

Study on diamond thin film deposited on graphite substrate by different pretreatment methods

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Nanocrystalline diamond thin film has been deposited on a graphite substrate by hot filament chemical vapor deposition system. The characteristics of diamond thin film growth on a graphite sheet were evaluated depending on the pretreatment methods which increase the nucleation density. Four kinds of pretreatments were studied including mechanical abrasion by nano-diamond powders, ultrasonication of graphite in solvents with nano-diamond powder suspension, electrophoretic deposition, and pretreatment with polyethyleneimine (PEI) to change the surface polarity, allowing the adsorption of negatively charged diamond particles onto the substrate surface. Electrophoresis and PEI pretreatment methods were found to be favorable of the diamond deposition to the graphite sheet. The serial process of the PEI-pretreatment and immersion into acetone solution of diamond nano-powders was concluded as an optimal condition, resulting in 100% film coverage of diamond film with the average grain size of 0.7-0.8 μm on the graphite sheet. It can be suggested that the diamond film deposited on graphite could replace current SiC deposited graphite carrier in MOCVD process.

Key words: Nanocrystalline diamond (NCD), Substrate pretreatments method, PEI Pretreatment.

Introduction

Motivation

Since graphite has excellent thermal conductivity, it can be used as a uniform heat spreader. Graphite has been used as a substrate holder for a metal organic chemical vapor deposition (MOCVD) on silicon wafers in many LED epitaxial fabs. However, graphite holder is easily attacked or eroded by the reaction chemicals at the high temperature of about 1500-1800 °C in the chamber and therefore SiC-coated graphite has been used commercially in order to protect any chemical reaction. The average thickness of SiC layer on the graphite holder is about 15 μm for commercial products.

Diamond has better anti-erosion and chemical durability at high temperature and therefore is proposed to replace SiC layer on top of the graphite holder. Diamond with high chemical stability is more favorable for a protection coating than SiC in the same thickness. Therefore, diamond coating on the graphite holder can extend the life time of graphite holder so as to reduce the processing cost for LED processing equipment.

Diamond coating by chemical vapor deposition

Due to the chemical stability, high hardness, high strength, high thermal conductivity, and low friction coefficient, diamond has been used for industrial

applications such as cutting tools, optical windows, heat spreaders [1], semiconductor equipments [2, 3], NEMS/MEMS [4-7], and biologically active substrates [8]. Diamond film can be classified into three groups in term of the grain size: microcrystalline diamond (MCD), nanocrystalline diamond (NCD) and ultra nanocrystalline diamond (UNCD). In general, the MCD is composed of over several hundred nanometer-sized grains. If the surface roughness and the friction coefficient are relatively high, it is difficult to apply an anti-friction coating. There are some reports proposed the MCD with high strength and low friction in order to overcome the problem [9, 10].

The formation of diamond includes explosion, high temperature high pressure, and chemical vapor deposition (CVD) which has the advantage of large coating area. Methods for CVD Diamond include hot-filament, microwave plasma, RF plasma and DC plasma based on the power supply of reaction gases. Methane as a carbon source and massive hydrogen as a carrier gas and a reaction gas are generally used in CVD. In 1952, W. C. Eversole firstly deposited diamond by hot filament chemical vapor deposition (HFCVD) [11]. Tungsten filament is usually used as a heat source for HFCVD. Since the tungsten filament can reach to high temperature of 1800-2400 °C, the reaction gases are easily decomposed. Therefore, many free radicals can be formed near the substrate. Nevertheless, the HFCVD has the processing advantages such as simplicity, low cost, large area deposition, and high deposition rate ranging of 0.5~8 $\mu\text{m/hr}$ [12].

