Exploring the validity of the charged cluster model for chemical vapour deposition diamond growth

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K.G. Saw

Physics Section, School of Distance Education, Universiti Sains Malaysia, Minden, 11800 Penang, Malaysia.

Tel:++ 604-6532280; fax:++604 6576000.

E-mail address: k.saw@aip.org.au

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Abstract

Diamond nucleation remains an unsolved problem. Recently the charged cluster model (CCM) was proposed as the nucleation and growth mechanism for low-pressure diamond where electric charges produced by gas activation are the nucleation sites. This paper explores the validity of the CCM by investigating the nucleation and growth of diamond on faceted sapphire substrates.

1. Introduction

The synthesis of low-pressure diamond using chemical vapour deposition (CVD) techniques is of commercial importance because of the high potential for various technological applications. Recently the charged cluster model (CCM) [1 – 5] was proposed as the nucleation and growth mechanism for low-pressure diamond where the electric charges produced by gas activation are the nucleation sites for the supersaturated carbon vapour. Charged nuclei are produced in the gas phase and the coarsening process of these nuclei eventually leads to the formation of charged clusters. If these clusters lose their charge only *after* crystallising on the substrate surface they maintain their diamond structure, and diamond crystals are eventually formed on the substrate. On the other hand if these clusters lose the charge to the substrates *prior* to landing on the substrate surface, graphite is formed on the substrate instead. Since the clusters do not lose their charge prior to landing on substrates with a low charge transfer rate (CTR), they maintain a diamond structure and land preferentially on surface structures such as an edge, forming a diamond film. Thus substrates with low CTR are thought to assist the preferential growth of diamond compared to graphite. A high density of the charged clusters is believed to provide a sufficient flux for subsequent diamond growth in the chemical vapour deposition (CVD) environment [6].

In this work diamond is deposited using the hot filament chemical vapour deposition (HFCVD) technique on single crystal α-(0001) sapphire substrates. Two aspects of the CCM will be investigated. The first aspect would be the diamond nucleation density. Since the CCM proposes that the initiation of the diamond particles on the substrate is not by surface nucleation but by the landing of charged nuclei on the substrate, a significant amount of diamond particles should be deposited. The atomic steps on the sapphire surface induced by annealing provide an opportunity to investigate whether the charged nuclei will land preferentially on these surface sites and eventually grow to become diamond particles as suggested by the CCM. Secondly, it would be interesting to investigate whether there is preferential deposition of diamond over graphite as sapphire substrates are insulating (low CTR) substrates.

2. Experimental details

Single crystal α-(0001) sapphire substrates were cleaned ultrasonically with solvents and then annealed in air for 1 - 3 h at the temperature of 1400°C. The annealing process induced a terrace-and-step surface topography. After the surface treatment, the substrate was inserted into the hot filament chemical vapour reactor (HFCVD) reactor. Diamond was deposited with 1 vol.% methane in hydrogen gas mixture at the filament and substrate temperatures of 2100°C and 850°C respectively. Diamond is deposited for 1, 2 and 4 h. Details of the HFCVD reactor were described elsewhere [7]. The deposition parameters were similar to those used by Hwang et al. [2] for the CCM and thus would serve as a good basis to investigate the validity of the CCM.

The formation of diamond on sapphire substrates was investigated using Auger electron spectroscopy (AES), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) as well as scanning electron microscopy (SEM). The AES and XPS measurements were performed using the Fisons MicroLab 310-F instrument. Data acquisition for the AES was performed at steps of 0.1 eV. The primary electron energy for the AES is 10 keV. The beam diameter was 100 nm while the beam current was 15 nA. The XPS measurements were taken with the Al Kα X-ray ($h\nu$ = 1486.6 eV) as the excitation source. The O 1s peak of the sapphire substrate at 531 eV binding energy, was used for charge correction. Single element scans were performed at a pass energy of 20 eV and at 0.1 eV steps between data points. The Raman measurements were taken at room temperature using a Dilor XY confocal micro-Raman spectrometer employing the 514.5 nm line from an Ar ion laser. The AFM analysis was done in air using a JEOL JSTM 4200A system in the non-contact mode. SEM was performed on the XL 30 Philips instrument.

3. Results and Discussion

Fig. 1 is an AFM image showing the typical faceted surface of the sapphire substrate induced by the annealing process. The height profile taken along the horizontal direction shows that the faceted surface has distinct steps separated by wide atomically smooth terraces. Fig. 2 shows the scarce formation of diamond particles on the sapphire substrate after a deposition period of 1 h. As the number of isolated diamond particles is very small, no nucleation density can be determined accurately. AFM analysis also reveals that the atomic steps on the substrate surface are stable in the HFCVD environment long enough to act as preferential sites for diamond formation if any were to occur. A reasonably high diamond nucleation density should have been obtained since the steps are found uniformly over the entire surface. However this is not observed. It should be noted that the number of diamond particles formed remains small despite longer deposition periods.

