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Fabrication of nanogranular diamond films by MPJCVD system

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Abstract

Nanogranular diamond films have been prepared by microwave plasma jet chemical vapor deposition system (MPJCVD) with argon-rich (Ar/H_2:90%) plasma. In this work, the plasma pre-carbonization (P.P.) pre-treatment was employed to obtain uniform and smooth (13.3 nm rms) diamond films with high nucleation density. The diamond films were fabricated in various Ar/H_2 concentrations from 0% to 100% and fixed at CH_4 concentration of 1%. It can be clearly observed that the grain size of diamond films changed from micrometer to nanometer scale and down to 5 nm at the concentration of 90% Ar/H_2. The reason is due to the rise of C_2 dimer in the plasma, which could be proved from the analysis of OES analysis.
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1. Introduction

Diamond possesses excellent physical and chemical properties that make it be a potential candidate for applications in future electronic devices and micro-electromechanical systems (MEMS). However, the surface roughness of typical CVD micro-crystalline diamond (MCD) films is too rough to introduce the industrial processes of semiconductor and electronic devices due to its apparent facet. One way of synthesizing nanogranular diamond films can effectively reduce the surface roughness. The grain size of ultra nanocrystalline diamond (UNCD) films is less than 10 nm [1-3], therefore it can make the effect of diamond facet greatly decreased. The reduced grain size could increase the grain boundaries containing non-diamond carbon (sp^2) in the diamond films that resulted in significant improvement in related electrical properties [4]. However, the surface roughness of diamond films is not only directly related with grain size but also with pre-treatment method of diamond growth.

The Microwave plasma jet chemical vapor system (MPJCVD) was designed and set up in our Lab., which could resolve the problem of varied distribution of plasma compared effectively with tube-type MPCVD system. The antenna with conical slow-wave structure plays the key role in this system. By this way, the input energy can restrict

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to the generation of maximum electric field position through conical antenna and stabilize the position and energy distribution of plasma. It can greatly enhance the dissociation rate and activity of reaction species through microwave coupled plasma jet, which can make the generation power by using sources (CH_4, Ar, N_2) and working pressure of CVD diamond process lower than general MPCVD. MPJCVD system could not only provide stable and uniform plasma distribution to achieve smooth diamond films but also save generation power and introduce gas source due to the plasma concentrated on antenna and with enough react species during growth processes.

In the typically synthesized process of diamond films, either the mechanical scratch or ultrasonication using diamond powders has been usually employed to enhance the nucleation rate on Si substrates. However, the nucleation density of pre-treatment with these two methods is not enough for growth smooth UNCD thin films, which can efficiently form MCD, but is not sufficient form UNCD due to the extremely small grain size of UNCD [5,6]. Bias enhance nucleation (BEN) is a superior technique to obtain UNCD with high nucleation density, which has several advantages over mechanical scratch or ultrasonic seeding pre-treatment such as better efficiency, stronger adhesion to substrates, and an integrated nucleation during growth in chamber [7-9]. However, BEN is limited to conducting substrates, which is not suitable to apply for non-conducting substrates and intermediate layer. In this present paper, the plasma pre-carburization (P.P.) method was first to improve nucleation rate on Si substrates and then combined with optimum Ar concentration to form extremely smooth UNCD films by superior MPJCVD system.

2. Experimental

The diamond films were prepared by using the home-made MPJCVD system. N-type mirror polished Si substrates were used to synthesize diamond films. Surface pretreatment of substrate was carried by plasma pre-carburization (P.P.), which involves two step processes. (1) 'carburization step'- substrates were exposed to C-H plasma (8% methane concentration) to produce a thin α-C layer with MPJCVD and (2) 'seeding step'– substrates were then took out the chamber and treated with ultrasonic seeding in alcohol solution by mixing nano-diamond powders (5 nm). The plasma chemistry used Ar gas gradually substitute H_2 gas from 0% to 100% (Ar/H_2) to investigate the process of MCD nanonization to form nanogranular diamond films. The other one deposition condition was fixed at 1% CH_4 concentration, microwave energy of 700 W, 3 hrs deposition time and deposition pressure under 35 torr, respectively. The surface morphologies of the films were observed using field emission scanning electro microscope (FE-SEM, Hitachi S-4700). Raman spectra of the diamond films were recorded with Renishaw Raman spectrophotometer, using an Ar laser at 514 nm. TEM observation was carried out using a Philips F30 microscope operated at 300 kv for high-resolution TEM image. The AFM image was obtained with scanning probe microscope (Digital Instrument NS3a) in tapping mode. Beside material analysis, we also used the in-situ plasma optical emission system (OES) to diagnosis the plasma reaction species with different compositions in this research work. Because of the plasma usually dominates the whole reactive and growth mechanism of diamond films in the typical CVD processes. The different reaction factors (CH, C_2, H_α and H_β) and concentrations of plasma played extremely important roles in the growth process of nanogranular diamond films. The analysis of plasma diagnosis was carried out by OES (B&WTEK BTC112E).