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Heteroepitaxy

Graphite and diamond are allotropic materials with different thermal expansion coefficients of $1.2 \times 10^{-6} \text{ K}^{-1}$ and $0.8 \times 10^{-6} \text{ K}^{-1}$, respectively. The general modes of heteroepitaxy growth are Volmer-Weber, Frank-van der Merwe and Stranski-Krastanow. The growth model can be described by the Volmer-Weber mode when the surface energy of the epitaxial materials is much larger than that of the substrate. The deposition model can be considered as Frank-van der Merwe mode while the surface energy of the epitaxial materials is close to or less than that of the substrate. The deposition of diamond with a well-known high surface energy can be attributed to Volmer-Weber mode [13].

Due to the large difference of the surface energy between the epitaxial materials and the substrate for heteroepitaxy, diamond with high surface energy cannot be easily deposited on non-diamond substrate [14]. For example, the nucleation density for the diamond deposition on silicon substrate is only 10^5 cm^{-2} [15]. Therefore, the nucleation process is considered as a key parameter for diamond film deposition.

Royer et al. [16] proposed an epitaxial growth model to predict that a certain orientation epitaxy could be obtained at the condition of two sets of parallel facets with very close distance where the mismatch between two crystalline materials could be reduced to a minimum and therefore could the strain. Mismatch dislocation theory was proposed by Van der Merwe [17, 18]. In order to reduce the strain energy induced by the lattice mismatch, one of the lattices formed a dislocation at a fixed distance to eliminate the strain.

The pretreatment on non-diamond substrate is necessary to reduce the difference of the surface energy between varied lattice constants for diamond film deposition. Iijima et al. [19] put a silicon substrate into the suspension of about 10 nm sized diamond powder by ultrasonication and found that some nano-diamond particles remained on the surface of the silicon by high resolution tunneling electron microscopy. The remained diamond particles were proposed to be the nucleation sites of diamond film. They proposed that the remained diamond scraps were the nucleation sites after scratch pretreatment by diamond powder. Other works demonstrates that diamond powders or carbide were used as intermediate layer to avoid carbon diffusion and therefore form the nucleation sites [20, 21]. Paul and David [22] found that the diamond nucleation is related to the topography of the substrate. Scratch slit or small angle on a substrate by diamond powder would result in the change of surface energy or contact angles and form a suitable nucleation sites. Liu and Dandy [23] showed that the grain size and topography of CVD diamond film would be affected by the nucleation density of diamond deposition. The nucleation density of CVD diamond increased with the density of the remained diamond particles, which could be improved by surface pretreatment.

Substrate pretreatment

In order to increase the nucleation density, many pretreatment methods have been researched including diamond powder scratching, ultrasonication in diamond powder suspension, bias enhanced nucleation (BEN), and hydrocarbon plasma assisted nucleation [24]. Liu et al. [25] reported that, for the NCD films on silicon substrates, the highest nucleation density of 10^{11} cm^{-2} with the highest residual stress was obtained by BEN among different pretreatment methods. Lee et al. [26] compared UNCD films by different pretreatment methods and showed that the highest nucleation density of 10^{11} cm^{-2} with the lowest surface roughness was obtained by pre-carburizing a silicon substrate and ultrasonication the substrate with diamond powder solution. Diamond films with different grain sizes correspond to their own suitable pretreatment methods. In addition, different pretreatment methods are required for diamond films on different substrates. For example, comparing a graphite substrate with a silicon one, aggressive pretreatment methods are not proper to apply on a graphite substrate since a graphite substrate less brittle characteristics than a silicon substrate delaminates easily. Affoune et al. [27] proposed electrophoretic deposition of nanosized diamond particles driven by the electrostatic force to impact and adhere onto the substrate based on the characteristics of the weak negative charge of diamond micro-particles. Adair and Singh [28] used polyethyleneimine (PEI) to change the electrical properties of the substrate with less harm on the surface. In this study, several kinds of pretreatment methods for HFCVD diamond were experimented as follows: 1. Ultrasonication; 2. Scratching; 3. Electrophoresis; 4. Electrophoresis after scratching; 5. Immersion into acetone solution with diamond nano-powders; 6. PEI pretreatment and immersion into acetone solution with diamond nano-powders.

