Structural analysis of hydrogenated diamond-like carbon coatings prepared using magnetron sputtering

Y L Su1*, S H Yao2, Y H Mao1, Z L You1

1Department of Mechanical Engineering, National Cheng Kung University, No.1, University Road, Tainan City 701, Taiwan
2Program in Technology Management, Chang Jung Christian University, No.1, Chang-Da Road, Tainan City 711, Taiwan

*E-mail: suyl@mail.ncu.edu.tw

Abstract. In this study, a series of hydrogenated diamond-like carbon (H-DLC) coatings were deposited using an unbalanced magnetron sputtering system. For hydrogenation, acetylene gas was used as the hydrogen source. The typical conditions for preparing DLC coatings were used, with additional acetylene gas being introduced into the depositing chamber. The acetylene flow rate was varied from 0 to 16 sccm at intervals of 4 sccm and finally set at 24 sccm. The chemical composition, microstructure, and phases of the resulting coatings were evaluated. Fourier transform infrared spectometry, X-ray photoelectron spectroscopy, and Raman analysis were performed, and specific mechanical properties were examined. The results indicated that hydrogenation influenced the H-DLC coatings due to the formation of sp³ bonding. The coating prepared at a flow rate of 8 sccm of acetylene exhibited the highest hardness of 15.4 GPa because it had the highest number of sp³ bonds.

1. Introduction

Protective coatings have been commonly used in industrial applications for several decades [1-2]. Amorphous carbon (including a-C and a-C: H) coatings, better known as diamond-like carbon (DLC) coatings, exhibit mechanical properties comparable to diamonds, such as high hardness. DLC coatings have been widely applied in diverse industries, such as in the fields of aerospace, automobiles, oil and gas, construction, and power generation [3-5]. Aisenberg and Chabot (1971) were the first to employ a deposition technique to prepare DLC coatings [6]. For more than 30 years, various deposition techniques have been developed for obtaining DLC coatings. Among them, magnetron sputtering is one of the most commonly used methods [7-8]. DLC coatings deposited using magnetron sputtering exhibit lower residual stress, higher loading capacity, and higher hardness than coatings prepared using other techniques, such as radio frequency and plasma-activated processes [9]. A published study sought to transition from DLC to a-C:H coatings and to achieve high deposition rates by applying carbon-carrying gas to working atmospheres [10]. Jacob and Moller controlled the ratio of sp² bonds to sp³ bonds to obtain various forms of C-H alloys in the ternary phase diagram of an amorphous C-H coating [11]. Liu et al. indicated that the acetylene flow rate and substrate temperature during the deposition determined the structures of DLC coatings [12]. Conditions such as the chamber atmosphere and preparation method considerably influence a coating’s final performance, while the addition of H also affects DLC coatings. Tillmann and Hoffmann found that the hardness decreased with increases in H content when the H content was more than 20 at.% [13]. Rabbani and Vogelaar prepared hydrogenated
DLC (H-DLC) coatings by using CH₄ gas and found that H addition led to an increase in the I₀/I₃ ratio and surface roughness (RMS) [14]. Piao et al. reported that increases in the H₂ flow rate did not lead to a remarkable increase in the deposition rate but caused a decrease in the I₀/I₃ ratio and surface roughness (RMS) [15]. Toro et al. determined that the deposition rate decreased with increases in the H₂ flow rate [16]. In this research, a series of H-DLC coatings with high H content was prepared by increasing the flow rate of acetylene up to 24 sccm. The influence of H addition on the coating structures was systematically investigated.

