

Research Article

A Low-Stress, Elastic, and Improved Hardness Hydrogenated Amorphous Carbon Film

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The evolution of hydrogenated amorphous carbon films with fullerene-like microstructure was investigated with a different proportion of hydrogen supply in deposition. The results showed at hydrogen flow rate of 50 sccm, the deposited films showed a lower compressive stress (lower 48.6%), higher elastic recovery (higher 19.6%, near elastic recovery rate 90%), and higher hardness (higher 7.4%) compared with the films deposited without hydrogen introduction. Structural analysis showed that the films with relatively high sp^2 content and low bonded hydrogen content possessed high hardness, elastic recovery rate, and low compressive stress. It was attributed to the curved graphite microstructure, which can form three-dimensional covalently bonded network.

1. Introduction

Hydrogenated amorphous carbon films with fullerene-like microstructure have attracted increasing attention due to their extraordinary properties of high mechanical hardness and low friction coefficient [1–4]. It can be as a protective coating in tooling components, such as knives, drill bits, dies, and molds, and as a coating on hard-disk platters and hard-disk read heads. Until now, hydrogenated amorphous carbon films with fullerene-like microstructure had been synthesized by our group and other groups with different techniques including dc pulse plasma chemical vapor deposition (CVD), magnetron sputtering (MS), ECR CVD, and ICP CVD [1–8].

In this paper, hydrogenated carbon films were deposited with dc pulse plasma CVD system. The as-deposited carbon films could be considered as nanocomposite thin films with fullerene-like microstructure in the diamond-like carbon (DLC) matrix based on our previous results [1, 2]. In order to study the evolution of structure and properties of films, a different content of H_2 was introduced to the mixture of methane and hydrogen as feedstock. The deposition pressure was kept constant. The result discloses the close relationship between sp^2 content, bonded hydrogen content and

hardness, elastic recovery rate, and compressive stress. The film deposited at hydrogen flow rate 20 and 50 sccm showed higher hardness and elastic and lower compressive stress.

2. Experiments

Hydrogenated amorphous carbon films were prepared on Si (100) substrates at different flux ratio of methane to hydrogen in the mixture which was about 1:0, 1:1, 1:2, 1:5, and 1:10 by dc-pulse plasma CVD technique. The flux of methane was kept constantly at 10.3 sccm. The deposition pressure was kept at 13 Pa. After deposition, optical profilometry, X-ray photoelectron spectra (XPS), reflection Fourier transform infrared (FTIR) spectra, and high-resolution transmission electron microscopy (HRTEM) were applied to probe the microstructure. Nanoindentation was applied to assess mechanical properties of the films.

3. Results and Discussion

Figure 1(a) shows the thickness and compressive stress of hydrogenated amorphous carbon films deposited with dc pulse plasma CVD versus H_2 flow rate. The film thickness

