphology. The uniform distribution of film particles became worse with the substrate temperature of 300°C, which would enhance scattering effect and weaken the transmittance of the films. The two factors affecting the transmittance of the film in relation to the sp3 bond and the surface morphology of the film were higher than factors that resulted in an increase in film transmittance due to a decrease in film thickness.
Figure 18 Metallographic microscopic images of the worn carbon-based films under different temperature.

Fig. 18 shows the metallographic microscopic images of the worn films at different substrate temperatures. It can be found that the worn films had obvious differences at different substrate temperatures. When the substrate temperatures were room temperature and 300°C, the carbon-based films at the edge of the wear marks had obvious peeling phenomenon, indicating that wear resistance of the carbon-based film was poor at both temperatures. When the sputtering temperature was selected to be 150°C, the edges of the wear marks were smooth, and were not easily peeled off after rubbing. Considering the wear resistance and optical properties of the DLC thin film, in this experimental scheme, the optimum substrate temperature was easily selected to be 150°C.

4. Summary
In this paper, the effects of Ar pressure, sputtering power and substrate temperature on the transmission and wear resistance of C-based films were studied by magnetron sputtering technique. The main conclusions are as follows:

(1) The carbon-based film prepared under different sputtering conditions belonged to the DLC film. An increase in the sp3 bond in the film is more preferably a diamond-like structure.

(2) The sp3 bond fraction increased as the Ar pressure increased, and decreased as the sputtering power increased or the substrate temperature increased.

(3) The content of sp3 bond had an important influence on the transmittance of DLC films. The higher the content of sp3 bond was, the higher the transmittance of DLC films would. However, when the content of sp3 bond was too large, the higher the internal stress and the worse the wear resistance of DLC films would be.

(4) The optimized deposition parameters were: Ar pressure of 0.7 Pa, sputtering power of 100 W, and substrate temperature of 150 °C.

Acknowledgments
Authors This work was funded by Ningbo Natural Science Foundation (No.2018A).

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