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Effect of hydrogen flow on the properties of hydrogenated amorphous carbon films fabricated by electron cyclotron resonance plasma enhanced chemical vapor deposition

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ABSTRACT

The hydrogenated amorphous carbon films (a-C:H, so-called diamond-like carbon, DLC) have exceptional physical and mechanical properties and have wide applications. In the present study, amorphous hydrogenated carbon films (a-C:H) have been deposited on a Si (100) substrate at different hydrogen flow using electron cyclotron resonance chemical vapor deposition (ECR-CVD). The flow of hydrogen changed from 10 sccm to 40 sccm and the flow of acetylene was fixed at 10 sccm. The microstructure and properties of the a-C:H were measured using visible Raman spectra, Fourier transform infrared (FTIR) spectroscopy, UV–VIS spectrometer, surface profilometer and nano-indentation. The results showed that the sp^3 content and sp^3–CH_2 structure in the amorphous hydrogenated carbon films increased with the hydrogen flow. The deposition rate decreased with the hydrogen flow. The residual stress and the nano-hardness of the amorphous hydrogenated carbon films increased with the hydrogen flow. Consequently, the a-C:H film become more diamond-like with the increase of hydrogen flow.

1. Introduction

Joint replacement surgery is most commonly applied on hips, knees, and shoulders. But the particles from the implanted joints caused by friction process lead to long-term loosing between the implant and the bone. Because of this, a wear-reducing coating on the metal component, which is also biocompatible, should dramatically extend hip implant life. Diamond-like carbon (DLC), with its extreme smoothness, hardness, low coefficient of friction and biocompatibility, is an excellent candidate for such an application [1]. Since the deposition of DLC was first reported by Aisenberg [2], numerous deposition techniques have been developed, such as sputtering deposition [3], cathodic arc deposition [4], pulsed laser deposition [5], plasma enhance chemical vapor deposition [6], etc. Among these techniques, ECR-PECVD (electron cyclotron resonance plasma enhanced chemical vapor deposition) method with pulse power has a number of features which make it an attractive method. For example, microwave ECR plasma creates a high ion density and electron temperature at low pressures. The hydrogenated amorphous carbon films (a-C:H) can be deposited from different source gases such as CH_4, C_2H_2, C_2H_4, C_6H_6, which can provide the source of carbon atoms. In addition, auxiliary gases like argon or hydrogen are also necessary because they can etch the sp^2 bonding and stabilize the sp^3 bonding. In other words, the auxiliary gas (hydrogen) affects the structure of a-C:H film. The high proportion of auxiliary gas (H_2) leads to high sp^3 content and the hydrogen flow was controlled 10 times than hydrocarbon [7] in the deposition process. However, for an artificial joint coating, the films with high hardness are adverse to decrease the wear debris and particles from joint cup (made by polyethylene). In order to decrease the hardness of the a-C:H film, this paper focused on the condition that the hydrogen flow was 1–4 times to the acetylene.

The properties such as mechanical property, adhesion force and biocompatibility were determined by the structure of the a-C:H films which used on the artificial joint. This paper reports the effect of hydrogen flow on the structure, especially the sp^3 content and the C–H related bond of a-C:H films deposited by ECR-PECVD.

2. Experimental procedure

The a-C:H films used in the present study had been deposited in the ECR-PECVD system shown schematically in Fig. 1 [8]. The system consists of a cylindrical vacuum chamber and a microwave plasma power to create plasma inside a 50 cm diameter quartz dome. The microwave was guided through a rectangular waveguide and introduced into the ECR magnetron excitation chamber through a quartz window. The top of the chamber was surrounded by a set of solenoids to provide the necessary magnetic field. The gases of hydrogen and acetylene were introduced into the excitation chamber and the flow rate was controlled by a calibrated standard mass flowmeter. The mixed gas was ionized in the excitation chamber and the ions deposited on the substrates forming a-C:H films.

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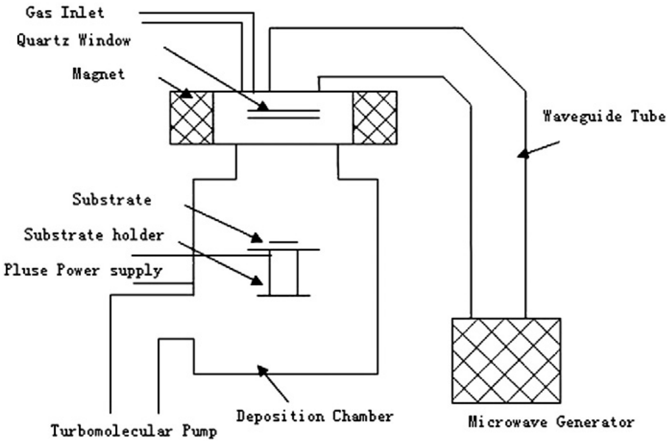

Fig. 1. Schematics of ECR-PECVD deposition systems for a-C:H [8].

In the present study, a-C:H films were deposited on single crystal silicon (100-oriented) and glass substrates in order to characterize the film microstructure. The substrates were firstly ultrasonic washed in acetone and then in alcohol. They were then secured to a substrate holder with silver paste. Prior to the deposition, the system was evacuated to below 10^{-3} Pa. The samples were sputter cleaned before deposition using argon plasma at −1200 V bias for 10 min.