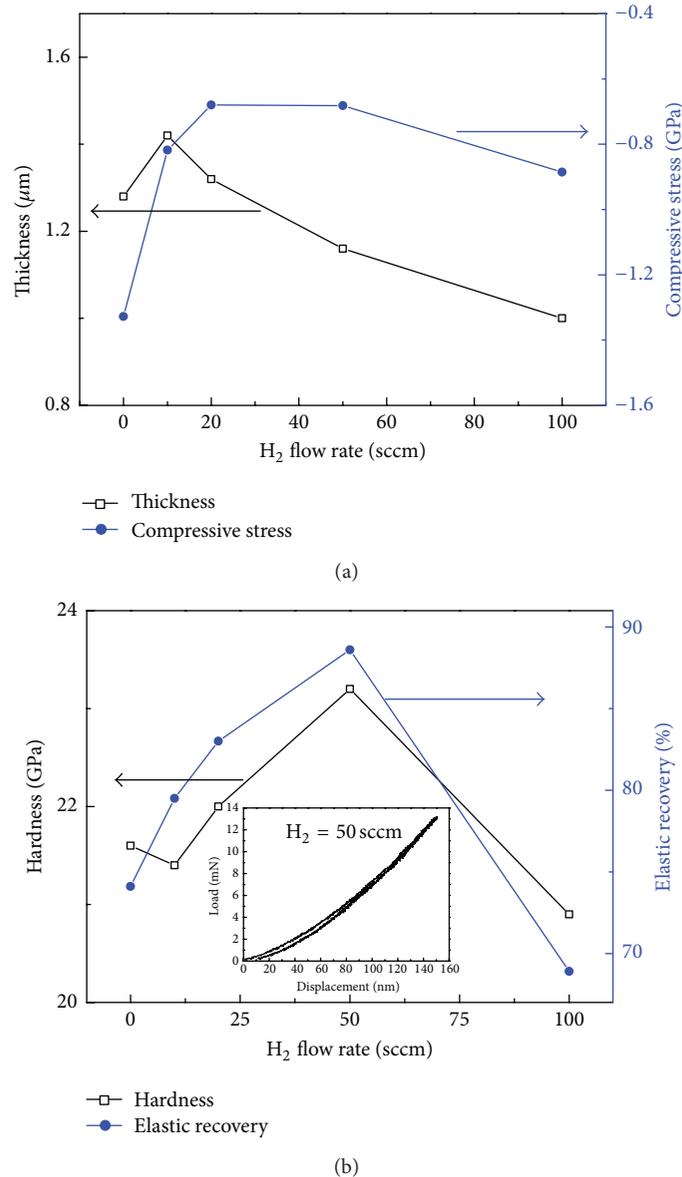


FIGURE 1: (a) Thickness and compressive stress of the as-deposited hydrogenated amorphous carbon films versus H₂ flow rate; (b) hardness and elastic recovery R of the as-deposited hydrogenated amorphous carbon films versus H₂ flow rate.

values were measured by surface profilometer. The compressive stress values were calculated by Stoney's equation with curvature radii that were measured by optical profilometry. It is obvious that the compressive stress value decreased quickly when H₂ was introduced into the mixture gas as feedstock. The values for the films deposited at H₂ 20 and 50 sccm are lower (~48.6%) than the film deposited without H₂ introduction. Generally, for amorphous carbon films, the decrease of compressive stress is corresponding to the structure transform of sp³-bonded atoms to sp²-bonded atoms.

Figure 1(b) exhibited the mechanical properties of the hydrogenated amorphous carbon films versus the H₂ flow rate. In our experiment, in order to minimise the effect of substrate, the maximum indentation depth was kept at 1/7 of the film thickness. Five replicate indentations were made

for each film sample. The elastic recovery R was defined as $R = (d_{\max} - d_{\text{res}})/d_{\max}$, where d_{\max} and d_{res} were the maximum displacement at the maximum load and the residual displacement after unloading, respectively [9]. This is a clear indication of plastic deformation regime. For the films deposited using dc-pulse plasma CVD versus the H₂ flow rate, the mechanical properties increased at the beginning, as shown in Figure 1(b). When the H₂ flow rate increased to 50 sccm, the hardness of the film was as high as ~23.2 GPa, 7.4% higher compared to ~21.6 GPa for the film deposited without H₂ introduction, and the elastic recovery R was as high as ~88.6%, 19.6% higher compared to ~74.1% for the film deposited without H₂ introduction. When the H₂ flow rate increased to 100 sccm, there was a sharp decrease for hardness and elastic recovery. The values were decreased to ~20.9 GPa

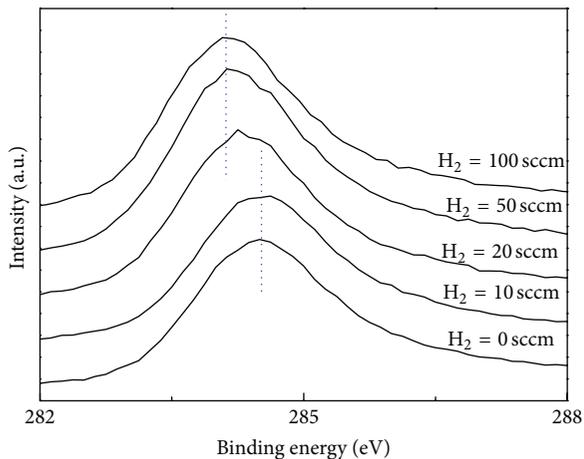


FIGURE 2: XPS spectra of as-deposited hydrogenated amorphous carbon films versus H_2 flow rate.

and ~68.9%, respectively. In order to reveal the reason of the transform and the origin of lower stress, higher hardness, and elastic recovery R , it is necessary to perform the films' structure probing to reveal the structure factor.