Experimental procedure

Polished graphites ($10 \times 10 \text{ mm}$ and 0.2 mm thick) were pretreated using different methods. There are three parallel tungsten wires with constant distance above the substrate. The temperatures of the tungsten wire or the graphite were adjusted by controlling the current of the tungsten wire. Before diamond deposition, the filament is carbonized by 2% CH_4/H_2 for 1 hour. After the surface pretreatment, diamond films were deposited by HFCVD. The experimental parameters of the deposition process are listed in Table 1.

Different pieces of graphite were pretreated by scratching, ultrasonication, electrophoresis, electrophoresis after scratching, PEI pretreatment or immersion into diamond powder (4~12 nm in diameter) solution. One piece of graphite was ground by diamond nano-powders between two silicon wafers for scratching pretreatment. For ultrasonication, a piece of graphite

Table 1. HFCVD Process Parameters in this study

	Deposition	Cooling
Distance between filament and substrate (mm)	10	10
Filament temperature (°C)	2000	cooling to 25
Substrate temperature (°C)	587-590	cooling to 25
Hydrogen flow rate (sccm)	250	250
Methane flow rate (sccm)	5	0
Reaction pressure (torr)	75	68
Duration (h)	5	1

was immersed into the solution of diamond nano-powders and acetone for 1 hour. Before electrophoresis, diamond nano-powders of 0.005 g/ml in acetone solution were ultrasonicated for several minutes to disperse the aggregation of diamond nano-powders. A piece of graphite as the anode in the electric field of 100 V/cm was then immersed into this ultrasonicated solution. PEI pretreatment was done by immersing a piece of graphite into a 0.45 wt% PEI solution for 12 hours to make PEI with positive charges adsorbed onto the graphite. After immersion into PEI solution, the graphite was immersed into acetone solution with 0.035 wt% diamond nano-powders for 12 hours. Diamond nano-particles with negative charges in acetone solution were attracted by the positive charges of the graphite surface after PEI pretreatment.

The surface morphology is inspected by a scanning electron microscopy (SEM, JSM-6330F, Jeol). The top-view SEM image can indicate the film coverage and the grain size and the cross sectional SEM image do the deposition rate and the diamond film thickness. Diamond quality was evaluated by Raman spectroscopy at the laser wavelength of 632.81 nm.

Experimental results and discussions

Different pretreatment methods

Some irregular layers of about 0.25~1 mm² were delaminated from the graphite substrate after 10 minutes ultrasonication. They were easily delaminated because of the weak bond between the graphite substrate and layers since they were broken firstly upon ultrasonication. The delaminated graphite exhibited the poor surface morphology and was not considered to proceed further CVD processes. Scratching pretreatment which destroys the substrate surface was not favorable for the post processes since the graphite surface became dim after grinding.

The adhesion of diamond nano-powders was done with different processing time at the applied electric field of 100 V/cm for electrophoresis. The graphite surface remained shiny after 3 minutes. After 5 minutes it became a little dim and exhibited the presence of some

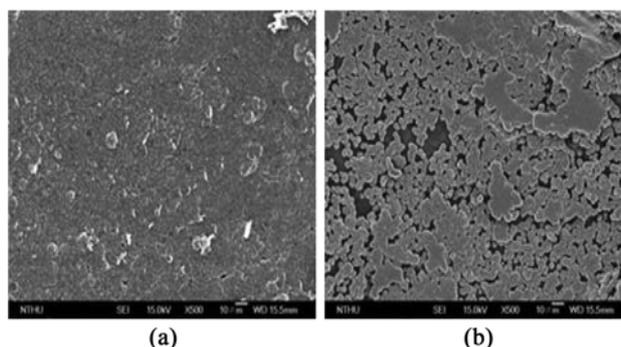


Fig. 1. SEM image of surface morphology after diamond deposition for 3 hours by PEI pretreatment with (a) horizontal immersion; and (b) vertical immersion of graphite sheet.

discrete dark spots. The surface appeared uniformly gray without shining after 8 minutes. Some island protrusions were found on the surface after more than 10 minutes. The longer the electrophoretic processing time, the more obvious the protrusion is. At the lower electric field of 50 V/cm, the protrusions still existed after 10 minutes. In order not to affect the following diamond film deposition, a low surface roughness is most important. Therefore, the optimal electrophoresis duration was decided to be 8 minutes.

