Effect of Nonbonded Hydrogen on Structure and Properties of DLC Films

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Abstract— a-C: H films were prepared on the surface of 316 L stainless steel, aluminum foil and single crystal silicon (100) wafer by PE-CVD. The effect of nonbonded hydrogen on the thermal stability and properties of the films was discussed. The analysis results show that the H elements in this a-C: H film mainly exist as free states of H molecules or H atoms. The graphitization stage of the a-C: H films prepared in this experiment are obviously divided into two stages by the precipitation of non-bonded H 564°C. At the same time, the escape of non-bonded H significantly resulted in the release of internal stress and significantly promoted the second stage graphitization. Under the action of hydrogen evolution and graphitization, the microstructure of carbon film is rearranged and agglomerated in a certain direction.

1. INTRODUCTION

Hydrogen-containing diamond-like carbon films (a-C: H) is a kind of material with outstanding mechanical properties, high resistance, high biocompatibility and excellent optical properties, which has attracted worldwide attention. However, under the condition of overheating, diamond-like carbon films usually undergo structural reorganization and performance transformation. Therefore, the excellent properties of some diamond-like carbons are severely restricted in practical application in some fields due to their limited thermal stability. This problem has become a great challenge for diamond-like carbon to achieve the expected performance in practical application.

Plasma enhanced chemical vapor deposition (PECVD) technology introduces C and H elements
into diamond-like carbon films by ionizing organic source gases during the deposition of diamond-like carbon films. Therefore, for a-C: H films, H in the films, as an inherent element, has an important influence on their thermal stability. However, the process and mechanism of H bonding to C atom escaping with the increasing temperature has become a relatively mature topic [1-9]. However, in diamond-like carbon amorphous films, the influence of non-bonded H (free H) that is not bonded to C on the structure and properties of the films has been rarely studied. Some studies [10, 11] have shown that H may exist in the thin film in the form of H molecules or H atoms (not bonded to C) through FTIR Spectrometer and Elastic Recoil Detection. Moreover, there are also reports in literature [10] that a-C: H thin films containing unbonded H exceeding 80% hydrogen content have been prepared by chemical vapor deposition. However, the research on the role and influence of unbonded H in diamond-like carbon films is limited.

In a word, many literatures have studied diamond-like carbon films containing bonded H, while films containing non-bonded H and the influence of non-bonded H on films have rarely been systematically studied. Therefore, the microstructure and properties of a-C: H films before and after annealing are studied in this paper, aiming at the limited thermal stability of a-C: H films, especially the existence mode of H in the films and its influence on the surface morphology, microstructure changes and mechanical properties, which is of great significance for deepening the understanding and practical application of H-containing diamond-like carbon films.

![Fig.1 DSC curve of a-C:H powders under a constant heating rate of 20 k·min⁻¹](image)

2. EXPERIMENTAL METHOD

In this experiment, a-C: H thin films were obtained by PECVD deposition on 316L stainless steel, silicon wafer and aluminum foil. In order to study the thermal stability of the thin film, DSC tests were carried out on the thin film powder in this experiment (Fig. 1 shows the DSC curve of a-C: H powder under the protection of high purity nitrogen (N₂, 99.999%) at a heating rate of 20 K/min), thus determining the annealing temperature of the a-C: H thin film. It can be clearly seen that the powder has endothermic phenomenon at 208 °C, 316 °C, 470 °C and 577 °C, which indicates that at these four temperatures, a-C: H thin films may undergo certain structural and mechanical changes. Therefore, the annealing temperatures were determined to be 230 °C, 330 °C, 430 °C, 490 °C, 560 °C, 590 °C, respectively. As that subscript of the sample anneal at this temperature, the sample numbers are denote as a-Cad: H, a-C230: H, a-C330: H, a-C430: H, a-C490: H, a-C560: H and a-C590: H, respectively, wherein the subscript ad represents as deposited sample without annealing treatment. The film powder is obtained by chemical peeling method from aluminum foil. The specific process is as follows: the aluminum foil deposited with a-C: H film is placed in hydrochloric acid solution, and the a-C: H film powder containing tungsten carbide transition layer can be obtained after the aluminum foil is dissolved. Because the WC transition layer has high thermal stability below 1000 °C and the diamond-like carbon film has excellent chemical inertness, it can be considered that the residual WC transition layer and the chemical peeling process have no significant influence on DSC results.
3. RESULTS AND DISCUSSION

3.1 Existence Forms of Hydrogen

Figure 2 shows the infrared spectra of a-C: H, a-C230: H and a-C590: H samples. According to the literature report [2-9], H bonds with C in the gaps between sp3 and sp2 clusters, thus forming CHn groups. It generally occupies a large atomic space and conducts that the a-C: H film is usually looser and has a smaller density than the a-C film. However, H bonded to C has a great influence on the stable film structure and film properties. In general, with the increase of annealing temperature, CHn groups decrease from 200 °C to 400 °C and almost completely disappear. The large amount of breakage of this C-H bond induces the transition of sp3 hybrid bond to sp2 hybrid bond in the film and the increase of sp2 hybrid carbon cluster. The rapid growth of graphite nanocrystals will also lead to the transformation of the thin film structure from diamond-like structure to graphite-like structure and the deterioration of mechanical and photoelectric properties.