The a-C:H films were deposited at different hydrogen flow and the acetylene flow, the total pressure were kept at 10 sccm and 0.5 Pa. The pulse bias voltage (400 V, 20 kHz, 20%) was supplied to the substrate in order to accelerate the ions down to the surface where the films were deposited. The microwave power was fixed at 400 W to avoid intense etching effect of hydrogen to silicon. The technical parameters of the deposition process of a-C:H films are given in Table 1.

The film thickness was measured using a stylus profilometer (Ambios XP-2). The Raman spectra (Nicolet almegaxr equipment) were taken at room temperature using the 514.5 nm excitation from an Ar laser. The spectra were typically recorded in the region from 1000 to 2000 cm^{-1}. The FTIR absorption characteristics of films were measured using diffuse reflectance Fourier transform infrared spectrometer (Nicolet 5700 RT-IR) in the 400–4000 cm^{-1} range. The optical gap of the films was deduced from transmittance and reflectance data obtained using UV–VIS spectrophotometer measurements in range of 200–900 nm. The residual stress was calculated by the method of measuring the curvature variation of silicon plate before and after deposition using a surface profilometer. The nanohardness of the films was measured by a CSEM nano-indenter with the loading rate of 2.4 mN/min and maximum depth of 70 nm.

3. Results and discussion

Fig. 2 showed the deposition rates of the a-C:H films deposited at different hydrogen flows. It showed that the deposition rates decrease with the increase of hydrogen flow. As a general rule, the deposition rates are determined by the balance between the deposition of hydrocarbon radicals and ions and the etching by ion bombardment [9]. With the increase of H_2 gas flow, the H^+ etching effect increases. At the same time, the content of carbon ion in plasma is reduced, the carbon ion flux onto substrates reduces too. Consequently, the deposition rate decreases with the increase of hydrogen flow.

Table 1
The processing parameters of a-C:H films preparation.

Sample no.	Gas flow/sccm		Deposition time/min	Microwave power/W	Thickness/ nm
	Acetylene	Hydrogen			
A	10	10	60	400	230
B	10	20	70	400	220
C	10	40	80	400	228

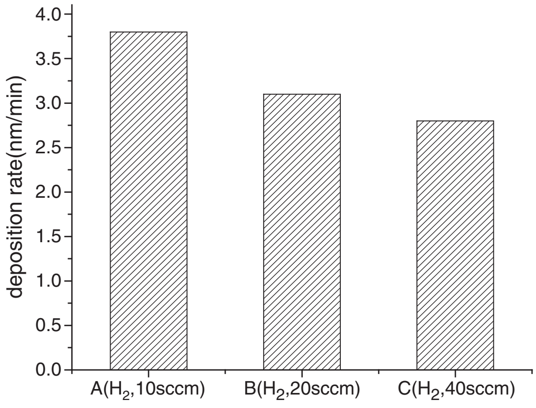

Fig. 2. The deposition rates of a-C:H films deposited at different hydrogen flow.

Raman spectroscopy is the best way to obtain the detailed bonding structure of a-C:H films. Fig. 3 shows the Raman spectra of the a-C:H films deposited at different hydrogen flow. It can be seen that all films have similar features in their Raman spectra in the 1000–2000 cm^{-1} region. The so-called G and D peaks show up at around 1560 and 1360 cm^{-1}, respectively, for visible excitation. The G peak is due to the bond stretching of all pairs of sp^2 atoms in both rings and chains. The D peak is due to the breathing modes of sp^2 atoms in rings [10,11]. The shape of the Raman spectrum is determined by these factors. The peak position and the I_D/I_G reflect the sp^3 content, the lower I_D/I_G ratio indicates larger percentage of sp^3. Table 2 shows the peak position and I_D/I_G which is calculated by fitting the Raman spectra using two Gaussian distributions. It shows that the position of the G peak shifted towards higher wave numbers as the hydrogen flow increased. The D peak position also shows a similar trend. The shift in the G peak and D peak positions and the I_D/I_G suggest an increase in the sp^3 bonding as the hydrogen flow increased, indicating the film becoming more diamond-like [12]. In other words, the sp^3 content increases with the hydrogen flow.

It also attempts to derive the sp^3 fraction from the optical spectra in the energy range 1–6 eV [13]. Typical absorption spectra of a-C:H films deposited on a glass substrate are presented in Fig. 4. The band gaps of a-C:H films are calculated by the well-known Tauc equation [14]. It shows that all curves show characteristically a similar performance. The band gaps of films are in the range of 3–4 eV, which indicates that the sp^3 fraction is dominating in the films [15]. The band gap of samples A, B and C are 3.34, 3.45 and 3.51 eV, respectively. It indicates obviously that the band gaps of the a-C:H

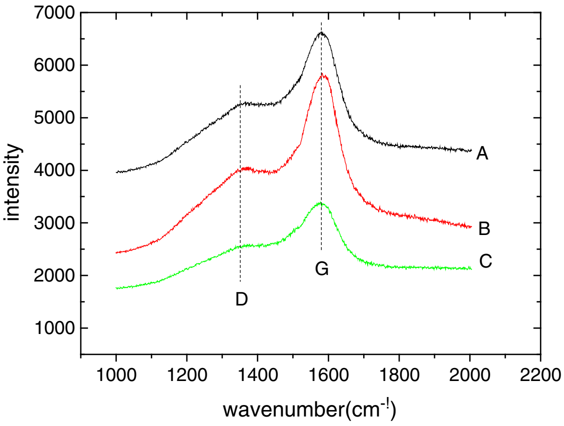

Fig. 3. Raman spectra of the a-C:H films deposited at different gas flow rate.