2. Experiment

2.1. Coatings

The H-DLC coatings were deposited using an unbalanced magnetron sputtering system (KD-550U, Taiwan), featuring four targets positioned orthogonally around the rotating specimen holder. SKH51 steel (HRC 65) and p-type (100) Si wafers were used as substrate materials. The steel was used for evaluating the mechanical properties, whereas the Si wafers were used for structural analysis. Three graphite and one Ti targets were used (300 mm × 109 mm × 10 mm, 99.5% purity, Nutek Material Co.). The sample holder rotated at a speed of 3 rpm. The targets were oriented towards the coated samples, and the distance between the samples and the targets was 13 cm. Each coating comprised a Ti interlayer followed by a TiC transitional layer and finally the main hydrogenated carbon layer. The Ar gas flow was maintained at a constant rate of 45 sccm during the deposition process. The Ti interlayer was deposited using one Ti target under a Ti current of 1 A and a bias voltage of −80 V for 10 minutes. The TiC transitional layer was prepared under a Ti current of 1 A, a C current of 2 A, and a bias voltage of −80 V for 6 minutes. The two layers (Ti interlayer, and TiC transitional layer, had a total thickness of near 0.1 µm, aiming at enhancing adhesion between the coating and the substrate. To prepare a series of main layers with varying H content, the flow rate of acetylene gas was varied from 0 to 16 sccm at intervals of 4 sccm and finally set at 24 sccm. The other conditions were fixed, with a bias voltage of −40 V and a C current of 2.5 A. Under the aforementioned conditions, amorphous (a-) C coatings were obtained. The coatings were named according to the acetylene flow rates at which they were produced. The coatings were given the following names: a-C, a-C:H04, a-C:H08, a-C:H12, a-C:H16, and a-C:H24.

2.2. Analysis equipment

A Fourier transform infrared (FTIR) spectrometer (Thermo Nicolet Nexus 470, Japan) was used to detect the H content in the coatings. The FTIR measurements were performed in the scan range of 2800–3500 cm⁻¹ with a resolution of 0.1 cm⁻¹. Raman measurements (HR800 Micro-PL, Horiba, Japan) were conducted at room temperature with the 633-nm line of a He–Ne laser in the working spectral range of 1000–2000 cm⁻¹. An X-ray photoelectron spectrooscope (PHI 5000 VersaProbe, Japan) was employed with monochromatic Al K-alpha radiation ranging from 282 to 290 eV. The OriginLab software (OriginLab Corporation, USA, Massachusetts), which was used in FTIR spectroscopy and Raman analysis, was also used to deconvolute the X-ray spectroscopy (XPS) spectrum according to the Gaussian–Lorentzian method. The ratios between the deconvoluted bands were calculated using the areas under each deconvoluted peak. The cross-sectional microstructure and thickness of the coatings were examined using a field emission scanning electron microscope (SEM) (HITACHI SU-5000, Japan). The Ra value was analyzed using a surface profilometer (Kosaka SE-300, Japan) with a cut-off of 0.25 mm. The nanohardness was measured using an LBI nanoindenter (UNAT-M, Germany) under an indentation load of 10 mN and depth of 100–130 nm. The adhesion was evaluated using a scratch tester (FM-POD-200NT, Taiwan) under a load of 0–100 N applied at a rate of 10 N/mm and increment of 1 N per second by a diamond head with a diameter of 30 µm. During scratching, a critical failure load (Lc) value was obtained, which was defined as the point when the friction coefficient rose abruptly.
3. Results and Discussion

Figure 1 displays the FTIR analysis results, which indicate the main peak at approximately 2920 cm\(^{-1}\), two shoulder peaks at 2980 and 2850 cm\(^{-1}\), and a small peak at 3010 cm\(^{-1}\). The main peak corresponds to the sp\(^3\) CH\(_2\) asymmetric stretching mode, while the two shoulder peaks to the sp\(^3\) CH\(_3\) asymmetric and symmetric stretching modes, respectively [17–19]. The small peak at 3010 cm\(^{-1}\) was from the sp\(^2\) CH\(_2\) asymmetric stretching vibration [20]. Considering the effects of flow rate of acetylene, in spite of no remarkable difference between the a-C:H04 and a-C:H08 coatings, the strength of peaks corresponding to the C-H stretch increased when the flow rate increased, which indicated increased bonding between C and H. In addition, the increased sp\(^2\) CH\(_2\) can be found.

![Figure 1. FTIR analysis results of the a-C:H coatings.](image)

Figure 2 illustrates the raw Raman spectra, and the Raman analysis results are listed in table 1. The data indicate that with increasing H content, the wave number of the G peaks first decreased and then increased. The a-C:H08 coating had the lowest wavenumber for its G peak. The D peaks exhibited an
opposite trend. When the number of sp³ bonds increased, the G peak shifted to a low position [21]. An increased fraction of sp³ bonding caused an increase in the degree of bonding distortion because of the rise in the shear-to-bulk-modulus ratio of the sp³ structure, which increased the defects in the C structure [22].

| Coating  | D peak position (cm⁻¹) | G peak position (cm⁻¹) | I_D/I_G |
|----------|------------------------|------------------------|---------|
| a-C      | 1364.1                 | 1581.1                 | 1.53    |
| a-C:H04  | 1363.8                 | 1579.9                 | 1.52    |
| a-C:H08  | 1372.4                 | 1571.1                 | 1.67    |
| a-C:H12  | 1366.9                 | 1575.9                 | 1.18    |
| a-C:H16  | 1362.1                 | 1580.9                 | 1.12    |
| a-C:H24  | 1367.7                 | 1583.8                 | 1.07    |

Figure 3. Typical XPS C1s spectra of coatings: (a) a-C, (b) a-C:H:08, (c) a-C:H16, and (d) a-C:H24.

