Thin Solid Films 518 (2010) 3492–3496

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Chemical diagnosis of DLC by ESR spectral analysis

Yukinori Yamauchi [a], Yasushi Sasai [b], Shin-ichi Kondo [b], Masayuki Kuzuya [a,*]

[a] Department of Pharmaceutical Physical Chemistry, College of Pharmaceutical Sciences, Matsuyama University, 4-2 Bunkyo-cho, Matsuyama, Ehime 790-8578, Japan
[b] Laboratory of Pharmaceutical Physical Chemistry, Gifu Pharmaceutical University, 5-6-1 Mitahora-Higashi, Gifu 502-8585, Japan

ARTICLE INFO

Available online 26 November 2009

Keywords:
Diamond-like carbon (DLC) film
Electron spin resonance (ESR)
Plasma enhanced chemical vapor deposition (PECVD)
Dangling-bond site

ABSTRACT

Diamond-like carbon (DLC) films were deposited utilizing plasma enhanced chemical vapor deposition (PECVD) with four precursor gases such as methane, ethylene, acetylene and benzene in gas phase. Electron spin resonance (ESR) spectra showed that dangling-bond sites (DBSs) observed in all films were characterized by an isotropic broad single line. The DLC film with unsaturated precursor gases had the higher film growth rate and the higher DBS accumulative rate. Although the DBS in DLC films were quite stable at room temperature under anaerobic conditions, the DBS decayed rapidly to level off toward a limiting value when exposed to air. The stability and reactivity of the DBS in DLC film were assumed to depend on chemical structure of organic gas used as precursor. The detailed-ESR study on DBS of the DLC films could be one of the powerful tools for diagnosing the micro-structural properties and the quality of films.

1. Introduction

More than three decades after the first report on the production of amorphous carbon films with properties approaching those of diamond, the deposition and characterization of such diamond-like carbon (DLC) materials is still a field of intense research activity [1]. The DLC thin films have widely used in a variety of industrial fields due to the attractive properties such as high hardness, low friction coefficient, optical transparency, chemical inertness, and high electrical resistivity [2,3]. Recently, the DLC is also an excellent candidate for use as biocompatible coating on biomedical implants, which is due to not only its excellent properties but also its chemical composition containing only carbon and hydrogen, which are biologically compatible with human cells [4,5].

The DLC films can be produced at low deposition temperature by various methods such as plasma assisted chemical vapor deposition, sputtering, and ion beam techniques. Depending on the deposition conditions and technique used, a variety of DLC materials, which have diverse ratio of both hydrogenated/unhydrogenated and sp^3/sp^2 carbon atoms, can be produced. Thus, the DLC is not a specific material but a group of materials with a wide range of atomic bond structure and properties. In this paper, diamond-like carbon (DLC) will be used as a general term of this group of amorphous carbon film, i.e. traditionally called plasma-polymerized thin film.

In general, the chemical properties of DLC films have been characterized mainly by visible Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). Although many activated sites such as radicals, dangling-bond sites (DBSs) and reactive species are formed and trapped in DLC films during the growth of the film, all spectra listed above cannot detect the microscopic structural changes. On the other hands, electron spin resonance (ESR) is a useful tool to obtain the information concerning the nature of the DBS as well as the characteristics of the resulting films. In this work, we have conducted the chemical diagnosis of DLC films prepared from hydrocarbons with different structural features, methane, ethylene, benzene and acetylene, by detailed-ESR study on the DBS formed in these kinds of DLC films.

2. Experimental

2.1. Preparation of DLC films and ESR spectral measurement

The DLC films were deposited using plasma RF generator with matching network system. Four kinds of gases, methane, ethylene, acetylene and benzene, were used as the precursor gas/vapor. Optical grade benzene liquid used as the precursor was supplied by Aldrich Co. and had a purity of over 99%.

A neutral glass capillary (1 mm i.d., 65 mm long) was placed in a specially designed ampoule with a side branch (30 mm i.d., 100 mm long) connected to a capillary tube (2 mm i.d.) at the upmost part of the ampoule. The ampoule was connected to a vacuum line and degassed. The preparation of DLC film by PECVD was carried out using inductively coupled plasma in the region encircled by the radiofrequency discharge coil at 13.56 MHz. The plasma state was sustained at 50 W of supplied power for prescribed period of time with the precursor gases flow rate of 50 mL/min. After the plasma irradiation was discontinued, the ample

---

* Corresponding author.
E-mail address: mkuzuya@cc.matsuyama-u.ac.jp (M. Kuzuya).

0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.11.032

reactor was kept *in vacuo* for 30 min to remove the remaining low-molecular weight materials and sealed. The ESR spectral measurements of DLC films formed on the glass capillary were performed by turning the ampoule upside down. The schematic representation is shown in Fig. 1.

ESR spectra were recorded with a JES-FA200 spectrometer (JEOL) with X-band and 100 kHz field modulation, and extra care was taken to ensure that the observed spectra were not saturated by keeping the microwave power level 0.01 mW. The ESR spectral intensity was determined by double integration. Measurements of *g*-values were made relative to the fourth signal from the lower magnetic field ($g=1.981$) of Mn^{2+} in MgO. The procedure is essentially the same as that reported earlier [6].