Raman measurements taken on the diamond particles show a strong peak between 1332 - 1333 cm^{-1} associated with good quality diamond. No broad peak associated with non-diamond carbon is observed in the 1500 – 1600 cm^{-1} range. Raman analysis on the sapphire surface in between the isolated diamond particles indicates no broad features in the range of 1500 - 1600 cm^{-1}. In view of the sensitivity of Raman spectroscopy using the 514.5 line from an Ar ion laser to sp^2 bonded carbon structures, the absence of a broad peak in this range is convincing evidence for the absence of graphitic or amorphous carbon. The Raman spectra for the various deposition periods of 1, 2, and 4 h are shown in Fig. 3.

The deconvolution of the XPS C 1s spectrum using a mixed Gaussian and Lorentzian function results in two peaks at binding energies of 283.3 and 285.0

eV. The peak at 283.3 eV is attributed to diamond while the lower intensity peak at 285.0 eV is due to unavoidable adventitious carbon from the ambient during the XPS measurements. Details of the XPS C 1s spectrum are presented elsewhere [8]. It is important to note that the C 1s peak attributed to the presence of aluminium carbide at 281.4 eV binding energy [9 - 10] is not observed. The absence of the aluminium carbide peak indicates that there is no formation of a carbidic interlayer between diamond and the sapphire substrate. The existence of a graphitic, diamond-like carbon or amorphous carbon intermediate layer is very unlikely, as in our previous work, we had analysed the underside of the delaminated diamond film as well as the sapphire substrate surface and found that diamond grew directly on the sapphire substrate [7].

Auger quantitative measurements in Fig. 4 reveal insignificant non-diamond carbon coverage on the sapphire surface even after 4 h of diamond deposition. The carbon-to-aluminium peak ratio is 0.1, which is similar to the ratio obtained from an uncoated as-received sapphire substrate. In addition, Auger C KLL analysis performed on the sapphire surface region in between the isolated diamond particles indicates no formation of a graphitic or amorphous carbon layer. The Auger C KLL spectrum obtained from the surface region in between the diamond particles is shown in Fig. 5 (a). The spectra obtained from amorphous carbon, graphite and diamond are shown in Fig. 5 (b) – (d) respectively for comparison. In the C KLL peak shape taken from diamond, the intensity of the fine structure shoulder B is greater than the shoulder A located at a slightly lower energy. On the contrary a low coverage of adventitious carbon from ambient contamination on the surface region between the diamond particles resulted in a small carbon peak with a large noise component as shown in Fig. 5 (a). Thus the Auger analyses are consistent with the Raman measurements that indicate no formation of a graphitic or amorphous carbon layer on the sapphire surface.

It should be noted that etch pits are observed on the substrate surfaces. Fig. 6 is a 2 μm x 2 μm AFM image showing etch pits on the sapphire substrate after 1 h of exposure in the HFCVD environment. In the atomic hydrogen hypothesis, the existence of the etch pits is easy to explain. Hydrogen undergoes a thermal dissociation reaction in the HFCVD environment. The atomic hydrogen from the dissociation of molecular hydrogen is actively involved in the etching process of non-diamond carbon and thus could also be the cause of the observed etch pits on the sapphire surface. Park and Lee [11] attributed the formation of etch pits on mirror-polished silicon substrates to the process of etching by atomic hydrogen. It should be noted that while the CCM suggests that hydrogen etches both diamond and graphite at the substrate temperature due to increasing carbon solubility, the etching effect on the substrate surface is unclear [5].

In summary we have investigated the growth of diamond on sapphire within the framework of the CCM. Scarce diamond formation is observed on the faceted sapphire surface. It is difficult to reconcile this observation with the high possibility of diamond formation according to the CCM. The lack of an intermediate layer and non-diamond carbon seems consistent with the CCM. However an alternative explanation for the absence of an intermediate layer is that sapphire is a thermodynamically stable substrate and it is unlikely to react with the source gases to form an intermediate carbide layer. As the etching effect on sapphire is unclear in the CCM, the observation of etch pits on the sapphire substrate surface can be better explained using the atomic hydrogen hypothesis. Further work needs to be done on other types of substrates or with different deposition conditions to ascertain the validity of the CCM.

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Figure Captions

Fig. 1. AFM image of the faceted α - (0001) sapphire surface induced by annealing at 1400°C in air.

Fig.2. Diamond particles on the reconstructed sapphire substrate after 1 h of deposition.

Fig. 3. Raman spectra of diamond particles deposited after 1, 2 and 4 h.

