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Fabrication and Characterization of High Quality Nano-diamonds by Hot Filament CVD

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Abstract: The hot filament chemical vapor deposition technique (HFCVD) is used to fabricate high quality nano-diamonds. In order to obtain a high density of nano-crystals of diamond that do not join together to form a continuous films, the nucleation density or rate need to be controlled by regulating the pre-treatment method for substrate, bias intensity and deposition time. After the experiments, the morphology and quality of the as-grown nano-diamonds are observed and analyzed by FESEM (field emission scanning electron microscopy). The results show that the as-deposited nano-diamonds (~220 nm) appear a well-defined morphology with (111) and (100).

Keywords: Nano-diamonds; Nucleation density; High quality; Hot filament CVD

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Introduction

Nano-diamonds have dual properties of diamond and nanomaterial, contributing to the fact that it has wide applications in many industrial sectors, e.g., lubricant, polishing slurry, electroplating solution, and composite materials [1]. Especially in the case of grinding and polishing, nano-diamonds has attracted intensive attention as the demand for high-precision products (i.e., advanced optical glass, computer hard disk substrate, optical elements, and semiconductor integrated circuit) has increased dramatically in recent years. It is well known that almost all industrial diamonds are manufactured by high pressure methods [2]. However, typically in this method, the diamond growth is over 1000 μm/h, which is too fast to grow nano-sized diamond crystals (<1 μm). Therefore, the nano-diamonds are fabricated by pulverizing from HPHT process or explosion shock-synthesis. Unfortunately, these nano-diamonds always have poor quality and contain catalytic impurities, which directly affect the grinding or polishing quality, especially for the case of the sensitive products like semiconductors [3].

Chemical vapor deposition (CVD) has attracted considerable attention due to deposit diamonds with low defect density, with well-defined morphology and size. Various research groups have reported the deposition of large single crystal diamonds using a variety of CVD methods [4-6]. It can be expected from the reported results that although the growth rate of CVD method is significantly lower than that of HPHT method, the high quality isolated diamonds are obtained directly by CVD method but not by HPHT method because isolated diamonds need to be purified and selected from catalytic impurities in HPHT method. Hence, it is possible to produce high quality nano -diamonds in quantity production by CVD method. But to our knowledge, there is very few related published work on CVD micro, or nano-diamonds [3,7]. Therefore, to obtain high quality isolated nano -diamonds in quantity production, many prominent problems need to be solved, in particular providing reasonable deposition conditions for controlling the diamond nucleation density and rate at a moderate value, under which the high density isolated crys-

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tals that do not join together to form a continues films are obtained on substrate.

In this paper, the hot filament CVD is adopted to fabricate nano-diamonds due to the moderated deposition rate and largest deposition area. Here we investigate the effect of the various pretreatment methods for substrate, bias intensity and deposition time on the density and quality of nano-diamonds. Afterwards, the morphology and quality of the as-grown nano-diamonds are observed and analyzed by FESEM.

Experiment

The nano-diamonds are fabricated in HFCVD reactor having a deposition area of 500 cm^2. They are deposited under various deposition conditions to investigate the nucleation density and quality of diamond crystals. The two kinds of the (100)-oriented silicon wafers (un-polished, mirror-polished) are used as substrate, which are prepared by scratching with diamond paste (0.5 μm) for different minutes (as listed in Table 1) and cleaning in an ultrasonic bath with acetone one times. In the deposition process, the tantalum wires (Φ0.7 mm) are used as the hot filaments, which are dragged to be straight by temperature springs and fixed 10 mm above the silicon wafer in parallel and equidistance manner. The studies of deposition conditions include bias intensity of 0-1.5A, and growth time of 0-2 h. Other deposition parameters are hold as constant, as illustrated in Table 2. It should be noted that compared with the deposition parameters in the conventional diamond films, the higher substrate temperature, higher deposition pressure, and lower acetone concentration are employed for depressing the nucleation rate and slightly enhancing the growth rate to grow isolated diamonds. This is attributed to the fact that a lowered super-saturation of growth species in the gas phase can depress the secondary nucleation, which contributes to fabricating high quality single crystal diamonds without growth defects [8].

Table 1 Sample pretreatment methods

Sample	Silicon wafer	Scratching duration
1	Un-polished	0 min
2	Mirror-polished	0 min
3	Mirror-polished	2 min
4	Mirror-polished	1 min

Table 2 Deposition parameters of diamond films by HFCVD

Parameters	Nucleation	Growth
The ratio of CH3COCH3 to H2	3%	2%
Pressure (Kpa)	2	3
Bias(A)	0.5	0.5-2
Substrate temperature (℃)	750-800	800-900
Filament temperature (℃)	2000±200	2200±200
During time	15min	0-2 h

The density and the surface morphology of CVD micro diamonds are analyzed by Scanning electron microscopy (SEM).

