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Amination of diamond film by ammonia microwave plasma treatment

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ABSTRACT

Functionalization of diamond films is important for various applications, such as electrochemical sensors. In this study, high quality diamond films were prepared by microwave plasma chemical vapor deposition (MPCVD). These surfaces were then functionalized by a surface amination modification (ammonia plasma) using the same system. The characterization results demonstrated that both the surface morphology and microstructure of the diamond films were not altered by the ammonia plasma treatment. The surface nitrogen content was assessed by XPS analyses, which revealed that amine groups ($-NH_2$) were generated on the diamond film surface efficiently. The $-NH_2$ concentration on modified diamond film surface was equal to 6.71% (denoted as $-NH_2$/100C). The contact angle of water was decreased as the hydrophilicity of the aminated diamond film was increased. Based on the optical emission spectrum (OES) study, •NH and $•NH_2$ radicals were generated in the microwave plasma, and are regarded as the crucial precursors for creating the amine group on diamond surface.

1. Introduction

The electrochemical detection of bio-molecules requires electrode materials with specific properties such as biocompatibility, stability, reproducibility and sensitivity [1–3]. Recently, diamond film has attracted much attention and been recognized as one of the best electrochemical sensor materials due to its unique physical and chemical properties [4,5]. The diamond film surface is chemically stable, exhibits favorable biocompatibility and shows an enlarged potential window together with a low background current, as compared to other sensor electrode materials such as silicon, gold or glassy carbon [6,7]. The immobilization of DNA molecules on diamond surface shows a higher stability as compared to other conventional substrates [8]. This novel DNA biosensor combines the outstanding electrochemical properties of diamond as a transducer with the controlled bonding of DNA molecules.

However, as-deposited diamond film is considered chemically inert to most reagents and its chemical modification is straightforward. During the last decade, progress has been made on the development of easy, controllable and specific surface modification methods for introduction of different functional groups on the diamond surface. These methods are based on chemical, photochemical, electrochemical and physical concepts. Among them, amine group modification is proved to be an efficient functionalization of diamond surface for the application of biosensor [9,10]. Such as covalent bonding of amine terminated alkyl chains [11,12], UV irradiation in ammonia gas [13], and the use of radio frequency plasmas of NH_3 [14].

To improve the detection efficiency, methods to achieve higher coverage of amine groups on the diamond film surface are needed. As for the aforementioned amination methods, the highest typical N concentration on diamond surfaces (H or O terminated diamond film) is 7%, with only a portion of these available for bio-functionalization [2]. Moreover, some of these amination methods are challenging to apply due to the equipment needed or the complex chemical reactions.

In this study, an ammonia microwave plasma treatment was performed to introduce the amine groups on the as-deposited diamond film surface. Due to the higher substrate temperature in contrast to other modification methods and the higher concentration of •NH (or $•NH_2$) radicals in the plasma, greater surface amination can be achieved. The modification mechanism is proposed based on the OES measurements of reactive species in the plasma and theory analysis.

2. Experimental

The diamond films were deposited on silicon substrates (10 × 10 mm) using a microwave plasma chemical vapor deposition (MPCVD) system with an output frequency of 2.45 GHz. The substrates were prepared by first dry abrading with diamond powder (10 μm diameter, bought from Polaris Company, China) and then cleaned ultrasonically in acetone solution for 15 min. CH_4 and H_2 were fed into the chamber at a total reactor pressure of 8.0 kPa. The temperature of the substrate was kept at 850 °C. After a 10-h film deposition, the CH_4 gas was turned off, and the H_2 flow was maintained until the sample was cooled down to room temperature or the needed temperature for amination process. The diamond film was grown with the average thickness 5 μm. Untreated diamond film was denoted as "as-deposited diamond film".

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To aminate diamond film, pure NH_3 gas (99.9%) was supplied at the end of the deposition, and the H_2 flow rate was reduced to 50 sccm to keep the plasma stable. Meanwhile, the input microwave power was reduced to 600 W and the chamber pressure was lowered to 2.5 kPa. After 15 min, the microwave plasma treatment is shut down and leaves the diamond film to cool down at room temperature in an ammonia flux. The diamond film after ammonia microwave plasma treatment was denoted as "amination diamond film".

The detailed deposition and amination parameters are shown in Table 1.

The diamond film morphology and microstructure were characterized before and after the ammonia plasma treatment by scanning electron microscopy (SEM, LEO-1450) and micro-Raman spectroscopy (JY-H2800, 532 nm, 3 mW). The information of element and/or group on surface of the as-deposited and amination diamond films was determined by XPS (AXIS ULTRA, Al Kα = 1486.6 eV). Amine group concentration was referred with respect to a carbon concentration in percents and denoted as $-NH_2$/100C or amine efficiency. Amine selectivity denoted as $-NH_2$/100N ratio gives information about selectivity of the process with respect to amine group. Active radicals in the plasma were detected by OES (71MS3011). Water contact angles of diamond films before and after amination process were measured by Contact measure instrument (Kruss DSA100) to evaluate the diamond surface activity briefly.

