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Highly dispersible diamond nanoparticles for pretreatment of diamond films on Si substrate

Shenjie Zhao [a], Jian Huang [a,*], Xinyu Zhou [a], Bing Ren [a], Ke Tang [a], Yifan Xi [a], Lin Wang [a], Linjun Wang [a,*], Yicheng Lu [b]

[a] School of Materials Science and Engineering, Shanghai University, Shanghai, 200444, China
[b] Department of Electrical and Computer Engineering, Rutgers University, Piscataway, NJ, 08854, USA

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ABSTRACT

High quality diamond film on Si substrate was synthesized by coating diamond nanoparticles prepared by polyglycerol grafting (ND-PG) dispersion as pre-treatment method. Transmission electron microscope indicates that ND-PG is much more dispersible than untreated nanoparticles in organic solvents. The surface morphology was characterized by scanning electron microscope while atomic force microscope was conducted to measure the surface roughness. Microstructure properties were carried out by Raman spectroscopy and X-ray diffraction. The results revealed an increase in nucleation density, an acceleration of growth rate and an improvement of film crystalline quality by using spin-coating ND-PG pretreatment.

1. Introduction

Diamond films have attracted lots of interest in both fundamental and applied sciences due to its unique mechanical, thermal, optical, electrical properties and outstanding chemical stability [1–3]. The nucleation is one of the key processes in the diamond film growth on foreign substrates such as silicon, Al_2O_3 and SiO_2 [4–6]. In order to ensure the formation of continuous and high quality diamond films, a high nucleation density is required at the initial stage of film growth. Numerous approaches including mechanical abrasion of the substrate surface [7–9], the addition of carbide forming or containing interlayers [10], through bias enhanced nucleation [11,12] as well as the attachment of diamond nanoparticles onto the surface for subsequent growth [13,14] have been used to increase the nucleation density. The most effective way among the above methods is to coat as many diamond nanoparticles (ND) as possible on the substrate surface that act as the seeds for epitaxial growth [15]. However, the agglomerates of ND can easily be over 100 nm which hamper the utilization of this process for high density nucleation. Although several techniques have been introduced to prevent the particles from aggregating, the problem has not been successfully solved so far. Chemical modification of ND powders has been reported to effectively reduce the size of ND aggregates down to the primary core particle size [16,17]. It is critical to find a suitable surface termination and functionalization of the diamond nanoparticles to avoid aggregating ranging from the establishment of a homogeneous initial surface termination, the covalent and non-covalent immobilization of different functional moieties, to the subsequent grafting of larger molecules onto previously functionalized ND [18]. NDs prepared by polyglycerol grafting have also recently begun to be studied for its high dispersability. Li Zhao et al. have developed a drug carrier based on ND with a surface coating of PG (ND-PG) [19]. The obtained ND-PG conjugate shows a very good dispersability in various solvents. The ND surface was covered with PG by means of ring-opening multibranching polymerization of glycidol at high temperature. ND-PG was synthesized when the polymerization was initiated at the surface functional groups, such as hydroxy and carboxylic acid groups [20]. Up to now, the studies on the nucleation of diamond films by using ND-PG pre-treated substrates have not been reported.

In this study, Si substrates were pretreated with ND-PG dispersion and common-used ND dispersion (untreated dispersion), respectively. Then, diamond films were deposited on pretreated Si substrates by microwave plasma chemical vapor deposition (MPCVD) method. The effects of ND-PG pre-treatments on nucleation and growth of diamond films were investigated in detail.

* Corresponding authors.
E-mail addresses: jianhuang@shu.edu.cn (J. Huang), ljwang@shu.edu.cn (L. Wang).

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Table 1
the process parameters for diamond film deposition.

Sample	Pretreated suspension	Nucleation H_2:CH_4:Ar (sccm)	Growth H_2:CH_4 (sccm)	Nucleation duration (h)	Growth duration (h)
S1	untreated	460:40:0	0	0.5	0
S2	ND-PG				
S3	untreated	445:35:20	0	0.5	0
S4	ND-PG				
S5	untreated	445:35:20	580:20	1	2
S6	ND-PG				

