



# Surface modification of amorphous carbon thin films by 1,3-dipolar cycloaddition

Yoshifumi Aoi <sup>\*</sup>, Akihiro Tada

Department of Materials Chemistry, Faculty of Science and Technology, Ryukoku University, Seta, Otsu 520-2194, Japan



## ARTICLE INFO

### Article history:

Received 14 March 2013

Received in revised form 23 May 2013

Accepted 22 June 2013

Available online 29 June 2013

### Keywords:

Chemical modification

Amorphous carbon

Nitrone

Surface characterization

## ABSTRACT

Amorphous carbon thin film surfaces were successfully modified by 1,3-dipolar cycloaddition of nitrones, generated by the condensation of 4-(trifluoromethyl)benzaldehyde and N-methylhydroxylamine. Amorphous carbon thin films were deposited by electron cyclotron resonance sputtering and consisted of mainly  $sp^2$ -hybridized carbon. The modification of amorphous carbon thin film surfaces with organic molecules was confirmed by X-ray photoelectron spectroscopy (XPS), Raman, and atomic force microscopy (AFM). F 1s, N 1s, and C 1s electron spectra revealed the existence of organic molecules on the surface of modified amorphous carbon thin films. The surface coverage increased with reaction temperature, reactant concentration, and reaction time.

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Carbon materials have attracted much attention in a vast range of applications such as protective coatings, energy storage, biosensors, and medical applications. Carbon exists in a variety of stable forms such as graphite, diamond, nanotubes, and fullerenes. They are promising as new materials because they exhibit remarkable electronic and optical properties. Carbon also forms a range of less-crystalline materials, including diamond-like carbon (DLC) and other forms of amorphous carbon consisting of a network of  $sp^2$  and  $sp^3$  bonding coordinations [1,2]. Amorphous carbon has attracted enormous interest in recent years due to its unique properties such as high hardness, low friction coefficient, and chemical inertness. Electrical and optical properties of amorphous carbon can be tuned by manipulating the  $sp^2$  and  $sp^3$  bonding ratio [1,2]. Amorphous carbon thin films can be deposited easily at room temperature. This suggests that it could be conveniently deposited on flexible plastic substrates and may be able to be easily integrated with other materials. There are several surface properties that make amorphous carbon a good platform for biosensors and bio-interfaces. The chemical inertness of amorphous carbon thin film makes it suitable for most biological environments. Additionally, amorphous carbon has well-known high biocompatibility and high hemocompatibility properties [3–6]. The amorphous carbon biocompatibility has opened new fields for applications in biology as protective coatings for implants, biosensors, and biochips [3,4,6–9]. Using the amorphous carbon thin films for biosensing platforms requires the modification of the inert

amorphous carbon surfaces with organic molecular and/or biomolecular species.

Modification of surfaces is an important objective in materials science. Many experimental efforts have been made to modify the surface of carbon materials [10]. Chemical modification of carbon nanotubes and graphene has been studied extensively [11,12]. Several attempts have been made to chemically modify diamond surfaces, in order to introduce specific sites into an unreactive surface [13], and many different methods have been developed. These include reactions involving radical initiators such as organic peroxides [14,15], halogenation of diamond surfaces with subsequent organic functionalization [16,17], electrochemical reduction of diazonium salts [18,19], the Prato reaction [20], and photochemical reactions [21]. However, the functionalization of amorphous carbon films with organic molecules remains relatively unexplored. Cullen et al. have investigated the spontaneous grafting of aryldiazonium salts onto amorphous carbon thin films [22]. Nakamura and co-workers have reported chemical modification of DLC films with perfluoroalkyl substituent by using photolysis [23]. Sun et al. have demonstrated photochemical functionalization of amorphous carbon thin films followed by covalent immobilization of DNA [24].