However, it is worth noting that, according to FIG. 2, only extremely weak peaks appear in the 2700 cm\(^{-1}\)-3200 cm\(^{-1}\) band, and the peaks disappear completely after annealing at 230 °C. Because of the characteristic peaks of carbon-hydrogen bonds in the range of 2700 cm\(^{-1}\) ~ 3200 cm\(^{-1}\) in the infrared spectrum, it can be confirmed from the experimental results that only a small amount of carbon-hydrogen bonds exist in the diamond-like carbon film prepared in this experiment, and CHn clusters completely disappear after annealing at 230 °C and above. This phenomenon is different from the research results of many scholars mentioned above [1-9].

Based on the above findings, mass spectrometry is used as a necessary means to verify the existence of H in the film (except for a small amount of H bonded to C) and to determine the precipitation temperature in this experiment. The results of mass spectrometry are shown in FIG. 3. When the experiment was carried out for 26.2 minutes and the temperature rose to 564 °C, the hydrogen intensity began to increase significantly compared with the previous 25 minutes. This indicates that H\(_2\) began to precipitate in the film at around 560 °C. Since CHn functional group does not exist at temperatures above 230 °C, almost all of the precipitated H in the film is not bonded to C. It can be seen that there are a large number of H in the non-bonded state in the film and it only starts to precipitate at high temperature. The precipitation temperature of about 564 °C also corresponds to the fourth peak at 577°C in the DSC analysis result. In summary FTIR and MS results fully verify that H in a-C: H thin films mainly exists in unbonded state in this experiment.

3.2 Raman Spectroscopy and X-ray Photoelectron Spectroscopy

In this experiment, Raman spectroscopy was used to analyze the microstructure of the film. As shown in Figure 4. The films prepared in this experiment all have the characteristics of asymmetric peaks, so the samples have typical diamond-like carbon structures. There is an absorption peak at 1539 cm\(^{-1}\), which is called G-peak. The peak corresponds to the SP2 lamellar cluster structure in the film and originates from the in-plane stretching vibration of the C-C bond in the graphite structure [12]. The
absorption peak at 1391 cm\(^{-1}\) is the D peak of a-C: H film, which corresponds to disorder the structure of graphite boundary (disordered carbon bond at grain boundary), originates from stretching vibration in graphite structure. After fitting, the peak intensities \(I_D\) and \(I_G\) of D peak and G peak can be obtained. It is generally believed that the intensity ratio of D peak to G peak, i.e. \(I_D/IG\), corresponds to the number of sp\(^2\) bonds. The larger the ratio, the more defects in C atomic crystal [13]. In amorphous carbon, the sp\(^3\)/sp\(^2\) value and \(I_D/IG\) value show reverse changes, that is, the smaller the \(I_D/IG\) value, the higher the sp\(^3\) hybrid carbon content.

![Fig.4 Raman spectra of a:C-H films annealed at specified temperatures](image1)

![Fig.5 Gaussian fitting results for Raman spectra of annealed films.](image2)

Fig.4 shows the change of G peak position and the change of \(I_D/I_G\) ratio (inverse ratio versus sp\(^3\) content) [14, 15]. In terms of test temperature, the changes of \(I_D/I_G\) and G peak positions are not obvious. However, the ratio of \(I_D/I_G\) increases obviously when annealed in the range of 430 \(\sim\) 490 ° C and 560 \(\sim\) 590 ° C, and the temperature range of the change is also consistent with the last two peak temperatures of DSC results. The shift of G peak to high band indicates that the size of sp\(^2\) clusters increases with the increase of annealing temperature, and the increase of the intensity of G peak above 430 ° C also indicates the change of sp\(^2\) cluster size. The increased \(I_D/I_G\) ratio is related to the rearrangement of sp\(^3\) carbon clusters and the transition from sp3 bond to sp2 bond, which also indicates that the graphitization transition of carbon films starts from this temperature [16]. Notably, as shown in the red dashed circle in figure 5, The graphitization process of a-C: H films in this experiment is obviously divided into two stages, which is different from the graphitization process of a-C: H films containing bonded hydrogen in other studies.

The graphitization of the first stage occurs under sufficient thermal drive, which is related to the poor thermal stability of the a-C: H film itself. In the second stage of graphitization, the precipitation of H reduces the internal stress formed during the deposition of the film and reduces the degree of structural distortion, thus the film reaches a more stable state through the effect of structural rearrangement and sp\(^2\) phase agglomeration at high temperature.

For the convenience of analysis, the C1s peaks were fitted in this experiment. To quantitatively obtain the sp\(^3\)-C/sp\(^2\)-C content in the film, The C1s spectrum was calibrated and the background peak was deducted by Shirley method. The graphite characteristic peak (284.4 eV) and diamond characteristic peak (285.6) were fitted by Gaussian-Lorentzian method [17]. Finally, the area ratio sp\(^2\)/sp\(^3\) of the characteristic peak was obtained.
As shown in Fig. 6, there is a low content of oxygen in the film, which is due to un-bonded oxygen adsorbed on the sample surface and a small amount of oxygen molecules remaining in the chamber [18]. Compared with a-C<sub>ad</sub>: H, with the increase of annealing temperature, the C1s peak position of a-C590: H shifts to the lower peak position by 0.4 eV due to the agglomeration of graphite phase, and the peak widened.

