

含氢四面体非晶碳膜的制备与结构及力学性能

许世鹏^{1,2}, 占发琦¹, 郑月红¹, 陈维铅^{1,2}, 喇培清¹

(1. 有色金属先进加工与再利用国家重点实验室, 兰州理工大学, 兰州 730050;

2. 甘肃省太阳能发电系统工程重点实验室, 酒泉职业技术学院, 甘肃 酒泉 735000)

摘 要: 采用化学气相沉积法制备具有优异力学性能的含氢四面体非晶碳膜有望满足工业应用的要求。通过自主设计的等离子体增强化学气相沉积实验系统制备含氢四面体非晶碳膜, 并对其微观结构与力学性能进行研究。随着偏压从-200 V 增加到-500 V, 薄膜硬度和弹性模量先增加后减少, 最大达到 34.0 GPa 和 282.0 GPa。压应力随着偏压的变化表现出相同的变化趋势。与传统等离子体增强化学气相沉积方法相比, 自主设计的等离子体增强化学气相沉积系统制备的碳膜硬度和弹性模量明显提升, 碳膜 sp^3 含量(摩尔分数)超过 62.3%, 制备出的碳膜具有典型的含氢四面体非晶碳膜特征, 而非含氢碳膜, 主要是由于水冷射频双螺旋电极与平板电极结合增强了粒子的轰击和离化率, 提高了薄膜 sp^3 含量。这为在工业中应用制备高硬度和弹性模量的含氢四面体非晶碳膜提供了可能。

关键词: 含氢四面体非晶碳膜; 力学性能; 等离子增强化学气相沉积; 微观结构

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Preparation, Microstructure and Mechanical Properties of Hydrogenated Tetrahedral Amorphous Carbon Films

XU Shipeng^{1,2}, ZHAN Faqi¹, ZHENG Yuehong¹, CHEN Weiqian^{1,2}, LA Peiqing¹

(1. State Key Laboratory of Advanced Processing and Recycling of Nonferrous Metals, Lanzhou University of Technology, Lanzhou 730050, China; 2. Key Laboratory of Solar Power System Engineering, Gansu Province, Jiuquan Vocational and Technical College, Jiuquan 735000, Gansu, China)

Abstract: Preparation of hydrogenated tetrahedral amorphous carbon (ta-C:H) films with good mechanical properties by plasma-enhanced chemical vapor deposition (PECVD) is expected to meet requirement in industrial application. This paper reported the microstructure and mechanical properties of (ta-C:H) films prepared by a self-designed PECVD technique. As the bias voltage varies from -200 V to -500 V, the hardness and elastic modulus first decrease and then increase, reaching the maximum values of 34.0 GPa and 282.0 GPa respectively. The evolution of compressive stress with bias voltage shows a similar trend. In this case, the hardness and elastic modulus of films prepared by the self-designed PECVD technique both are improved, compared with those by the conventional PECVD methods. The mole fraction of sp^3 hybridized bond is greater than 62.3% when the bias voltage changes from -200 V to -500 V. Carbon films were deposited using the self-designed PECVD technique, showing the typical characteristics of ta-C:H films. This can be attributed to the increased ion bombardment and ionization due to the incorporation of a water-cooled radio frequency double helix electrode and a plate electrode resulting in an enhanced sp^3 content. This paper provides a promising technology to fabricate ta-C:H films with high hardness and elastic modulus for industrial applications.

Keywords: hydrogenated tetrahedral amorphous carbon films; mechanical properties; plasma-enhanced chemical vapor deposition; microstructure

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第一作者: 许世鹏(1987—), 男, 博士研究生, 副教授。

通信作者: 喇培清(1971—), 男, 博士, 教授。

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First author: XU Shipeng (1987—), male, Doctoral candidate, Associate Professor.

E-mail: shipeng4425660@126.com

Correspondent author: LA Peiqing (1971—), female, Ph.D., Professor.