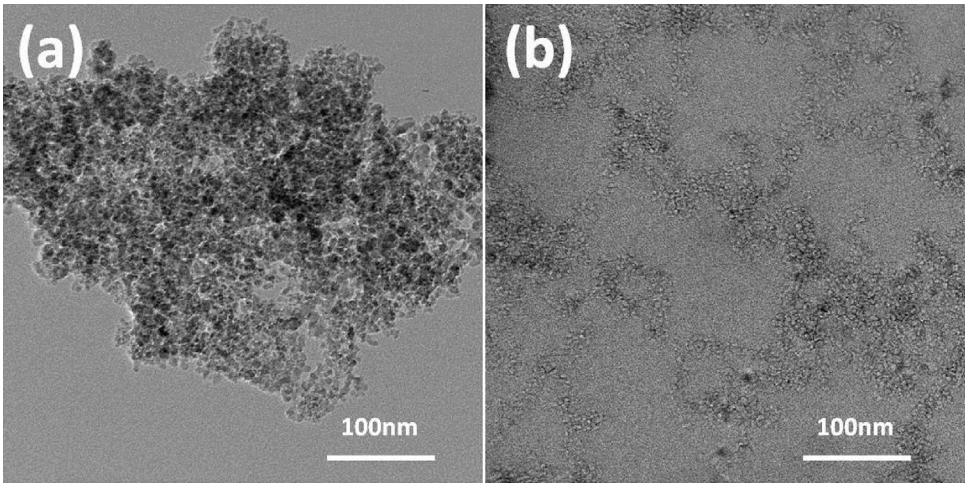

Fig 1. TEM images of two different diamond dispersions: (a) untreated diamond nanoparticles and (b) diamond nanoparticles prepared by polyglycerol grafting (ND-PG).

2. Experiment details

Concentrated sulfuric acid and 60% nitric acid (3:1 v/v) were mixed to treat the as-received ND powder with a median diameter of 10 nm produced by explosion method. The treated powders (60 mg) in glycidol (6 mL) were sonicated in an ultrasonic bath at 25 °C for 2 h. The well-dispersed suspension was magnetically stirred at 140 °C for 1 h and then left to cool to room temperature [20]. The resulting brownish gel was diluted with methanol (60 mL) via an ultrasonic bath for 5 h until the gel was all disappeared. The resulted sallow cream is the ND-PG stable dispersion.

For comparison, the common-used ND stable dispersion was prepared. The same powder (300 mg) was dispersed in acetone (250 mL) and then sonicated in an ultrasonic bath for 30 min. The above clear liquid (100 mL) was left alone for 4 days and was diluted with acetone (150 mL) again. The untreated suspension is the grey cream after standing for another 3days.

The ND-PG and untreated suspensions were coated on $20 \times 20\ mm^2$ (100)-oriented Si substrates using spin coater, respectively. Then, an optimized diamond film deposition process was employed by a MPCVD system with a hydrogen-methane mixture precursor. During the whole process, the microwave direct power was kept at 2.5 kW. The nucleation pressure was 20 Torr whereas the growth pressure was 45 Torr. To investigate the contribution of each stage of the process, we prepared 6 different samples with 3 groups tabulated in Table 1: Samples S1 and S2 coated with different dispersions just nucleated for 0.5 h without argon opposed to samples S3-S6; samples S5 and S6 grow 2 h after nucleation. The detailed deposition parameters are as follows in Table 1.

Transmission electron microscope (TEM, JEOL LTD JEM-2010F) was carried out to observe the dispersibility of ND-PG and untreated ND in organic solvents. The cross section and surface morphology of two different films were observed using scanning electron microscope (SEM, JEOL LTD JSM-7500F). Films were investigated by atomic force microscope (AFM, Bruker Scientific Instrument Hong Kong Multimode 8) to characterize the surface roughness working in noncontact mode, which can reflect the nucleation density. Raman spectrometer (JY, HR800UV) excited by 514.5 nm wavelength laser were used to study the film composition and uniformity. The crystalline phase, microstructure and vibration modes of films were analyzed by X-ray diffraction (XRD) operated on D/MAX 2200 diffractometer with Cu Kα radiation (λ = 1.54 Å).

3. Results and discussion

The diamond cores in as-prepared ND-PG and untreated ND in organic solvents were clearly observed by TEM in Fig. 1a and b, which shows that untreated particles have been aggregated severely. In stark contrast, ND-PG particles were separated successfully, which is beneficial to the subsequent nucleation process. ND-PG particles were very stable with high dispersibility in various solvents and we have not observed any precipitates and significant change in the diameter distribution for more than half a year. This characteristic of ND-PG particles is crucial to the nucleation and growth of diamond films.