3. Results and discussion

3.1. diagnosis and analysis of plasma

The optical emission spectra of the diamond films grown at various Ar concentrations are shown in Fig. 1. In the whole spectra, the C_2 swan system (467.7, 516.5, 558.8, nm etc.) and H_α (656.2 nm) have been observed through in the wavelength ranged from 300 to 700 nm [10-12]. The related species of Ar also could be observed over the 700 nm in the spectrum. From the analysis of OES indicated the intensity of C_2 gradually increased and the H_α gradually decreased with increasing the Ar concentration in the growth process. While the Ar/H_2 ratio was over 50%, the spectra indicated the domination in the plasma change from H_α to Ar specis. Moreover, C_2 dimer intensity increased greatly at Ar concentration over 90% (Ar/H_2). The H_α could remove the amorphous carbon and non-diamond phase, but the C_2 dimer could enhance secondary nucleation formation in growth process of diamond films [13]. In order to

improve the surface smoothness of diamond films, reducing grain size of diamond is necessary due to microcrystalline diamond have apparent facet. So the secondary nucleation rate could be raised in the growth process. Using of Ar gas to substitute H_2 gas could effective to raise the C_2 specie concentration in plasma especially in our MPJCVD system. It could be confirmed from the OES analysis. The OES spectra indicated the C_2/H_α value is 1.58 at 35 torr working pressure with 100% Ar concentration process in MPJCVD system. Above results indicated that the formation of UNCD diamond films with enough secondary nucleation could be obtained by this system without using 100% Ar concentration.

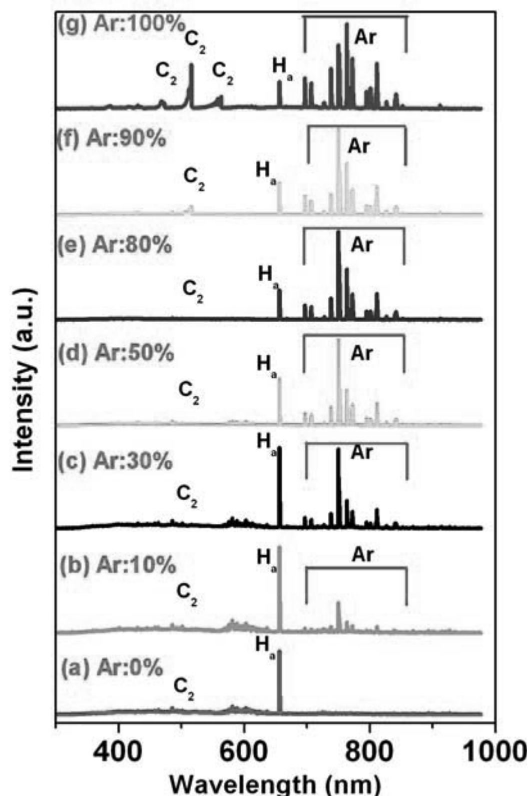

Fig. 1 OES analysis for diamond films grown at various Ar concentrations (a)0%, (b)10%, (c)30%, (d)50%, (e)80%, (f)90%, and (g)100%