E-mail: pqla@lut.edu.cn

1 Introduction

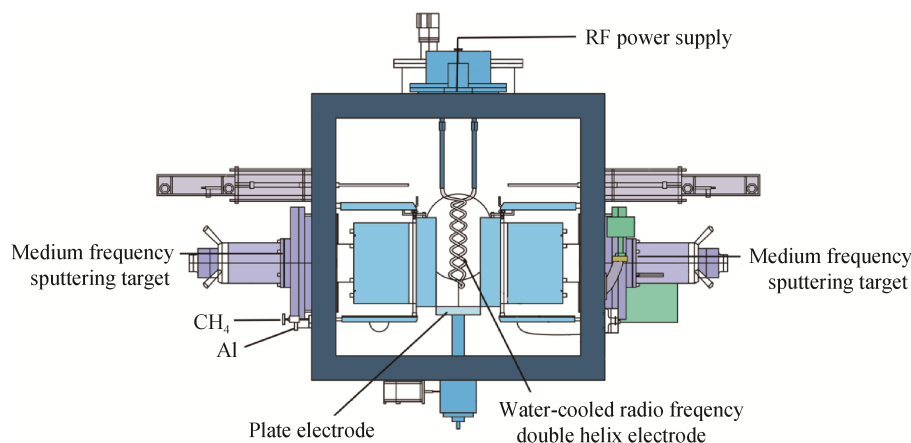
Hydrogenated tetrahedral amorphous carbon (ta-C:H, fraction of C—C sp^3 bonds $\geq 60\%$) materials have been widely used as protective coatings in the industrial fields of microelectromechanical systems, medical equipment and precision molds/dies because of their outstanding performance, including high hardness, smooth surface, low friction coefficient, good corrosion resistance, chemical and biological inertness and high biocompatibility^[1–4]. There are a few ways to obtain ta-C:H films. The incorporation of hydrogen into ta-C films has been accomplished using a variety of processing methods, including filtered cathodic vacuum arc (FCVA), direct and pulsed source, pulsed laser ablation, and sputtering processes. The maximum hardness of 38.15 GPa was obtained for ta-C:H films^[5]. The ta-C:H films were grown on Si substrates using a distributed electron cyclotron resonance (DECR) plasma reactor, an electron cyclotron wave resonance (ECWR) source, a plasma beam source (PBS) and high power impulse magnetron sputtering (HPIMS)^[6–11]. The Young's modulus and hardness of ta-C:H films reached maximum values of 280 GPa and 45 GPa by applying DECR plasma^[11]. However, from an industrial viewpoint, achieving good mechanical properties of ta-C:H films grown by plasma-enhanced chemical vapor deposition (PECVD) from a hydrocarbon precursor is desirable because of its advantages of low deposition temperature, high deposition rate, simple equipment and low cost compared to other preparation methods. Actually, this method more easily forms hydrogenated amorphous carbon films (a-C:H, fraction of C—C sp^3 bonds of 30%–60%), which do not achieve excellent mechanical properties due to the low degree of ionization of the deposition flux and dispersion of the ion energy. For instance, a-C:H films were prepared by PECVD with different bias voltages and showed lower elastic modulus and hardness values of 80.7 GPa and 10.7 GPa^[12]. Furthermore, a-C:H films were also deposited on

stainless steel and Si substrates by radio frequency PECVD, and their maximum hardness was only 19 GPa^[13]. For comparative analysis, different literature-reported values of the elastic modulus, hardness and thickness of ta-C:H/a-C:H films deposited by some fabrication methods are listed in Table 1^[5, 11–17]. The hardness values of ta-C:H/a-C:H films prepared by conventional PECVD are lower than those of films deposited in other ways, which is considered the current key barrier to extensive applications.

In this work, we focused on ta-C:H films prepared using a self-designed PECVD technique with different bias voltages and analyzed the change in mechanical properties from the microstructure. The mechanical properties of ta-C:H films fabricated by the self-designed PECVD technique were obviously improved compared with those of films fabricated by conventional PECVD due to the high C—C sp^3 hybridization content in the matrix. This work lays the foundation for expanding ta-C:H film applications.

2 Experimental

Fig. 1 shows a schematic diagram of the self-designed PECVD system. The anode and cathode were a water-cooled radio frequency double helix electrode and a plate electrode, respectively, which were different from those in other systems. The incorporation of a water-cooled radio frequency double helix electrode and a plate electrode increases the mean free path for ion motion and promotes ion bombardment, thus significantly enhancing the film quality. P-type silicon (100) wafers with a thickness of (545 ± 15) μm were used as the substrate, and thinner Si wafers with a thickness of (290 ± 15) μm were also used to accurately measure the residual stress. The background pressure was evacuated to a vacuum of 5×10^{-4} Pa. Prior to deposition, the substrates were ultrasonically cleaned in acetone for 10 min and dried with nitrogen. Argon plasma was adopted to clean the substrates at a flow rate of 190 mL/min and a constant bias voltage of -600 V for



RF is radio frequency.