Since the adhesion between diamond nano-powders and the graphite sheet is very weak after electrophoresis, the movement of the graphite sheet should be careful in order not to make diamond nano-powders fall off. The graphite sheet can be horizontally or vertically placed in diamond nano-powders solution after PEI pretreatment. Fig. 1 shows SEM images of the surface morphology after diamond deposition for 3 hours by PEI pretreatment with the horizontal and vertical immersion of graphite sheets into diamond nano-powders solution. In case of the horizontal immersion, a continuous diamond film with some small holes is obtained. In case of the vertical immersion, some regions of the graphite were exposed though a regional continuous diamond film. Therefore, the horizontal immersion of the graphite sheet was thought to be a better condition for a continuous diamond film. During the adsorption of diamond nano-powders on the graphite sheet in diamond nano-powders solution, diamond particles can either be attracted by the static force or be precipitated for the horizontal immersion process and hence more diamond nano-powders can be deposited on the graphite sheet.

Diamond film deposition experiments for different pretreatment methods

Fig. 2 shows SEM images of film coverage/surface morphology after diamond deposition for 5 hours by different pretreatment methods. Fig. 2(a) shows the case of non-pretreatment, indicating that microcrystalline diamonds were distributed nonuniformly. The coverage is about 62-65%. In case of scratching, more uniform distribution of small crystalline diamonds are seen and