3.2. Surface morphology and microstructure of diamond films grown with various Ar concentrations

The surface morphologies of diamond films grown at various Ar concentrations by MPJCVD are shown in Fig. 2. From SEM images indicated that the morphology could be controlled by introducing of argon gas. When the diamond films grown at CH_4/H_2 atmosphere (no Ar), the diamond films have well facet with average grain size about 400 nm as shown in Fig. 2(a). At argon concentration of 10%, the diamond films consist of many fractional facets around the big facet indicated the nanonization of microcrystalline diamond have been achieved by introducing of Ar as shown in Fig. 2(b). Further increase of Ar concentration in growth process induced the nanocrystalline diamond films with smoother surface and unclear facet as shown in Figs. 2(c)-(e). The nanocrystalline diamond films synthesized by 90% Ar concentration have best smooth surface as sown in Fig. 2(f). It could be observed that film surface not only consisted of nanoscale grain size to reduce the effect with diamond facet but also efficiently made the cluster size down to nanometer scale without appear cluster. Because of the limit from the maximum resolution of FESEM, the real grain size of diamond films grown with 90% Ar concentration process could not be clearly observed by SEM. Fig. 3 shows the plane view HRTEM image and corresponding SAD pattern of diamond films deposited with 90% Ar concentration process. The average grain size of the diamond film is about 5 nm. Nanogranular grains are embedded in the amorphous carbon matrix. The inset image of the corresponding SAD pattern indicated that the diamond grains have random orientation from the sharp ring diffraction pattern. In addition, the Raman spectra analysis was performed to indicated that the diamond films

gradually changed from the microcrystalline (MCD) to nanocrystalline (NCD and UNCD) diamond films as the Ar concentration increased (not shown here). The decreased intensity of D_f at 1332 cm^{-1} is due to the reduced grain size of diamond films.

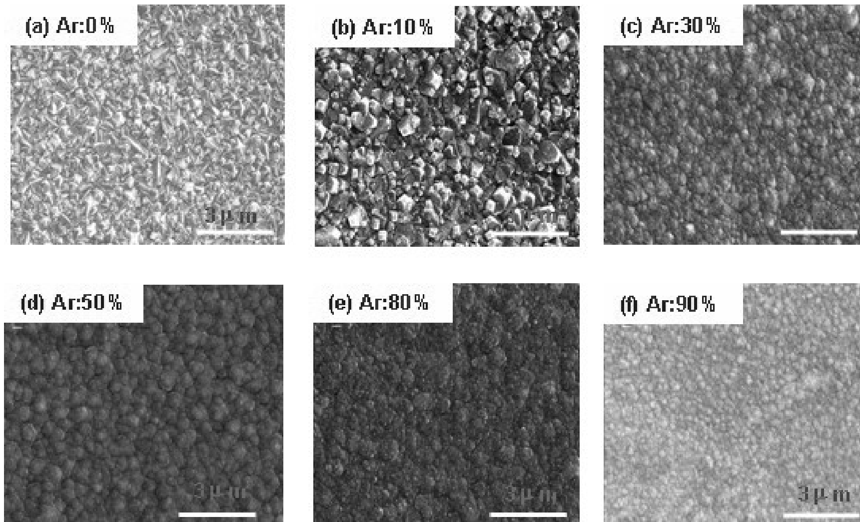

Fig. 2 SEM images for diamond films grown at various Ar concentrations (a)0%, (b)10%, (c)30%, (d)50%, (e)80%, and (f)90%, respectively

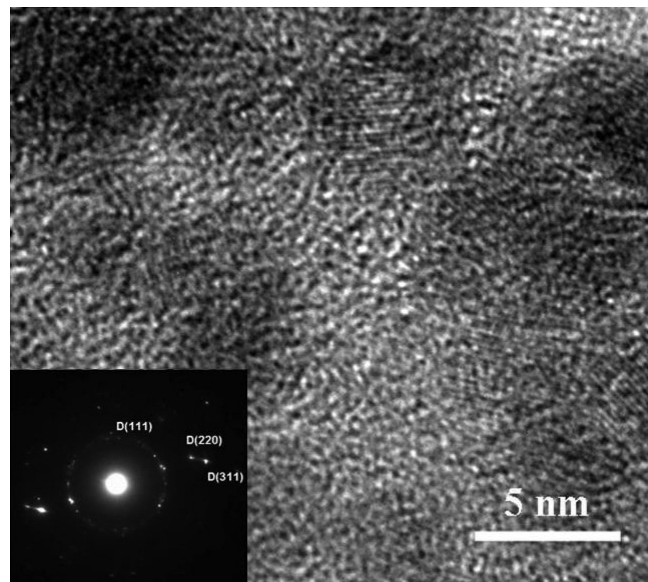

Fig. 3 HRTEM image and corresponding SAD pattern of UNCD films synthesized with Ar 90% concentration