Fig. 1 Schematic diagram of the self-designed PECVD system

15 min to remove the existing impurities and oxides from the substrate surface and improve the adhesive strength between the film and substrate. The film deposition process was carried out in a gas mixture of CH_4 (5 mL/min) and Ar (50 mL/min) (Gas produced by Lanzhou Yulong Gas Limited Company) at a working pressure of 4 Pa and a radio frequency power of 500 W. The bias voltage was changed from -200 V to -500 V (namely, -200 , -300 , -400 , -500 V). The thickness of the film was kept at approximately (130 ± 10) nm by varying the deposition time from 80 min to 110 min. During the whole deposition, the sample holder always rotated at a speed of 5 r/min. Nanoindentation (NANO G200, USA) in the continuous stiffness measurement (CSM) mode was employed to characterize the mechanical properties of ta-C:H films. Eight indentations were made for each specimen to accurately determine the hardness value. The residual stress was calculated from the curvature of the film/substrate composite using Stoney's equation. Visible Raman (InVia-reflex, England) spectroscopy, X-ray photoelectron spectroscopy (XPS) (AXIS SUPRA, Japan) and electron energy loss spectroscopy (EELS) (Tecnai F20, USA) were conducted to analyze the microstructure and composition of the films.

3 Results and discussion

Fig. 2 shows the evolution of the hardness, elastic modulus and compressive stress of the deposited ta-C:H films as a function of bias voltage. The insert in Fig. 2 shows load versus displacement curves. As the bias voltage increases from -200 V to -400 V, the hardness and elastic modulus monotonically increase from 19.5 GPa and 166.0 GPa to 34.0 GPa and 282.0 GPa. However, the hardness and elastic modulus decrease to 20.1 GPa and 238.0 GPa with a further increase in the bias voltage to -500 V. The evolution of the compressive stress with bias voltage shows a similar trend. Changing the bias voltage in the range of -200 V to -400 V leads to an increase from 1.5 to 2.9 GPa for compressive stress, which then gradually decreases to 1.9 GPa at a bias voltage of -500 V. Of particular interest is that, generally, the hardest a-C:H film is deposited by PECVD at approximately 21 GPa (partial research data are shown in Table 1), where the hardness is increased by approximately 61.9% to 34.0 GPa by the self-designed PECVD system. Because the indentation depth is 50 nm (the maximum indentation force is set at 1 mN), the hardness results of the ta-C:H films include the influence of the hardness of the Si substrate (13 GPa), but this influence is relatively small^[12–13]. Therefore, ta-C:H films can be fabricated by this system to enhance the film mechanical properties for adaptation to the application requirements of industry.

Since the mechanical properties are closely related to the sp^3 bond content and microstructure distortion in the film deposition process^[18]. Fig. 3(a) presents the visible Raman spectra of the ta-C:H films deposited

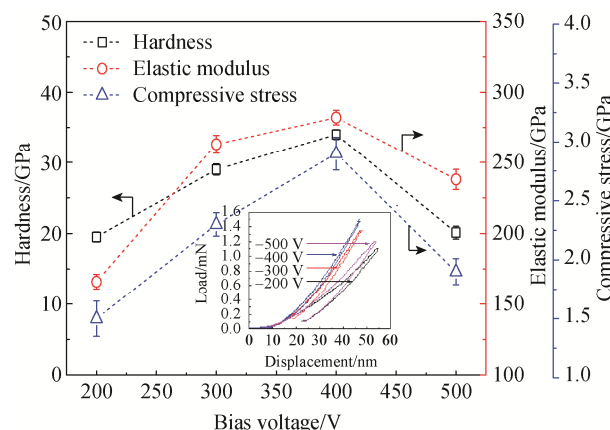


Fig. 2 Hardness, elastic modulus and compressive stress of ta-C:H films as a function of bias voltage

Table 1 Hardness, elastic modulus and thickness data of ta-C:H/a-C:H films prepared by different methods reported in the literature