Figure 2 shows the C1s core level XPS spectra of hydrogenated amorphous carbon films versus different H_2 flow rates. In this paper, Au thin film about 0.2 nm was deposited on the test surfaces so as to minimize the charging effect in the XPS analysis. The C1s peak can be decomposed into two peaks: sp^2 and sp^3 . The one around 284.3 eV corresponded to sp^2 carbon atoms, and that around 285.2 eV corresponded to sp^3 carbon atoms [10]. The C1s binding energy position of the film deposited without H_2 introduction is ~284.6 eV. As the H_2 flow rate increased, except at the H_2 flow rate of 10 sccm, a clear chemical shift to lower binding energy showed at H_2 flow rate of 20, 50, and 100 sccm. We concluded that the sp^2 carbon structure increased with the increased H_2 flow rate. It was likely that excess H_2 flow rate increased the impact of ion etching and impingement and led to the structure transformation from sp^3 to sp^2 . In particular, the binding energy positions of C1s at the H_2 flow rate of 50 and 100 sccm are very close to the binding energy of C1s for pure graphite, 284.3 eV [11]. Combined with the data of stress, hardness, and elastic recovery R , the reason for the improved properties of the film deposited at H_2 flow rate of 20 and 50 sccm should be the increased sp^2 structure. It mainly existed in the form of fullerene-like curved graphite structure. The increased binding energy level at H_2 flow rate of 10 sccm is due to the defects (dangling bonds) in the films that were ended or occupied by H atoms when H_2 was introduced, which prompted the formation of sp^3 structure.

In order to get a better understanding of the bonding structure of all the samples, reflection FTIR spectra were invoked to determine the C-H bonding configuration. The bonded hydrogen content in films can be applied as a probe to detect the structural environment of the attached carbon atoms due to the localized nature of the C-H vibration. FTIR spectrum was widely used in this sense to characterize the

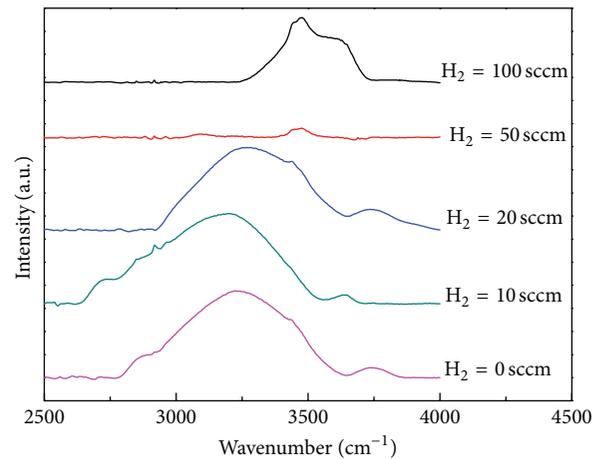


FIGURE 3: Reflection IR spectra of as-deposited hydrogenated amorphous carbon films versus H_2 flow rate.

C-H bonding in hydrogenated carbon films. It is known that the FTIR intensity of amorphous carbon films is relevant to the hydrogen incorporation.

Generally, the peaks in the range of 2800–3300 cm^{-1} are attributed to the different stretching vibrations of C-H bonds. The C-H stretching modes can break down into three regions, the $sp^1 \equiv C-H$ modes centre on 3300 cm^{-1} , the $sp^2 =CH_n$ modes lie from 2975 to 3085 cm^{-1} , and $sp^3 -C-H_n$ modes lie from 2850 to 2955 cm^{-1} [12]. Figure 3 shows the reflection FTIR spectra of as-deposited hydrogenated amorphous carbon films versus the H_2 flow rate. For the film deposited without H_2 introduction, the peak was broad, and it can conclude $sp^3 -C-H_n$, $sp^2 =CH_n$, and $sp^1 \equiv C-H$ complexes. However, by carefully examining the peaks, it is also found that there is a clear chemical shift to high wavenumber at H_2 flow rate of 20, 50, and 100 sccm, and the peak intensity at the flow rate of 50 sccm decreased sharply, indicating a reduction of bonded hydrogen in carbon films. At the H_2 flow rate of 10 sccm, since the defects (dangling bonds) in the films probably could be ended or occupied completely by H ions generated by methane and H_2 , which prompt the formation of sp^3 structure, the peak position has a little shift to lower wavenumber. The analysis of increased sp^3 content is consistent with that provided by XPS. When H_2 content further increased, impact of ion etching and impingement increased, and $sp^3 -C-H_n$ changed into $sp^2 =CH_n$ and $sp^1 \equiv C-H$. As the H_2 flow rate was increased to 50 sccm, mounts of C-H bonding were destroyed; -H easily combined each other to form H_2 and led to a loss of hydrogen content in the as-deposited film. It is obvious that the structure was gradually turned into sp^2 . When H_2 flow rate increased further, impact of ion etching and impingement was strong and led to porous structure in film. We suggest that this is the reason for the absorption peak of H_2O at a wavenumber of 3400–3700 cm^{-1} for the film deposited at H_2 flow rate of 100 sccm. Combined with XPS spectra, the reason of the improved properties of the film deposited at H_2 flow rate of 20 and 50 sccm should be the