Fig. 2a and b show the SEM images of nucleation films on Si substrates spin-coated with untreated ND dispersion (sample S1) and ND-PG dispersion (sample S2), respectively. There are only small amounts of ball-like diamond particles can be observed on spin-coated substrates with untreated ND dispersion, whereas sample S2 presents a more coalesced film with a higher diamond particles density. As a well-known fact, the ball-like diamond particles in the SEM images are diamond clusters made up of nano-crystallites. The results show a significant increase of the nucleation density by spin-coating ND-PG dispersion.

In microwave methane–hydrogen plasma, noble gases were found to have a profound effect on plasma chemistry, including additional ionization and dissociation. Upon adding a noble gas such as argon, the emission intensity of various species changes and the growth rate of diamond are enhanced [21]. Meanwhile the addition of argon to plasmas can increase the electron density of the plasma and modify diamond film morphology [22], which

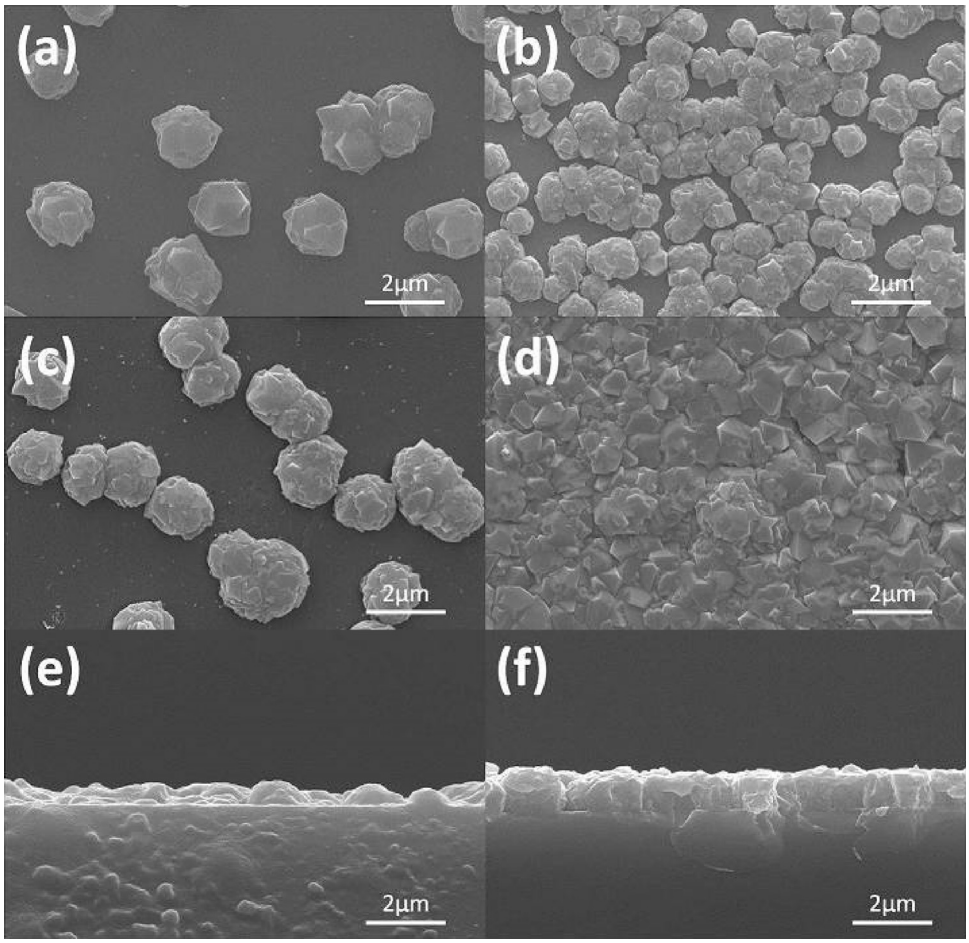

Fig. 2. SEM images of S1–S4: (a) surface of sample S1, (b) surface of sample S2, (c) surface of sample S3, (d) surface of sample S4, (e) cross section of sample S3 and (f) cross section of sample S4.

means that the introduction of argon to the deposition atmosphere can lead to the enhanced nucleation on substrates [23]. Compared to samples S1 and S2, argon was added during the nucleation of samples S3 and S4. The surface morphology of S3 and S4 can be seen in Fig. 2c and d. From the images, we can find continuous films are formed on substrates with spin-coated ND-PG dispersion, indicating that the nucleation density is significantly increased by introduction of argon. Fig. 2e and f show the cross section SEM images of S3 and S4, respectively. Sample S4 is thicker than S3, which means that coating ND-PG dispersion can not only increase the nucleation density, but also accelerate the growth rate.