In this paper, we report the application of 1,3-dipolar cycloaddition of nitrones, generated by the condensation of 4-(trifluoromethyl)benzaldehyde and N-methylhydroxylamine, to covalent surface modification of amorphous carbon thin films. 1,3-Dipolar cycloaddition, usually referred to as click chemistry, is popular whenever a simple, fast and irreversible reaction [25]. This reaction has been widely applied to the organic modification of fullerene  $C_{60}$  [26,27], carbon nanotube [27–30], and graphene [31–33]. The presence of the organic groups on the amorphous carbon thin film surfaces was verified by X-ray

<sup>\*</sup> Corresponding author. Tel.: +81 77 543 7465; fax: +81 77 543 7483.  
E-mail address: [aoi@rins.ryukoku.ac.jp](mailto:aoi@rins.ryukoku.ac.jp) (Y. Aoi).

photoelectron spectroscopy (XPS). The surface morphologies were investigated by atomic force microscopy (AFM). The effects of the reaction temperature, reactant concentration, and reaction time on the surface coverage were also investigated.

## 2. Experimental

### 2.1. Preparation of amorphous carbon thin films

Amorphous carbon thin films were prepared by electron cyclotron resonance (ECR) plasma sputtering. The background pressure of the deposition chamber before deposition was less than  $1 \times 10^{-3}$  Pa using a diffusion pump and Ar gas was introduced to the chamber at  $1 \times 10^{-1}$  Pa during sputtering. The sputtering was performed at the frequency of 2.45 GHz microwave at 400 W. The substrate bias was +20 V. A Si (100) wafer was used as the substrate. Before deposition, the substrate was ultrasonically cleaned with acetone. All substrates were pre-sputtered (the target bias was off) for 2 h, and this was followed by ECR plasma sputtering at the target bias of  $-400$  V for 1 h. During the deposition, substrate temperature was increased to 343–353 K.

### 2.2. Surface modification of amorphous carbon thin films

Amorphous carbon thin film surfaces were modified by 1,3-dipolar cycloaddition. For the reaction, the amorphous carbon thin films were diced into  $1 \times 1$  cm<sup>2</sup> pieces. 4-(Trifluoromethyl)benzaldehyde, N-methylhydroxylamine hydrochloride, and 1,3,5-trimethylbenzene (all from Tokyo Chemical Industry) were used as received. The amorphous carbon thin film was immersed in 1 mL of mixed solution of 4-(trifluoromethyl)benzaldehyde and N-methylhydroxylamine in 1,3,5-trimethylbenzene under stirring. Concentration ratio of 4-(trifluoromethyl)benzaldehyde to N-methylhydroxylamine was kept to 1:1.1. The concentration of 4-(trifluoromethyl)benzaldehyde was varied from 0.1 to 1.5 mol dm<sup>-3</sup>. The reaction solution was heated in the range of 298–413 K, and the reaction time was varied from 1 to 168 h. After the reaction, the modified amorphous carbon thin films were sequentially rinsed and sonicated in 1,3,5-trimethylbenzene and ethanol.

### 2.3. Characterization

X-ray photoelectron spectroscopy (XPS) was carried out on an Ulvac Phi XPS-1600R by using a Mg K $\alpha$  1253.6 eV X-ray source. Survey scans were collected over the kinetic energy range 0–1200 eV with 23.5 eV pass energy and 0.2 eV energy step. Higher resolution scans were made over a range of 20 eV around the peaks of interest with 23.5 eV pass energy and 0.025 eV energy step. In order to determine the peak area, peak fitting was performed with Gaussian functions after a Shirley background subtraction. Peak areas were obtained from the Gaussian component areas. Raman spectroscopy was performed using a Jasco NRS-2100, with an Nd:YVO<sub>4</sub> laser excitation line at 532 nm. Spectra were collected with 5 s exposure time, 5 accumulations, and a laser power of 100 mW. Atomic force microscopy (AFM, Seiko Instruments SPA-300) measurements were carried out in a tapping mode with a frequency of 310 kHz and 256 scan lines. Rms roughness values were calculated over  $1 \times 1$   $\mu$ m<sup>2</sup>.