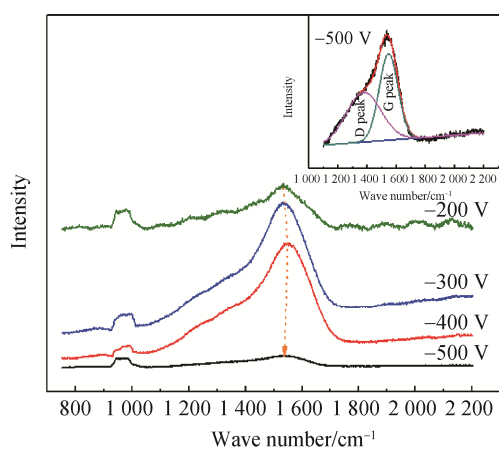
Hardness/ GPa	Elastic modulus/ GPa	Thickness/ nm	Preparation method	Reference
10.7	80.7	283.0	PECVD	[12]
19.0	140.0	400.0	PECVD	[13]
18.1	126.6		PECVD	[14]
14.0	90.0	3 710.0	PECVD	[15]
21.0	153.0	3 000.0	PECVD	[16]
61.0			PBS	[17]
38.2	410.1		FCVA	[5]
45.0	280.0	70.0–190.0	DECR	[11]

with different bias voltages. The peak at approximately $900\text{--}1\,000\text{ cm}^{-1}$ in the spectra is the second-order signal of the silicon substrate, indicating the good transparency of the deposited films. The broad asymmetric Raman peak in the range of $1\,100\text{--}1\,800\text{ cm}^{-1}$ can be deconvoluted into a G peak centered at $1\,540\text{ cm}^{-1}$ and a D peak centered at $1\,340\text{ cm}^{-1}$ (the insert in Fig. 3(a)), showing the typical characteristics of hydrogenated amorphous carbon films^[15, 19–21]. Fig. 3(b) illustrates the fitted result for the G peak position, I_D/I_G and full width at half maximum of the G peak (FWHM(G)) of the deposited ta-C:H films. When the bias voltage changes from -200 V to -400 V, the G peak position shifts upward from $1\,537.2$ to $1\,546.9\text{ cm}^{-1}$, while I_D/I_G decreases from 1.013 to 0.898, indicating an increase in the sp^3 bond content (in mole) in the films. With a further increase in the bias voltage to -500 V, a dramatic decrease and increase are found for the G peak position and I_D/I_G , respectively, which become $1\,542.5\text{ cm}^{-1}$ and 1.05, respectively, implying a decrease in the sp^3 bond content^[22–25]. The FWHM(G) monotonically increases from 137.7 to 168.3 cm^{-1} as the bias voltage changes from -200 V to -400 V and then decreases to 152.3 cm^{-1} for the case of -500 V. FWHM(G) is mainly sensitive to structural disorder arising from bond angle and bond

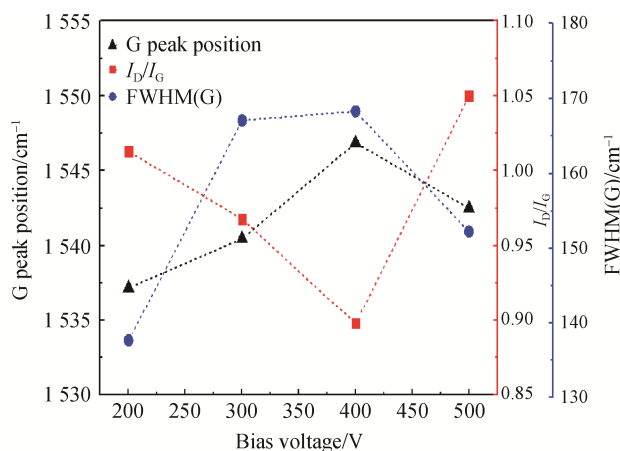
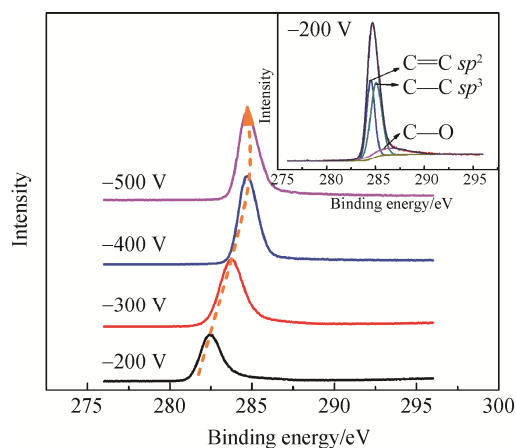
length distortions, and less structural distortion leads to a lower FWHM(G) [22–24]. More disordered carbon and lower sp^2 clustering in the localized structure can thus be concluded to be obtained when the bias voltage is less -400 V, showing decoupling of topological disorder from structural disorder. Nevertheless, a further increase in the bias voltage to -500 V resulted in an inversion of the trends, where the disorder of the localized structure decreased with the conversion from sp^3 to sp^2 .