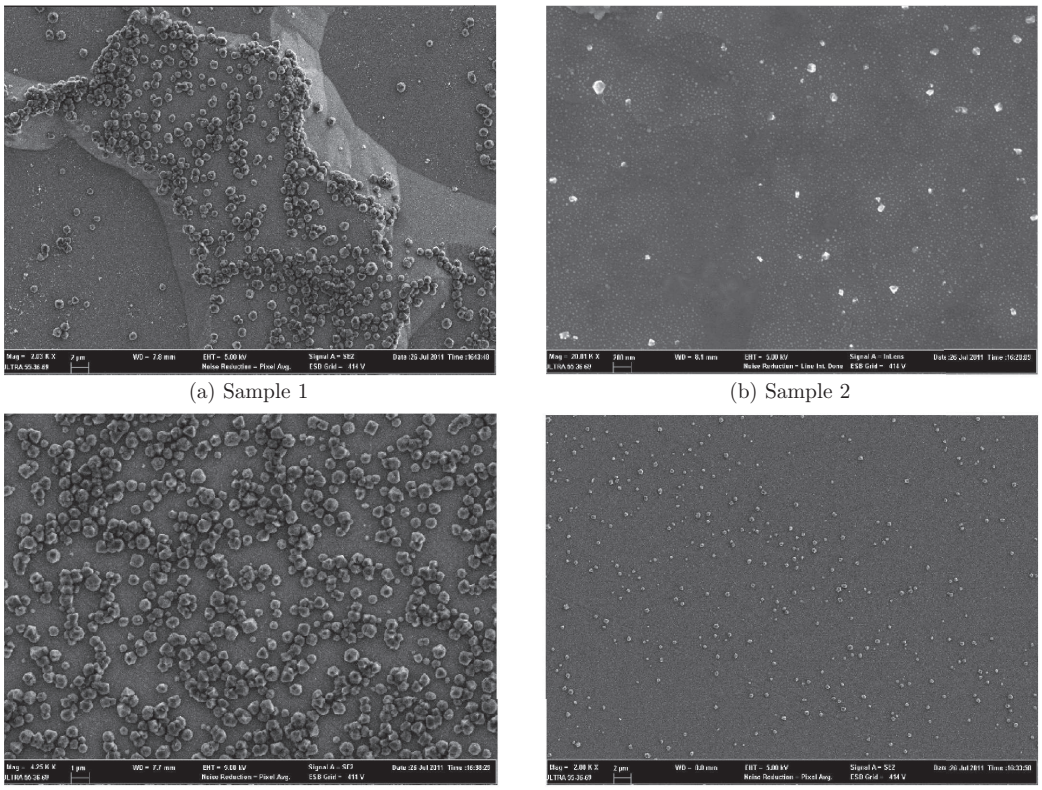
Results and discussion

Several experiments perform in order to gain the technique for depositing nano-diamonds and to gain insight into the process. A first experiment consisted in varying the pretreatment methods for (100)-oriented silicon substrate while holding the other deposition parameters as constant; in a second experiment the bias intensity is changed; in a third experiment the deposition time is varied.

Influence of the pretreatment methods for substrate

The diamond crystals are grown on four kinds of substrates which are prepared with various pre-treatment methods, when the bias current, growth time, and other parameters are fixed at 0.5 A, 1.5 h, and values as listed in Table 2. The as-deposited diamond crystals under the various substrates are observed and analyzed by FESEM (as shown in Fig. 1). With the unpolished silicon wafer (Sample 1), obviously, the distribution of diamond crystals is significantly non-uniform (some crystals are isolated while some crystals join together to form continuous films). This is attributed to the fact that the unpolished substrate is rather rough and the surface morphology of that is fairly non-uniform. With the mirror-polished Si substrate (Sample 2), it is observed from Fig. 1(b) that the diamonds does not readily nucleate and grow, owing to its high surface free energy and the low sticking probability of diamond precursors [5]. Nevertheless, the distribution of diamond nuclei is found to be relatively uniform on the highly polished surfaces, being beneficial for producing single crystal diamonds with homogeneous nano-grain size. Therefore, to enhance the nucleation density and rate on the highly polished surfaces, the mirror-polished Si substrate are scratched with diamond paste (0.5 um) for several minutes. In the case of scratching for 2 minutes (Sample 3), the well-facted diamond crystals with mean size of 600 nm are obtained but some of them are agglomerated, indicating that the nucleation density is too high to produce isolated crystals. While in the case of scratching substrate for one minute (Sample 4), the diamond crystals (∼400 nm) are all isolated, and evenly distributed on the substrate. According to the above results, it is expected that the nucleation den-

sity or rate strongly depends on the surface morphology of substrate, moreover, coarsened the substrate surface is favorable for enhancing the nucleation density and growth rate.