Shown in Fig. 4 is the AFM image of diamond films grown with 90% Ar concentration process. The surface roughness is 13.3 nm (rms) with the scanning area 5 μm × 5 μm. This result showed that surface pretreatment with plasma carburization and grown nanogranular diamond at growth stage by MPJCVD could achieve ultra smooth surface. The reduction of the grain size can decrease the effect from facet. However, the P.P. pretreatment could provide a smooth base for diamond nuclei rapid formation with uniform distribution on this α-C layer. Fig. 5 shows the Raman spectra of the P.P. layer growth with 10 min deposition time by MPJCVD. The spectra clearly indicated this layer consist of two peaks around 1350 and 1580 cm^{-1}, respectively, which are assigned to D-band and G-band due to the typical characteristic of amorphous carbon phase from carbon related materials [14]. The P.P. step mainly served two purposes: (1) to form a soft allotrope layer on Si substrate for nanometer diamond powder seeding with ultra-sonication as well as (2) to reduce the nucleation incubation period and thus increased nucleation rate at initial stage of UNCD film growth [15].

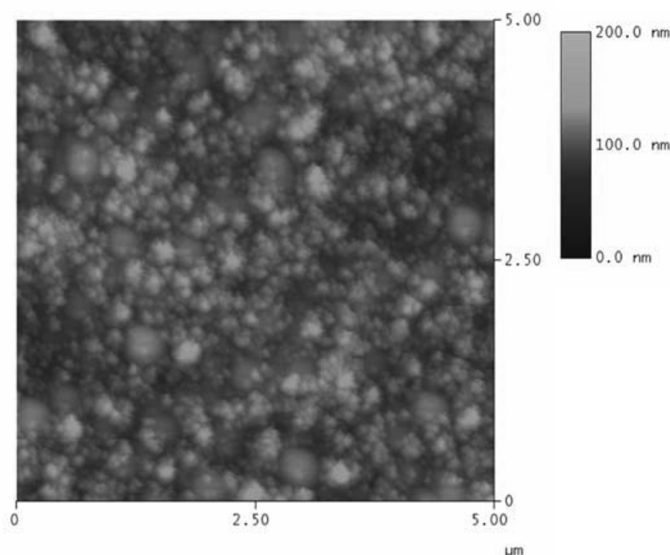

Fig. 4 AFM image of UNCD films synthesized with Ar 90% concentration process. It shows that the surface roughness of UNCD films (Rms: 13.3 nm) with the scanning area 5μm × 5μm

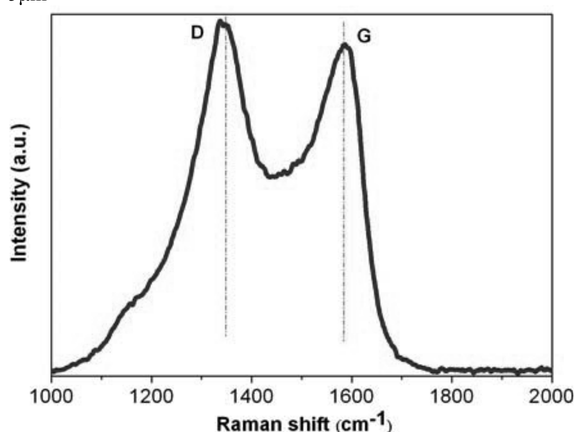

Fig. 5 The Raman spectra of the plasma precarbonization (P.P.) layer grown with deposition time of 10 min by MPJCVD. It demonstrates that P.P. layer mainly consist of amorphous carbon

4. Conclusions

Synthesized diamond thin films at Ar concentrations ranged from 0% to 100% by using microwave plasma jet CVD were investigated. The surface smoothness of diamond films was significant enhanced with the increase of Ar concentration and resulted in reducing the gain size from MCD (aparent facet) to UNCD (nanogranular crystal). The grain size of diamond films could down to 5 nm with extremely smooth surface (13.3 nm rms) at the concentration of 90% Ar without substrate heating process by using plasma precarbonization (P. P.) seeding method via MPJCVD process. The growth of UNCD by MPJCVD system can enhance the dissociation rate of introduction gas in order to achieve growth process with saving energy (lower Ar concentration and microwave power) and lower temperature (low working pressure), which will be of great aid in the industrial development for modern multi-applications.

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