2.2. XPS spectral measurement

To confirm the chemical composition of the DLC films formed on neutral glass plate (5 × 5 mm) by PECVD, X-ray photoelectron spectrum (XPS) measurement was carried out using the conventional photoelectron spectroscopy apparatus, Shimadzu ESCA 3400. The Mg Kα line (1253.6 eV), used as X-ray source, was incident at 45 with respect to the surface. The total energy resolution was approximately 0.5 eV. The base pressure in the photoelectron analysis chamber was maintained at least 5×10^{-6} Pa. In order to investigate the chemical composition of bulk phase in DLC film, XPS sputter depth profiling was performed using 10 keV argon ion beam. The ion beam was restored over an area of 4 mm × 4 mm and the analysis diameter was 800 μm, ensuring that the signal was measured from the center of the sputtered area. The sputter rate was 10–20 nm min^{-1}.

3. Results and discussion

3.1. ESR spectra

Fig. 2a shows the ESR spectra of immobilized DBS observed in DLC films prepared with four kinds of precursor gases such as methane, ethylene, benzene and acetylene. All spectra are characterized by an isotropic broad single line with ΔH_{msl} of 1.82–1.91 and *g*-value of 2.000–2.001 which is consistent with carbon center radicals and not glass radicals. It can be seen that the spectral features are almost the same with each other and they were unchanged at any stage of plasma treatment. These spectral features have been observed in ESR spectra of DLC films formed from phenylacetylene (PA), styrene (ST) and hex-3-yne (3H), reported earlier [6].

Fig. 3 shows the progressive changes in ESR spectral intensity (determined by double integration) of the DBS in all DLC films in the course of PECVD. It is clear in all cases that the spectral intensity increases linearly as the reaction proceeds, but the rate varies with the precursor gases used for PECVD. A notable feature in Fig. 3 is that the spectral intensity of DLC film with acetylene is markedly larger than for the other films. In our previous report, we have observed the similar results that the spectral intensity of DBS in DLC formed from PA was much larger than that from PS [6]. From these results, a large number of the DBS in film from acetylene and PA stem from their effective structural features for DBS formation, an alkyne hydrocarbon (triple bond) containing non- or mono-substituted group in acetylene and PA. These results indicate that the unsaturated π-bond of precursor molecule strongly involves the formation of DBS where free radicals are trapped in the cross-linked polymer matrices formed by PECVD. The rate of DBS formation has been found to be well correlated with the rate of film formation by PECVD [6].

The spectral intensity of DBS observed in all cases is almost unchanged at room temperature for a long period of time so long as the films are kept under unaerobic conditions, indicating that all the DBS are immobilized and do not readily undergo termination at room temperature (data not shown). On the other hand, the spectral intensities observed after exposed to air are appreciably reduced relative to those of the spectra before exposed to air as shown in Fig. 2b. This indicates that considerable amount of DBS are reacted with oxygen and terminated to the stable diamagnetic molecules at room temperature. Fig. 4 shows progressive changes of relative ESR spectral intensity of DBS in DLC films formed from methane, ethylene, benzene and acetylene on standing at room temperature under aerobic conditions, together with that of PA, ST and 3H, reported earlier, for the comparison purpose. It is seen that the spectral intensity quite rapidly decreases with time under aerobic conditions toward a limiting value. After standing for a few hours, the spectral intensity tends to level off and persisted essentially unchanged for a

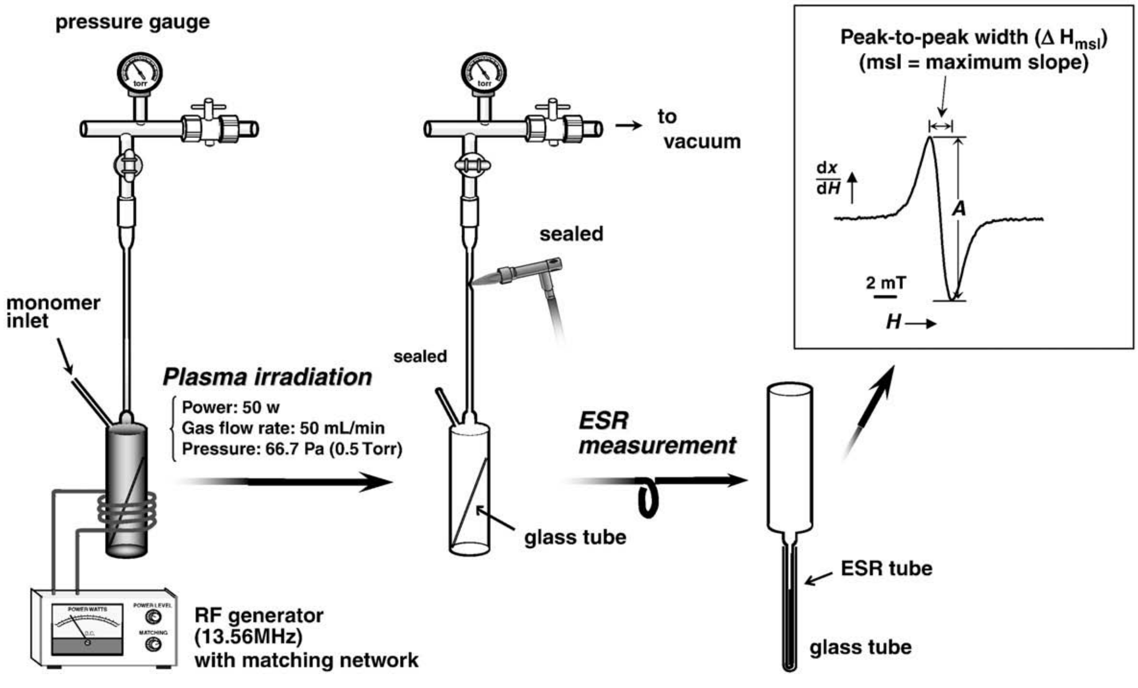

Fig. 1. Schematic representation for PECVD and ESR spectral measurement of the DLC films.