The position of the C1s peak and the fitted area ratio sp<sup>2</sup>/sp<sup>3</sup> have been plotted in figure 7. The area ratio is relatively stable below 430°C, but when the temperature rises to 430~490°C and 560~590°C, the sp<sup>2</sup>/sp<sup>3</sup> ratio increases obviously. For the convenience of comparison, the test results of Raman spectra I<sub>d</sub>/I<sub>g</sub> also plotted in the figure with green dashed lines. By comparison, it is obvious that the results of XPS and Raman spectra are highly consistent, so the results of XPS and Raman spectra together support the view of stage graphitization.

![Fig.6 XPS spectra of the C1s core level spectra of the films annealed at specified temperatures.](image)

![Fig.7 The result of XPS, the dotted green line represents the experimental data](image)
3.3 characterization of microstructure

Figure 8 is the microscopic surface morphology of the a-C: H films treated by annealing at different temperatures, which is $4 \times 10^4$ times larger under SEM. And the surface randomly presents a granular bulge with a diameter of 100-300 nm. With the increase of annealing temperature, it can be found that the particles show a growing trend: after annealing at different temperatures, the area of particles increases from 0.15$\mu$m$^2$ to 0.28$\mu$m$^2$. When the annealing temperature rises to 560°C and 590°C, the circular particle bulges on the surface show a regular linear arrangement, and the sample thickness is between 1.14 and 1.21$\mu$m after annealing at different temperatures. The surface features of circular protrusions are consistent with the findings of Catena A. et al. on the carbon film surface with PET as the substrate.

Catena A. [16, 19] et al. deposited a-C: H films by RF-PECVD method with C$_2$H$_2$ as gas source. According to the Catena A. study, with the deposition process (>500nm), the film surface shows the phenomenon of condensation and large particle area, that is, particles begin to merge. It is precisely because of this grain merging property that the texture features of the substrate are covered and disappeared. This study also indicates that the growth pattern of layered growth. Besides, the bombardment of the surface by high-energy ions in the plasma during the deposition of the film will not only lead to a higher degree of interaction and combination of the sp$^3$ structure in the film, but also cause protruding particles.

![Fig.8 SEM micrographs of annealed a-C: H films](image)

To study the change of micro-morphology more clearly, the surface roughness of the annealed a-C: H films was analyzed by 3D white light interferometer and the statistical results were drawn in the figure.

![Fig.9 Average roughness of specimen annealed at specific temperatures](image)
The annealing temperature of the first four samples in Fig. 9 is lower than 430°C, and its surface roughness is between 0.018μm and 0.025μm, which does not change much. However, when the annealing temperature is higher than 430°C, the surface roughness increases monotonously with temperature. This change is related to the surface structure of the circular bulge [16,19], i.e., The surface particles are agglomerated and grown. Notably, the roughness change between a-C_{490: H} and a-C_{560: H} is more drastic.

Moreover, for a-C_{560: H} and a-C_{590: H} samples, the roughness values measured along the linear alignment direction are 0.017μm lower than those measured perpendicular to the linear alignment direction. This phenomenon is considered to be related to the structural change of the film, that is, the graphitization of the film, the precipitation of hydrogen and the growth of particle size affect the surface roughness of the sample. It should be noted that the linear rearrangement of the a-C: H film surface was not found during the first stage of graphitization, i.e., In samples with annealing temperatures below 490°C, no obvious change in roughness was found with different lateral and longitudinal measurements. And the phenomenon coincides with the precipitation and internal stress release of hydrogen 560°C to 590°C. This is because the sp² phase rearranges and agglomerates along a specific direction that is more conducive to the release of internal stress, producing a special texture when the shear stress exceeds the critical stress [20]. From this point of view, the characteristics of the linear rearrangement can also be considered as the transformation characteristics of the film from diamond-like structure to graphite structure.

4. CONCLUSION
In this paper, hydrogen-containing diamond-like carbon films were prepared by PECVD. After annealing at different temperatures, it is found that hydrogen atoms in hydrogen-containing diamond-like carbon films do not bond with carbon atoms to form CHₙ groups, which mainly exist in the form of hydrogen molecules or free states of hydrogen atoms. Hydrogen-containing diamond-like carbon films are affected by the precipitation of unbonded hydrogen at 564°C, and the graphitization stage is obviously divided into two stages. The escape of non-bonded hydrogen from hydrogen-containing diamond-like carbon films leads to obvious internal stress release and promotes the second stage graphitization. Under the action of hydrogen precipitation and graphitization, the microstructure of the carbon film rearranges and agglomerates along a specific direction, and the surface shows the characteristics of particle growth, roughness increase, linear arrangement of particles, etc.

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