It was learned from the FTIR results that the H addition led to the formation of C-H and C=C bonds. Figure 3 displays the typical XPS results. Because the C-H bonding energy is very close to the C-C bonding energy, deconvolution is not meaningful. Thus, the C-C peak comprised C-C and C-H bonds.
As seen in these figures in Figure 3, the height of the C-C peak increased and then decreased with increasing H\textsubscript{2} flow rate, with the a-C:H08 coating exhibiting the highest C-C peak. The fractions of C-C and C=C bonds were calculated using the XPS spectra (table 2). The a-C:H08 coating showed the highest fraction of sp\textsuperscript{3} bonding. Diesselberg et al. indicated that sp\textsuperscript{2} bonding changes to sp\textsuperscript{3} bonding with a small amount of H addition [23]. When the H content continues to increase, the fraction of sp\textsuperscript{3} bonding decreases and that of sp\textsuperscript{2} bonding increases [24]. The results here are consistent with these findings from previous studies.

**Table 2.** The calculated bond fraction in the XPS C1s spectra.

| Sample     | C-C (%) | C=C (%) |
|------------|---------|---------|
| a-C        | 53.1    | 46.9    |
| a-C:H04    | 60.2    | 39.8    |
| a-C:H08    | 66.7    | 33.3    |
| a-C:H12    | 58.9    | 41.1    |
| a-C:H16    | 58.7    | 41.3    |
| a-C:H24    | 47.5    | 52.5    |

Figure 4 displays the SEM micrographs of the surface morphologies and cross sections of the coatings. The coating thickness increased from 1.4 to 3.1 μm with an increase in the acetylene flow rate. The a-C:H08 coating (figure 4c) exhibited the densest cross-sectional structure. The a-C:H24 coating (figure 4f) presented the least dense structure due to high H content. No columnar structure was observed on any of the coatings, which suggested the formation of amorphous coatings.

**Figure 4.** SEM micrographs of the surface morphologies and cross sections of the coatings: (a) a-C, (b) a-C:H04, (c) a-C:H08, (d) a-C:H12, (e) a-C:H16, and (f) a-C:H24.

Table 3 lists the characterization results of the coatings. All the coatings had very smooth surfaces with ultralow Ra values. The scratching test results indicated that the coatings had comparable adhesion strength except for the poor adhesion of the a-C:H24 coating [20, 25–26]. Table 4 provides the results of the nanohardness test and the calculated $H/E\textsuperscript{2}$ values. The three indices in 4table 4 exhibit an increasing trend with a small addition of H. The a-C:H08 coating showed the maximum value for all
three indices. As the H content continued to increase, the nanohardness and modulus of elasticity decreased drastically.

Table 3. Thickness, surface roughness, and adhesion of the coatings.

| Coating     | Thickness (μm) | Ra (nm) | Lc (N) |
|-------------|---------------|---------|--------|
| a-C         | 1.4           | 37      | 83     |
| a-C:H04     | 1.9           | 33      | 73     |
| a-C:H08     | 2.0           | 34      | 75     |
| a-C:H12     | 2.1           | 36      | 83     |
| a-C:H16     | 2.6           | 38      | 80     |
| a-C:H24     | 3.1           | 36      | 68     |

Figure 5 illustrates the relationship between the hardness and sp³ bonding fraction of the coatings. As the sp³ bonding fraction increased, the nanohardness increased. The a-C:H08 coating had the highest hardness. The a-C:H16 coating had a nanohardness of merely 7 GPa, which indicates the increased sp² C-H bonding.