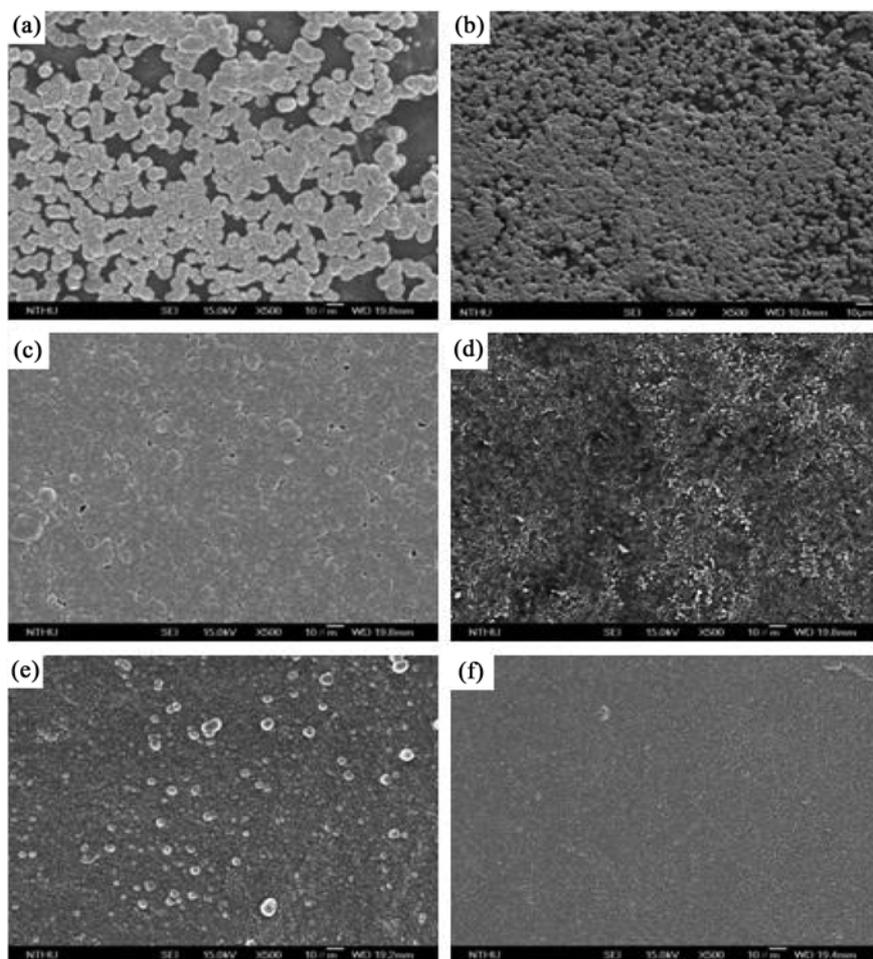


Fig. 2. SEM images of film coverage/surface morphology by different pretreatment methods.

(a) non-pretreatment, (b) scratching; (c) electrophoresis; (d) electrophoresis after scratching; (e) immersion into acetone solution with diamond nano-powders, and (f) PEI pretreatment and immersion into acetone solution with diamond nano-powders

the trend of continuous diamond film are seen to be able to develop in some regions (Fig.2(b)). The coverage is improved to be 77-79%. Fig. 2 (c) shows the result of the substrate after electrophoresis pretreatment. A continuous diamond film is seen with some holes. Small facets are also observed and the coverage approaches to 98-99%. The morphology of the diamond film on the graphite having scratching pretreatment before electrophoresis is shown in Fig. 2 (d). The deposited diamond film with small crystals covers all surface of the graphite sheet. The color of the diamond film changes depending on the viewing angles and the roughness and uniformity are poor. The phenomena may be originated from a large amount of scratches and sharp angles on the graphite surface after scratching pretreatment. With these scratches and sharp angles, the applied electric field becomes nonuniform and hence the nucleation sites are distributed with the nonuniform electric field. After diamond deposition, the dark and bright regions were observed. Fig. 2 (e) shows the case of the immersion of a graphite sheet into acetone solution with diamond nano-powders. A

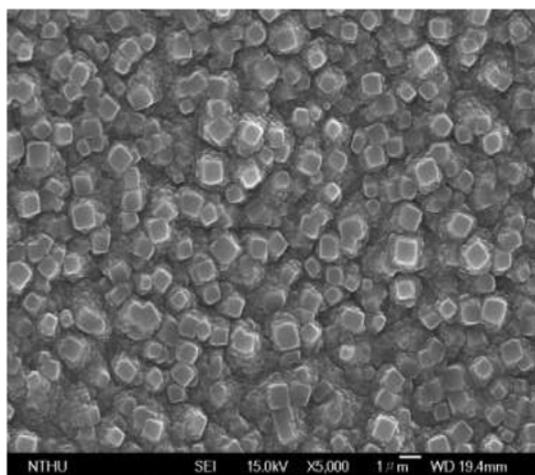
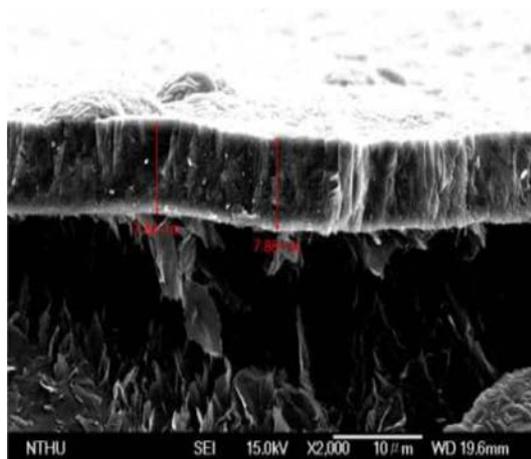
continuous film without any hole was obtained. Some aggregated diamond particles of about 3-10 μm are observed on the surface. Fig. 2 (f) shows the result after the pretreatment of PEI and immersion into acetone solution with diamond nano-powders. A continuous film with small crystals is seen. The coverage is almost 100% and the roughness and uniformity are good. It is concluded that this case is the best condition. The experimental results of diamond deposition with the different pretreatment methods are summarized in Table 2.