Fig. 4. Auger wide survey spectra of (a) uncoated as-received sapphire substrate surface and (b) surface region in between deposited diamond particles on the faceted surface.

Fig. 5. The Auger C KLL spectra obtained from (a) the sapphire surface region in between the diamond particles; (b) amorphous carbon; (c) graphite; and (d) diamond.

Fig. 6. AFM image showing etch pits on the sapphire surface after 1 h in the HFCVD environment.

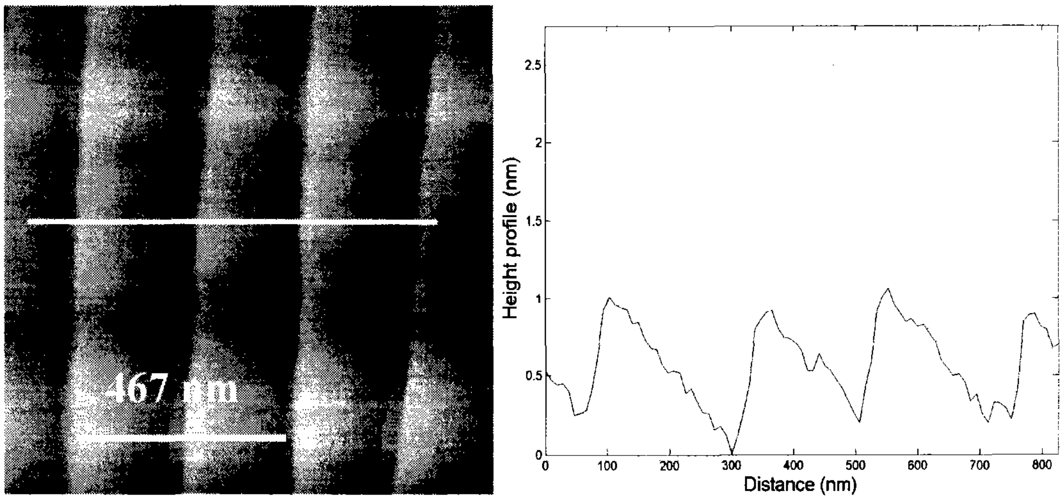

467 nm
Height profile (nm)
2.5
2
1.5
1
0.5
0
Distance (nm)
0
100
200
300
400
500
600
700
800

Fig. 1

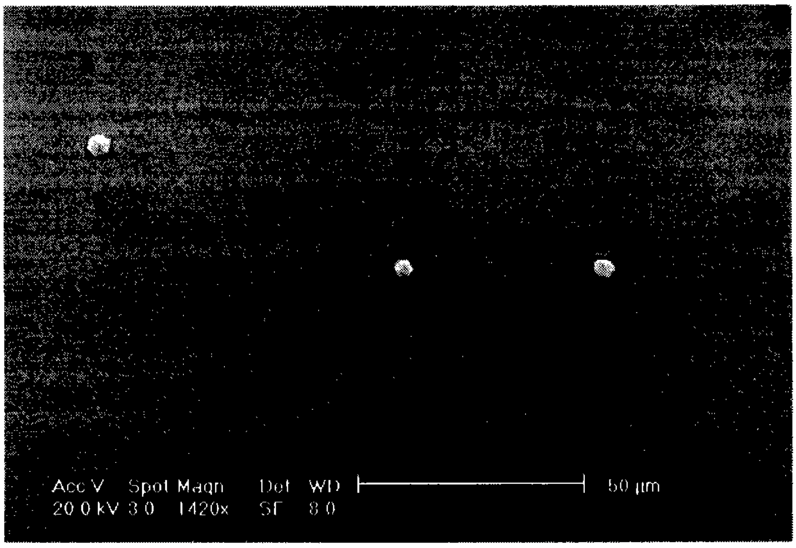


Fig. 2

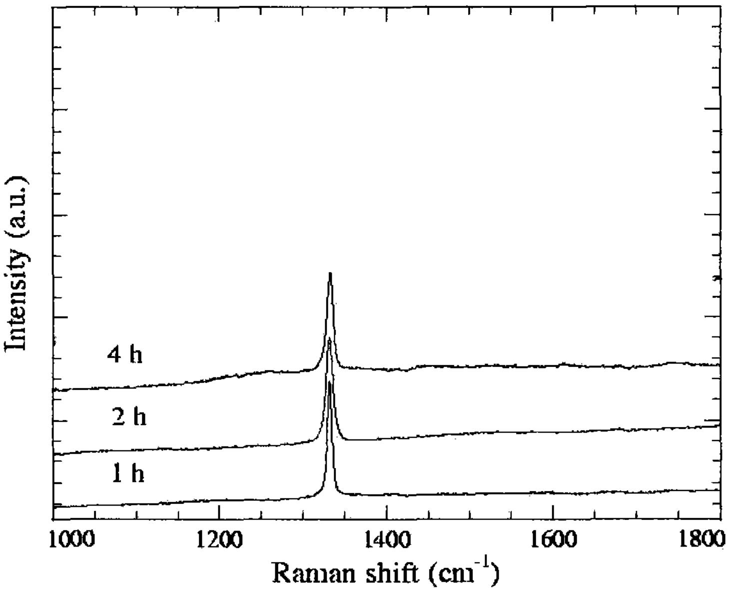

Intensity (a.u.)
4 h
2 h
1 h
1000
1200
1400
1600
1800
Raman shift (cm^{-1})