Fig. 3(c) presents the combined XPS measurement of the microstructure of the as-deposited ta-C:H films. The binding energy of XPS C1s shifts toward a higher value as the bias voltage increases from -200 V to -400 V, which implies an increased sp^3 bond content. However, as the bias voltage increases further, the binding energy

of C1s shifts toward a lower value, representing a higher sp^2 bond content. All the XPS C 1s spectra are deconvoluted into three peaks: the $\text{C}=\text{C}$ (sp^2) bond at approximately (284.0 ± 0.4) eV, the $\text{C}-\text{C}$ (sp^3) bond at approximately (285.1 ± 0.4) eV and the $\text{C}-\text{O}$ bond at approximately (286.6 ± 0.2) eV; thus, the sp^3 and sp^2 bond contents in the films can be estimated from the related peak areas [26]. Fig. 3(d) presents the sp^3 content of ta-C:H films as a function of bias voltage. Similar to the Raman results, the XPS data reveal that as the bias voltage changes from -200 V to -400 V, the sp^3 bond content in the deposited ta-C:H films increases from 51.7% to 71.8%, whereas the sp^3 bond content decreases to 61.2% when the bias voltage reaches -500 V. The XPS data confirm the correctness of the Raman results.



(a) Visible Raman spectra

(b) G peak position, I_D/I_G ratio, FWHM (G)

(c) XPS C1s peak

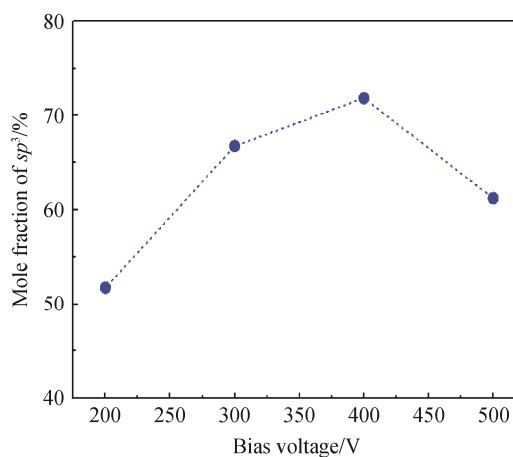
(d) sp^3 content

Fig. 3 Change in Raman spectra and XPS of ta-C:H films as a function of bias voltage

Raman spectroscopy and XPS can provide inaccurate quantitative characterization of the sp^3 bond content of carbon films. EELS spectra are employed to assess the local carbon bonding and characterize the sp^3 bond content. A cross-sectional scanning transmission electron microscopy (STEM) image of the -200 V sample is presented in Fig. 4(a). The processed carbon K-edge spectra of the -200 V sample and highly oriented

pyrolytic graphite (HOPG) are presented in Fig. 4(b). As Raman and XPS spectra reveal that its sp^3 bond content is the lowest, the -200 V sample is chosen for the EELS measurement. HOPG serves as a standard. The π^* peak centered at 285 eV is fitted with a Gaussian function, while the σ^* peak is integrated within the small energy window from 290 to 305 eV (insert of Fig. 4(b)). The fraction of sp^2 bond carbon atoms x is given by the

formula^[27–28]:

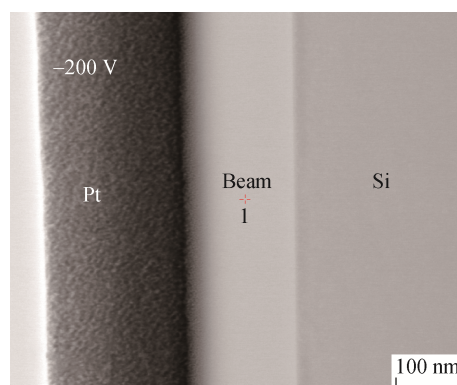
$$\frac{I_{\pi^*}(\text{film}) / I_{\sigma^*}(\text{film})}{I_{\pi^*}(\text{standard}) / I_{\sigma^*}(\text{standard})} = \frac{3x}{4-x} \quad (1)$$

The content of sp^3 bonds reaches 62.3% for the deposited carbon film (bias voltage, –200 V) according to the calculation, and since Raman and XPS spectra reveal that the sp^3 content of this film is the lowest, this implies that the sp^3 hybridized bond content is greater than 62.3% as the bias voltage changes from –300 V to –500 V. Therefore, carbon films are deposited using the self-designed PECVD technique that show the typical characteristics of ta-C:H films.