Fig. 3 shows the surface morphology of diamond film by PEI pretreatment for 5000 times. Crystal facets are seen and the grain sizes are about 0.7-0.8 μm . The cross sectional image of diamond film deposited on the graphite by PEI pretreatment is shown in Fig. 4. The film thickness is 7.8 μm with the deposition rate of 1.56 $\mu\text{m/hr}$.

Fig. 5 shows Raman spectra of diamond film depending on the different pretreatment methods. The D band ranging from 1140 cm^{-1} and 1350 cm^{-1} and The G band of about 1580 cm^{-1} were detected. With decreasing the grain size, the band near 1140 cm^{-1} becomes obvious,

Table 2. Diamond deposition results by different pretreatment methods

Pretreatment methods	Film coverage (%)	Grain size (μm)	Surface morphology	Raman spectrum
Non-pretreatment	62-65	9-11	Low film coverage	Intensity of G band is much higher than that of D band.
Scratching	77-79	2-3	Small grain sizes are uniformly distributed. Some discrete protrusions are connected.	Intensity of G band is slightly higher than that of D band. Nanocrystalline diamond exists.
Electrophoresis	98-99	1.0-1.5	A continuous film with some small holes. Small facets are observed.	Intensity of G band is slightly higher than that of D band. Nanocrystalline diamond exists.
Electrophoresis after scratching	100	1-2	A continuous film without any hole. The surface is composed of smaller grains. The roughness and uniformity is not good.	Intensity of G band is slightly higher than that of D band. Nanocrystalline diamond exists.
Immersion into acetone solution with diamond nano-powders	100	0.15-0.30	A continuous film without any hole. Some aggregated diamond particles of about 3-10 μm are observed on the surface.	Intensity of G band is about that of D band. Nanocrystalline diamond exists.
PEI pretreatment and immersion into acetone solution with diamond nano-powders	100	0.7-0.8	A continuous film without any hole. The surface is composed of small grains. The roughness and uniformity are good.	Intensity of G band is about that of D band. Nanocrystalline diamond exists.

**Fig. 3.** Surface morphology of diamond film by PEI pretreatment (5000X).**Fig. 4.** Cross section image of diamond film on the graphite by PEI pretreatment.

attributed to nano-diamond. Except the case of non-pretreatment, nano-diamond is more or less observed. The pretreatment can increase the nucleation density and constrain the grain size. The slight deviation of the diamond peak in all these figures to 1335 cm^{-1} indicates the existence of residual stress resulting from the difference of the thermal expansion coefficients between diamond and graphite. Except the case of non-pretreatment, G band moves to a lower Raman shift. This may be attributed to the torsion of bonding angle of sp^2 bond. The intensity of G band is slightly higher than that of D band for the pretreatment methods of scratching, electrophoresis and electrophoresis after scratching. The intensity of G and D bands are approximately the same for the pretreatment of immersion into acetone solution with diamond nano-powders and PEI pretreatment.

Conclusion

Different kinds of pretreatments were studied including mechanical abrasion by nano-diamond powders, ultrasonication of graphite in solvents with nano-diamond powder suspension, electrophoretic deposition, and pretreatment with PEI. The quality of diamond film deposited by HFCVD was compared among different pretreatment methods. Electrophoresis and PEI pretreatment methods are favorable of the diamond deposition to the graphite sheet. 100% film coverage of diamond film with the average grain size of 0.7-0.8 μm on the graphite sheet were obtained by the use of the sample which was PEI-pretreated and immersed into acetone solution of diamond nano-powders. This method is concluded as an optimal condition. It can be