(a) Sample 1 (b) Sample 2

(c) Sample 3 (d) Sample 4

Fig. 1 The shape and surface morphology of non-diamonds under different periods of the deposition.

Influence of the bias current

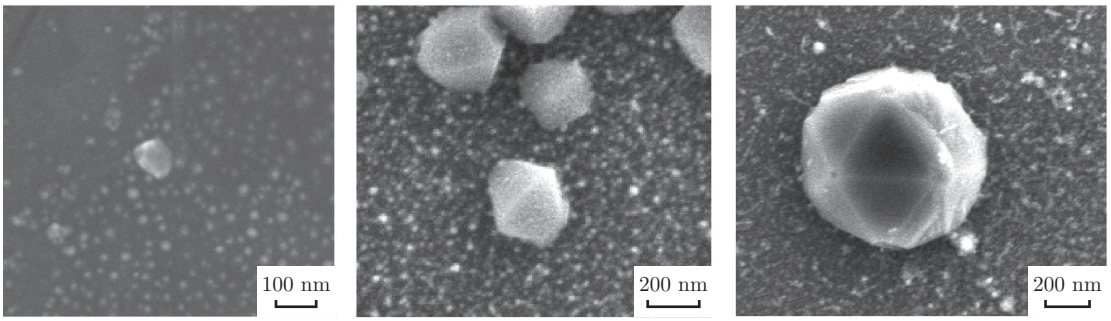
The diamond crystals are deposited at bias current of 2-1A when the pre-treatment method is the same as that in Sample 4, and the growth time is fixed at 1 h. The results of the experiments are shown in Fig. 2. Apparently, the nucleation density and the mean size of diamonds increase with enhancing the bias intensity. The diamond crystals have joined together to form a continuous films at bias of 2 A, and the mean size of crystals is about 1 μm. Hence, it is impossible to produce isolated nano-diamonds under the bias of 2 A. In the case of the bias of 1.5 A, the estimated nucleation density is about 1.1×10^{10} m^{-2}, and the mean size of crystals is about 500 nm, whereas many crystlas are found to be agglomerated. However, when the bias intensity is about at 1A, the majority of crystals (∼220 nm) with well-defined morphology are isolated from others, and the estimated nucleation density is about 8.6×10^{9} m^{-2}. In addition, it is found that the lower bias intensity adopted, the more diamond crystals with the euhedral diamond faces and low growth defects are obtained. Therefore, it can be infered that the bias intensity play an important role on the nucleation density, orientation of the nuclei, and the size of the crytals.

Influence of the deposition time

The diamond crystals are deposited at the growth time of 0.5-2 h when the pretreatment method is the same as that in Sample 4, and the bias current is fixed at 1 A. Apparently, the mean size of the diamond crystals increase stable with the deposition time (in Fig. 3). However, the size of the crystals is too inhomogeneous (20 nm∼100 nm) and the shape of that is irregular below 30 minutes of deposition. After 1hour of deposition, the mean size of crystals is comparatively homogeneous ranging from 200 nm and 220 nm; moreover, the euhedral diamond faces appear smooth and flat without indications of growth spirals or excrescences. Subsequently, it is observed that the diamond crystals become larger (800 nm) at 120 min deposition time, and even some are close to 1 μm. Nevertheless, compared with the surface morphology of the diamonds at the 60 min, the growth defect and secondary nucleation are detected on the crystals at 90 min.

As discussed above, it is concluded that in the early

stage of growth, the shape of diamond crystals are irregular and the size of the crystals is inhomogeneous; in the stable stage of growth, the crystals with euhedral diamond faces are well distinguishable on substrate, whereas it is noted that the well-faceted crystals nearly exceed 200 nm; as the crystals grow to above 500 nm, the growth defects are detected. Therefore, the 200 nm diamonds with euhedral diamond faces are fabricated after one hour deposition time.



0.5 hours of deposition | 1 hours of deposition | 2 hours of deposition

Fig. 2 The shape and surface morphology of non-diamonds under different periods of the deposition.

Conclusion

Hot filament chemical vapor deposition technique (HFCVD) is adopted to produce high quality nano-diamonds with the euhedral diamond faces. The effect of pre-treatment for substrate, the bias intensity and deposition time on the density and size of the nano-diamonds are investigated. According to the experimental results, it is found that the nucleation density or rate strongly depends on the surface morphology of substrate, and indicated that the mirror-polished silicon wafer which are prepared by scratching with diamond paste for just one minutes is more effective way for producing the high density single crystal nano-diamonds. The results also indicated that the bias intensity is a predominant factor in controlling nucleation density and the size of the diamond crytals. Furthermore, the mean size of the diamond crystals are found to be increased stable with the deposition time, and the nano-diamond crystals (∼200 nm) with well-faceted morphology are successfully fabricated under bias current of 1 A after 1 hour deposition time.

Acknowledgements

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