The surface roughness of the nucleation diamond films S1-S4 was investigated with AFM. Fig. 3 shows the surface roughness of the samples from AFM. As can be seen from the figure, the nucleation films pre-treated with ND-PG dispersion have lower surface roughness, while those treated with common-used ND dispersion have greater roughness. The higher nucleation densities and uniform coverage of substrates with ND-PG dispersion is the reason for smoother surface of the nucleation films. Compared with sample S2, the surface of S4 is relatively smoother by adding argon in the deposition atmosphere which is consistent with the SEM results.

To get thicker and high quality films, the nucleation duration of the samples S5 and S6 increased to 1 h followed by 2 h growth. SEM images for the surfaces of samples S5 and S6 are in Fig. 4a and b. Growth leads to larger grains for both the sample S5 and S6. The same as the above analysis, it is evident that unlike the film seeding with untreated ND, the film seeding with ND-PG presents highly uniform coverage of the substrate as a result of higher nucleation

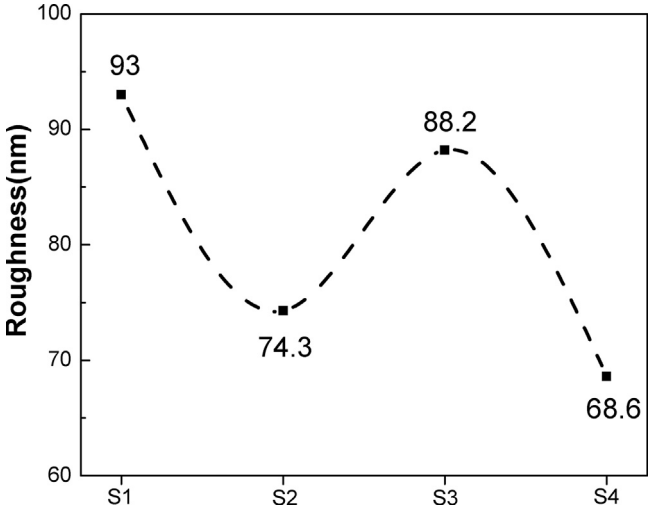

Fig. 3. Surface roughness of sample S1, S2, S3 and S4 from AFM.

density, which is also clear that the deposition rate of ND-PG films is faster.

Raman spectroscopy is always used to characterize diamond, graphite and amorphous-carbon components in the grown diamond films. Fig. 5 shows the Raman spectrum for samples S5 and S6. A strong Raman peak at the 1332 cm^{-1} can be observed for both films, which is the characteristic peak of the diamond. Another rela-

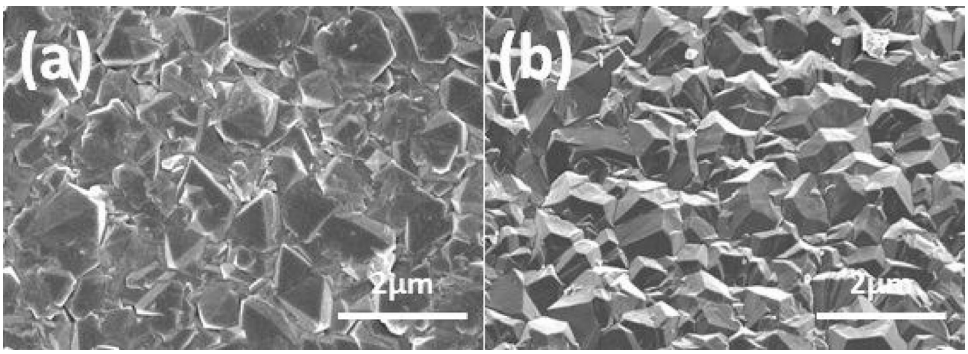

Fig. 4. SEM images (a) sample S5 and (b) sample S6.