3. Results and discussion

3.1. Film quality

The morphology of diamond films before and after ammonia microwave plasma treatment is shown in Fig. 1a and Fig. 1b, respectively. For the aminated diamond film, the NH_3 flow rate was 80 sccm with 600 W microwave power input and 15 min treatment time. As seen in these two figures, the diamond film consists of many well facetted diamond grains with an average grain size of 2 μm. Clearly, the film morphology is unaffected by the NH_3 microwave plasma treatment.

The microstructure of the diamond films before and after ammonia plasma treatment was studied by Raman spectroscopy. Characteristic spectra are presented in Fig. 2. One sharp peak at 1332 cm^{-1} due to sp^3 C–C bond can be observed in as-deposited diamond film, which implies that a high quality diamond film was deposited on silicon by MPCVD. After amination for 15 min, the peak in 1500 cm^{-1} is increased slightly, which originates from an increase in the nondiamond carbon content on the surface [15]. For the most part, however, the microstructure of the aminated diamond was not significantly affected by the treatment.

3.2. Surface group analysis

To characterize the changes in the atomic composition on the diamond film after aminated at various NH_3 flow rates, XPS analysis was conducted. These aminated diamond films were treated at various NH_3 flow rates (20, 40, 60, 80 sccm, respectively) and 50 sccm H_2 gas flow rate, a microwave power of 600 W and pressure of 2.5 kPa, time of 15 min. The results showed that increased ammonia flow produces increased nitrogen coverage based on the increased N 1s core level intensity near 402 eV. Not only the peak intensity increased, but also the binding energy shifts from 401 to 399 eV.

For functionalization, not all of the incorporated nitrogen can be linked to biomolecules. It is the primary amines that are most active. According to previous literatures [2,16], the N 1s peak at 399 eV can be ascribed to "C–NH_2" termination, which is especially important for bio-functionalization. The N 1s peak at 401 eV is less active and less desirable for biosensors. The signal at this position can be assigned to nitrogen atoms linked to 2 carbon atoms, as double carbon–nitrogen

Table 1
Diamond films deposition and amination parameters.

	Experimental parameters	
	Deposition	Amination
Microwave power (W)	1800	600
Pressure (kPa)	8.0	2.5
Substrate temperature (°C)	850	300
Hydrogen flow rate (sccm)	200	50
Methane flow rate (sccm)	3	0
Ammonia flow rate (sccm)	0	20/40/60/80
Duration time (min)	600	15

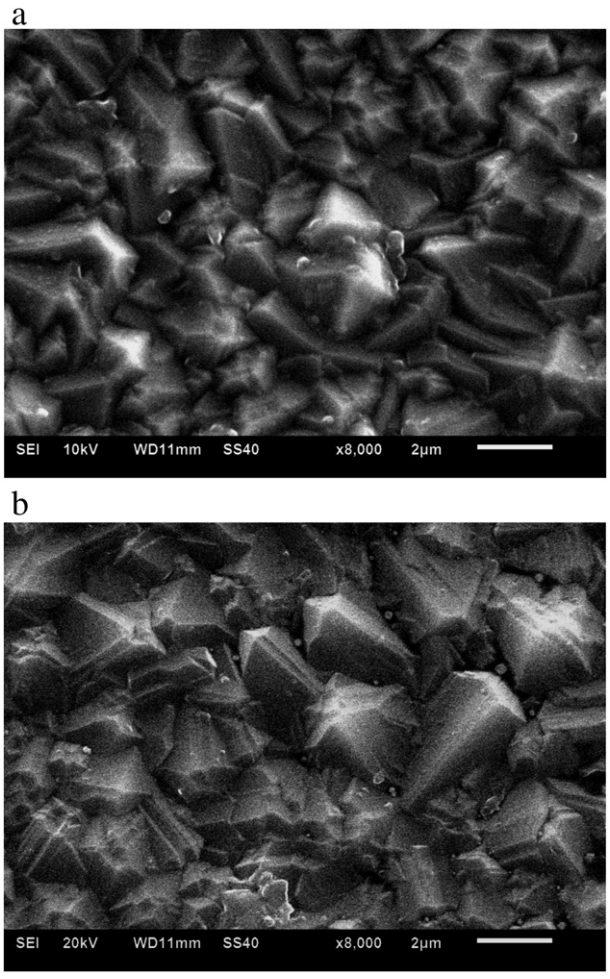

Fig. 1. SEM morphology of diamond film before (a) and after amination (b).

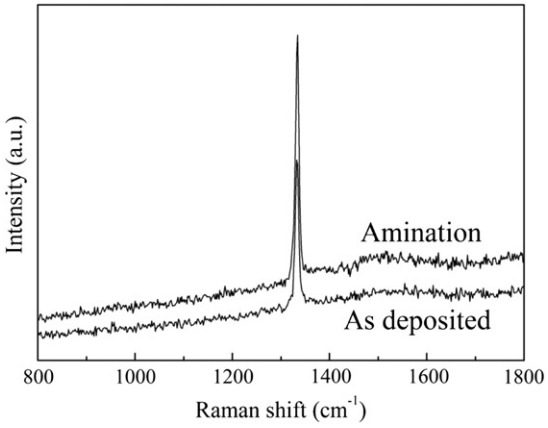

Fig. 2. Raman spectra of diamond films before and after amination.