Fig. 3

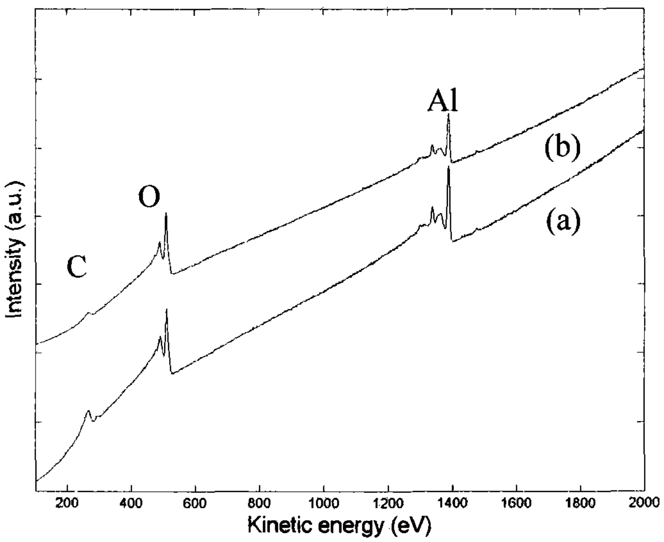
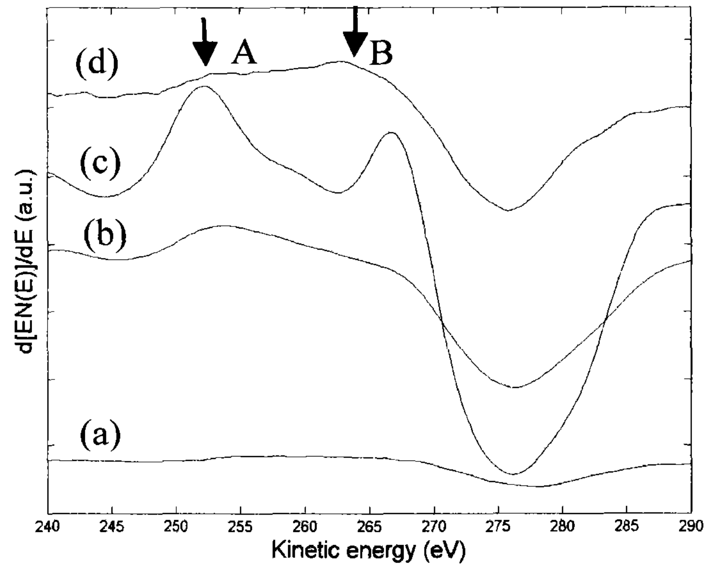

Al
O
C
(b)
(a)
Intensity (a.u.)
200
400
600
800
1000
1200
1400
1600
1800
2000
Kinetic energy (eV)

Fig. 4


(d)
A
B
(c)
(b)
(a)
d[EN(E)]/dE (a.u.)
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245
250
255
260
265
270
275
280
285
290
Kinetic energy (eV)

Fig. 5

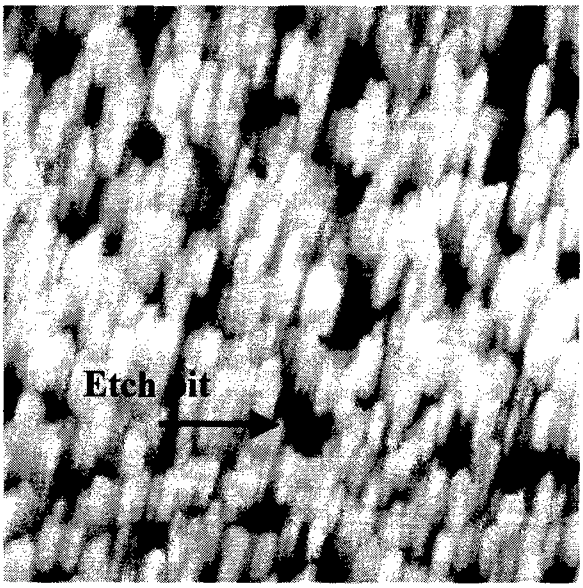

Fig. 6