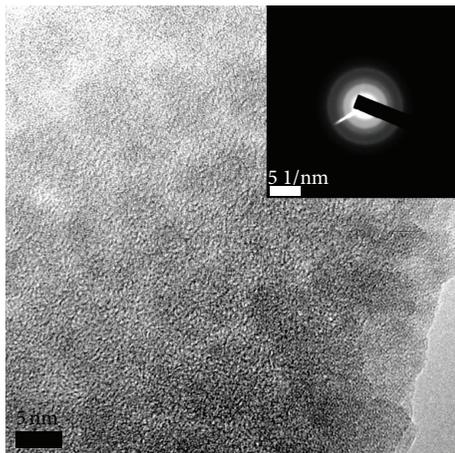


FIGURE 4: TEM images of as-deposited hydrogenated amorphous carbon films versus H_2 flow rate of 50 sccm. The scale bar represents 5 nm.

increased sp^2 structure that mainly existed in the form of fullerene-like curved graphite structure, and the reason for poor properties of the film deposited at H_2 flow rate of 100 sccm should be the porous structure of the film formed in deposition process.

Figure 4 shows the HRTEM image of the hydrogenated amorphous carbon film deposited at H_2 flow rate of 50 sccm by dc pulse plasma CVD, displaying amorphous structure. There is no obvious ordered fullerene-like curved graphite structure. The corresponding SAED pattern indicates the amorphous structure of the film and displays three corresponding measures of spacing of 1.15, 2.00, and 3.50 Å. The two rings at 1.15 and 2.00 Å coincide with those observed for amorphous carbon structure, whereas the ring at 3.50 Å matches well the interplane spacing of hexagonal basal planes of graphite (0002) [13]. The appearance of a broad feature at 3.50 Å indicates the presence of defective graphitic planes and confirms the formation of fullerene-like structure in as-deposited films. However, the fullerene-like features in our HRTEM image are not so clear compared to the other reports [2, 14]. The reason is mainly from the too large thickness for HRTEM samples. Meanwhile, the HRTEM image can be seen from our previous reports. Combined with XPS and FTIR spectra results, it was reasonably concluded that the improved mechanical properties were corresponding to increased curved graphite (fullerene-like) structure. We speculated the reason why there was no obvious curved graphite structure that was from the impact of ion etching and impingement and led to a poor order of the structure.

It was obvious that the improvement of mechanical property versus H_2 flow rate was due to the change of microstructure. It was much different from conventional hydrogenated amorphous carbon films, in which the mechanical properties decreased as sp^2 bonding structure increased; in other words, a high concentration of sp^2 graphitic bonds indicates soft film. Recently, the nanostructure of the films may also play dominant role in determining the mechanical properties of amorphous carbon films [1, 2]. This thought is supported

by the recent report that the mechanical properties of DLC films probably are not only dominated by sp^3 fraction but also the degree of the sp^2 bonding arrangement. In this paper, combined with XPS results, according to our and other researchers' reports, fullerene-like microstructure in the hydrogenated carbon matrix could be considered as the structure factor for the lower compressive stress, high hardness, and high elasticity. The film can possess lower stress, higher hardness, and higher elasticity by adjusting sp^2 content and bonded hydrogen content.

4. Conclusion

In summary, the evolution of structure and mechanical properties of the hydrogenated amorphous carbon films with fullerene-like microstructure was investigated. The results showed that at hydrogen flow rate of 50 sccm, the deposited hydrogenated amorphous carbon films exhibited lower compressive stress (lower 48.6%), higher elastic recovery (higher 19.6%, near elastic recovery rate 90%), and higher hardness (higher 7.4%) compared with the films deposited without hydrogen introduction. Structural analysis showed that the film with relatively high sp^2 content and low bonded hydrogen content possessed high hardness, elastic recovery rate, and low compressive stress. It was attributed to the curved grapheme microstructure, which can form three-dimensional covalently bonded network. Meanwhile, when excess H_2 was introduced, impact of ion etching and impingement was strong and led to porous structure in film.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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