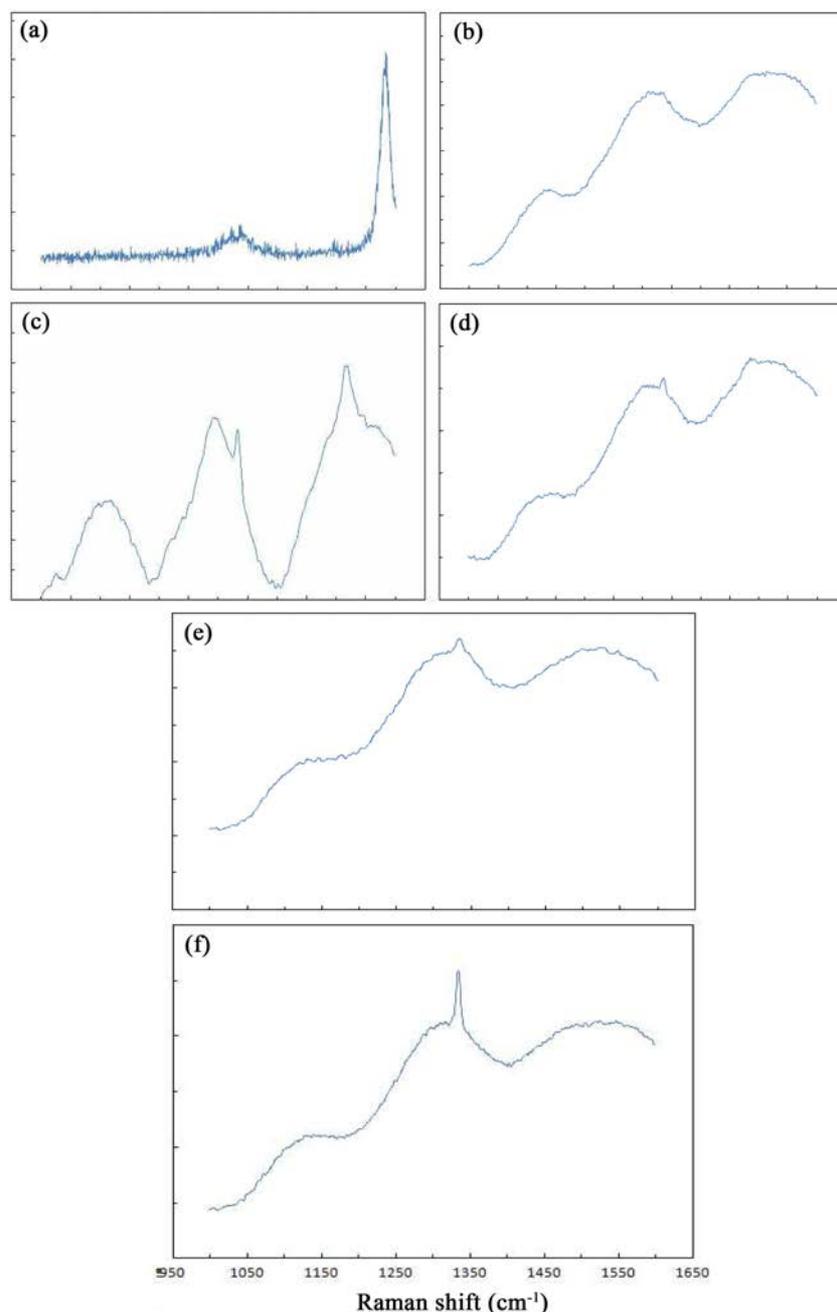


Fig. 5. Raman spectra of diamond film by different pretreatment methods. (a) non-pretreatment; (b) scratching; (c) electrophoresis; (d) electrophoresis after scratching; (e) immersion into acetone solution with diamond nano-powders, and (f) PEI pretreatment and immersion into acetone solution with diamond nano-powders.

suggested that the diamond film deposited on a graphite carrier used in metal organic chemical vapor deposition (MOCVD) can replace currently used SiC deposited graphite carrier and increase the life cycle of the carrier.

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