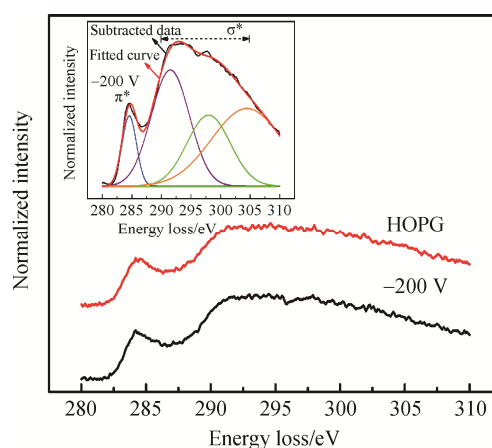
Regarding the microstructure distortion during film deposition, the equilibrium bond angle of graphite is 120° , and that of diamond is 109.471° , while the equilibrium bond lengths of graphite and diamond are 1.42 Å and 1.54 Å, respectively. A previous study revealed that the high compressive stress of diamond-like carbon (DLC) films originates mainly from the distortion of bond angles and/or bond lengths, which were less than 109.471° and 1.42 Å, respectively^[29]. Increasing the bias voltage from –200 V to –400 V leads to increases in the fraction of distorted bond angles and bond lengths (from Raman FWHM(G) analysis) and, as a consequence, to the enhanced experimental residual stress (Fig. 2). Nevertheless, as the bias voltage further increases from –400 V to –500 V, a larger heat-affected zone can be produced, and the generated accumulation of atomic energy relaxes the distorted structures, including bond angles and bond lengths, thus promoting the transformation of the hybrid structure from sp^3 to sp^2 and sp . This combined contribution agrees well with the experimental results, where a significant reduction in residual stress and sp^3 bond content is visible^[29–30].

Meanwhile, we can see from the combined Raman and XPS data that the hardness and elastic modulus of the ta-C:H film deposited by the self-designed PECVD technique are mainly dominated by the sp^3 bond content^[18]. When the sp^3 bond content is the highest, the hardness of the deposited ta-C:H film is the largest. The sp^3 bond is promoted by maximizing ion bombardment, thus influencing the hardness and elastic modulus of ta-C:H films^[31]. During the deposition process, increasing the bias voltage within a certain range will increase the ion bombardment, resulting in a higher degree of ionization in the plasma, but further increases of the bias voltage beyond this range can bring about accumulation of atomic energy that relaxes the distorted structures, thus promoting a decrease in the sp^3 bond content. Additionally, incorporating a water-cooled radio frequency double helix electrode and a plate electrode also increases the mean free path for ion motion and promotes ion bombardment, thus significantly enhancing the sp^3 content^[31]. Namely, the hardness and elasticity modulus of ta-C:H films fabricated by the self-designed PECVD technique are obviously improved, which can be attributed to increased ion bombardment and ionization

due to the incorporation of a water-cooled radio frequency double helix electrode and a plate electrode.



(a) STEM image



(b) Carbon K-edge spectra

Fig. 4 Carbon K-edge EELS spectra obtained from the –200 V sample and HOPG

4 Conclusion

In summary, a self-designed PECVD technique incorporating a water-cooled radio frequency double helix electrode and a plate electrode has been successfully employed to deposit high hardness ta-C:H films. The hardness and elastic modulus of the films increased from 19.5 GPa and 166.0 GPa to 34.0 GPa and 282.0 GPa for the bias voltage in the range of –200 V to –400 V, while they significantly decreased to 20.1 GPa and 238.0 GPa under the bias voltage of –500 V. The change in compressive stress with bias voltage showed a similar trend to that of hardness. Of particular interest, our result was that the mechanical properties of ta-C:H films deposited by the self-designed PECVD technique were obviously improved compared with conventional PECVD due to the high C—C sp^3 hybridization content in the matrix. The sp^3 bond content exceeded 62.3% for all samples. The films showed the typical characteristics of ta-C:H films. This provides a promising route to fabricate ta-C:H films with high performance for precision component applications.

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