Table 4. Nanohardness, modulus of elasticity, and H³/E² values of the H-DLC coatings.

| Coating     | Nanohardness (GPa) | Modulus of elasticity (GPa) | H³/E² |
|-------------|---------------------|-----------------------------|-------|
| a-C         | 13.3                | 191.8                       | 0.064 |
| a-C:H04     | 13.4                | 192.1                       | 0.065 |
| a-C:H08     | 15.4                | 198.8                       | 0.092 |
| a-C:H12     | 13.9                | 182.6                       | 0.081 |
| a-C:H16     | 7.0                 | 99.8                        | 0.034 |
| a-C:H24     | 5.4                 | 66.1                        | 0.036 |

Figure 5. Correlation between the nanohardness and sp³ fraction of the coatings.

The FTIR spectroscopy, Raman analysis, and XPS indicated that H addition led to the formation of sp³ C-H bonding, and the sp³/sp² bond fraction varied with H addition. sp³ C-H bonding was less
favorable than sp³ C-C bonding. Moreover, due to the significant difference in the atomic sizes of C and H, sp³ C-H bonding was considered as a defect, and the overall C structure was distorted. However, a small number of defects produced by the appropriate amount of H atoms may enhance the performance of H-DLC coatings. The a-C:H08 coating, which exhibited the highest hardness, had an optimal number of defects caused by H addition.

4. Conclusions
DLC coatings are widely applied in industries and require enhancement. In this study, acetylene gas with a flow rate up to 24 sccm was introduced during deposition to obtain a group of H-DLC coatings. The obtained H-DLC coatings exhibited an amorphous structure. The H content increased with increasing acetylene flow rate. Hydrogenation led to the formation of various types of bonds with hybridized spⁿ states. The fraction of sp³ bonding in the coatings varied with the H content. The a-C:H08 coating grown with 8 sccm acetylene had the highest fraction of sp³ bonding. This coating also exhibited the highest nanohardness of 15.4 GPa. A certain small amount of sp³ bonding in the H-DLC coatings enhanced their hardness.

Acknowledgment
The authors wish to express their gratitude to the Ministry of Science and Technology for financing this research under the grant MOST 105-2221-E-006-071. The support from the Centre of Noble Equipment, NCKU, Taiwan is also acknowledged.

References
[1] Butter R S and Lettington A H 1995 J Chem Vapor Depos 3 182-92
[2] Huang M S, Yang Y S, et al. 2012 J Polym Eng Sci 32 389-99
[3] Loir A S, Garrelie F, et al. 2004 J Thin Solid Films 453–454 531–6
[4] Veerasamy V S, Luten H A, et al. 2003 J Thin Solid Films 442 1–10
[5] Dai H Y, Zhan C, et al. 2016 J Optik 127 2512-5
[6] Aisenberg S and Chabot R 1971 J Appl Phys 42 2953-8
[7] Grill A 2003 J Diamond Relat Mater 12 166–70
[8] Smietana M, Szmidt J, et al. 2008 J Diamond Relat Mater 17 1655–9
[9] Bordin D and Coelho P 2018 J Dent Mater 3123 e1-e10
[10] Rubio-Roy M, Corbella C, et al. 2009 J Diamond Relat Mater 18 923-6
[11] Jacob W and Moller W 1993 J Appl Phys Lett 63 1771-3
[12] Liu W J, Guo X J, et al. 2009 J Thin Solid Films 517 4227-32
[13] Tillmann W and Hoffmann F 2011 J Surf Coat Technol 206 1705-10
[14] Rabani F and Vogelaar B M 2004 J Diamond Relat Mater 13 170-9
[15] Piao J X, Kumar M, et al. 2016 J Surf Coat Technol 307 1119-23
[16] Toro R G, Calandra P, et al. 2017 J Surf Interface Anal 6 60-71
[17] Wang Y, Ye Y, et al. 2011 J Surf Coat Technol 205 4577-81
[18] Dai H, Chen J, et al. 2013 J Non-Cryst Solids 363 77-83
[19] Wu Y, Li H, et al. 2014 J Tribol Int 71 82-7
[20] Tomasella E, Meunier C, et al. 2001 J Surf Coat Technol 141 286-96
[21] Diesselberg M H, Stock -H, et al. 2004 J Surf Coat Technol 188 612-6
[22] Robertson J 1992 J Surf Coat Technol 50 185-203
[23] Neuville S and Matthews A 2007 J Thin solid films 515 6619-53
[24] Ishihara M, Suzuki M, et al. 2005 J Diamond Relat Mater 14 989-93
[25] Cheng Y H, Wu Y P, et al. 1999 J Diamond Relat Mater 8 1214-9
[26] Grill A and Patel V 1993 J Diamond Relat Mater 2 1519-24