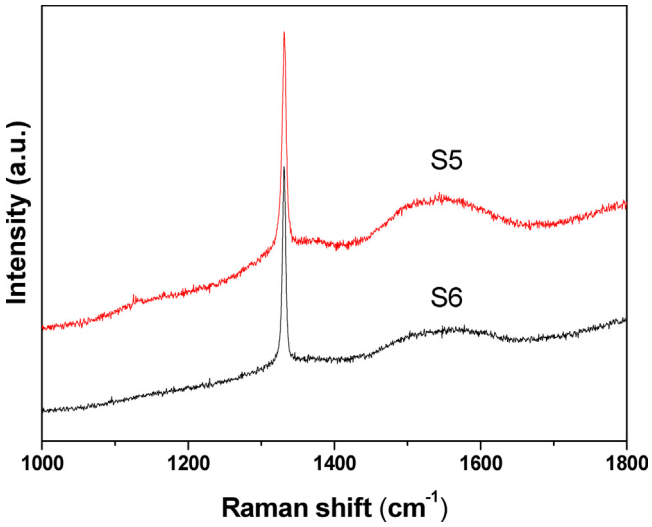

Fig. 5. Raman spectrum for samples S5 and S6.

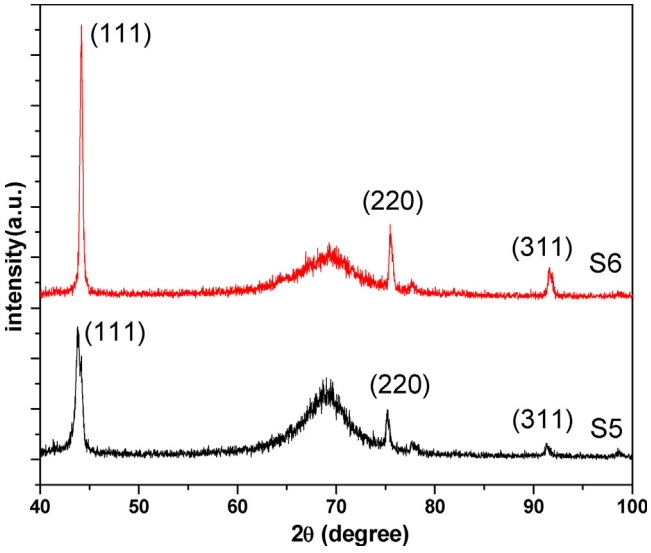

Fig. 6. X-ray diffraction patterns of samples S5 and S6.

tively weak broad peak existed in range of 1500 ~ 1600 cm^{-1} is the characteristic peak of non-diamond carbon [24]. For sample S5, the weak peak from ~1140 cm^{-1} (accompanied by a very small shoulder at 1490 cm^{-1}) attributed to transpolyacetylenes which appears in many CVD diamonds films [25].

The Raman signal for non-diamond carbon phase is about 75 times of that for diamond, so the non-diamond carbon content (C_{nd}) can be estimated [26]:

$$C_{nd} = \frac{1}{1 + 75 \times \frac{I_{dia}}{I_{nd}}} \quad (1)$$

Where I_{dia} refers to Raman peak intensity for diamond phase and I_{nd} refers to the intensity for non-diamond carbon phase. According to the formula (1), the results from Fig. 5 suggest a higher quality diamond with lower content of non-diamond carbon in S6.

In order to test the quality of the obtained diamond film, XRD pattern of samples S5 and S6 with a scanning range 40°–100° (2θ) is in Fig. 6. Three major diffraction peaks at 43.90°, 75.30° and 91.49°, originating from (111), (220) and (311) lattice plane of diamond cubic structure (JCPDS 06-0675) respectively [27] were showed in both the samples. It clearly shows that all the diffraction peaks of S6 are stronger than those of S5 and the FWHM of 43.9° in S6 is 0.334 which is much smaller than that in S5. It means better crystallinity and fewer defects in S6. To put it other way, the quality of ND-PG film is better than untreated one.

A point that needs to be emphasized here is that the diffraction peak of Si substrate at about 69.50° was stronger in sample S5 than in sample S6, which means that sample S6 is thicker and bigger coverage of substrates.

4. Conclusions

The diamond nano-particles prepared by polyglycerol grafting (ND-PG) so highly dispersible that easily dispersed in organic solvents, which is an effective method to reduce the agglomerates of diamond nanoparticles. We used the ND-PG stable dispersion to coat Si substrates before diamond films preparation. The results demonstrate that the choice of ND-PG can increase nucleation density and obtain highly uniform diamond films with lower surface roughness. Moreover, the ND-PG pretreatment can effectively speed up the growth rate and improve the crystalline quality of the film.

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