## 3. Results and discussion

### 3.1. Characterization of amorphous carbon thin films

Thickness of the film was ca. 250 nm. Survey scan (not shown here) shows the presence of carbon and oxygen. Oxygen is probably incorporated into the sample due to exposure to the atmosphere before XPS measurement and/or accidental incorporation during the

deposition. On the other hand, the absence of any peaks around 400 eV indicates that no nitrogen is incorporated into the film during deposition. Fig. 1(a) shows the C 1s electron spectrum of the amorphous carbon thin film on a Si wafer. The C 1s electron spectra had a single asymmetric peak that is characteristic of amorphous carbon film. Peak asymmetry arises from the presence of carbon atoms in sp<sup>2</sup> and sp<sup>3</sup> bonding configurations and from the presence of small amounts of surface oxides [34,35]. The main peak position was 284.5 eV assigned to sp<sup>2</sup> carbons. It can be considered that the main bonding configuration of carbon atoms in our amorphous carbon films is sp<sup>2</sup>.

Raman spectroscopy is a suitable tool for the characterization of carbon-based materials. Fig. 1(b) shows the Raman spectrum of the amorphous carbon thin film. The spectrum consists of two broad peaks around 1590 and 1370 cm<sup>-1</sup>: the G-band and D-band respectively. The G-band is due to E<sub>2g</sub> symmetry corresponding to the bond stretching vibration of the in-plane pairs of sp<sup>2</sup> sites, and the D-band is due to A<sub>1g</sub> symmetry corresponding to the breathing vibration of 6-fold aromatic rings [36,37]. Intensity ratio, I(D)/I(G) and G-band position have been reported to depend on the sp<sup>2</sup> content in the film [37]. The I(D)/I(G) and G-band position of our amorphous carbon film were about 1.9 and 1590 cm<sup>-1</sup>, suggesting that the main bonding configuration of carbon atoms is sp<sup>2</sup>.

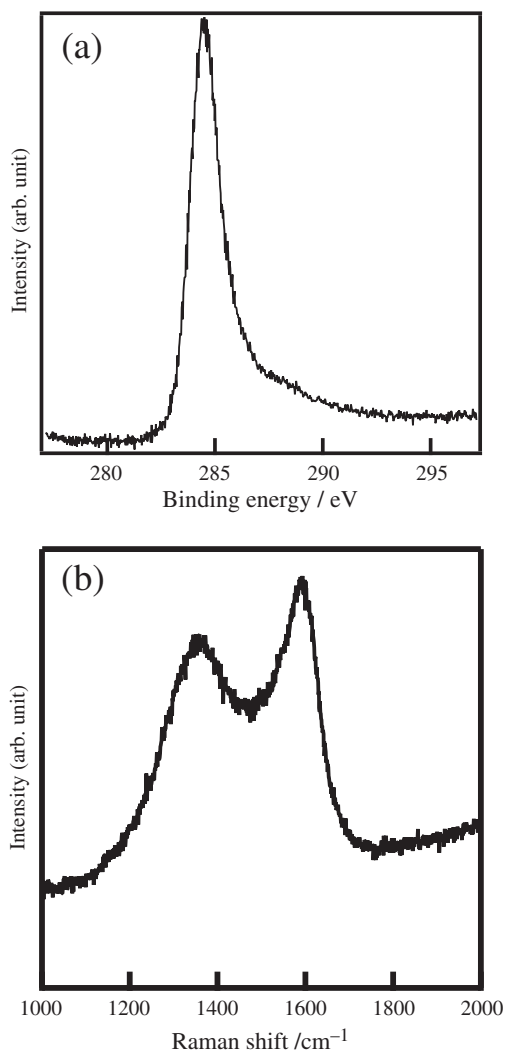


Fig. 1. (a) XPS C 1s electron spectrum and (b) Raman spectrum of pristine amorphous carbon thin film.

Download English Version:

<https://daneshyari.com/en/article/7111556>

Download Persian Version:

<https://daneshyari.com/article/7111556>

[Daneshyari.com](https://daneshyari.com)