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Abstract
For biomedical and electronic applications, it is highly desirable to deposit
smooth diamond films with crystal sizes in the nanoscale range. We present
experimental results of chemical vapour deposition diamond growth from CH_4
with incremental substitution of H_2 with He or Ar gases; the concentrations of
the inert gases were varied between 0 and 98 vol%. Results show that initially
the addition of either argon or helium increases the growth rate and significantly
alters the film structure and crystallinity up to 60 vol%. With additions of argon
or helium greater than 60 vol% in the gas phase the growth decreases and there
is degradation of the crystal structure. In general, nanocrystalline diamond has
been deposited at dilutions in excess of 90 vol% helium or argon.

1. Introduction

Since the early 1980s the unique combination of physical and chemical properties and
applications of diamond films have attracted considerable scientific and technological
interest [1, 2]. By far the most successful method for depositing diamond films is through the
use of chemical vapour deposition (CVD). This technique generally employs carbon containing
precursor gas mixtures such as CH_4, diluted in hydrogen [3]. Under standard CVD conditions
polycrystalline diamond films are formed; these films, however, are too rough and have too
variable a morphology for many industrial, biomedical and consumer applications [4, 5].

For biomedical and electronic applications, it is highly desirable to deposit smoother films
with decreased crystal size. In general, diamond coatings with a crystallite size of 10–100 nm
range are known as nanocrystalline diamond (NCD). There are several ways in which NCD
may be deposited by CVD including growth from fullerene precursors with argon dilution. A
number of workers [6–12] have proposed various mechanisms for the growth process using inert
gas dilution to conventional HF or MWCVD systems or NCD growth through the deployment

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Table 1. The experimental parameters for HFCVD deposition.

Set-up		Deposition parameters
Substrate	Silicon	5 mm^2
Filament	Tantalum	0.50 mm (d)
Temperature	(Filament)	1650–1800 °C
Temperature	(Substrate)	650–850 °C
Pre-treatment	Diamond powder	1 μm
Reactive gases	Methane	1 vol%
	Hydrogen	1–100 vol%
	Helium	0–90 vol%
	Argon	0–98 vol%

of CO_2 [13, 14] or in CO rich environments [15]. However, the use of inert gas dilution with carbon containing species is the least complex approach to growing nanocrystalline and more recently ultrananocrystalline diamond (UNCD) [7–12].

Gruen *et al* [7–12] have investigated the use of inert gas dilution using MWCVD systems; however, very little work has been carried out on inert gas dilution of NCD using HFCVD [16]. Lin *et al* [17] have observed growth of NCD from Ar/CH$_4$/H$_2$ systems and well faceted diamond deposition was achieved using an Ar concentration of >90 vol%. With an Ar mixture >95.5 vol% there is a noticeable transition in morphology and structure from microcrystalline to nanocrystalline, through to UNCD, in atmospheres greater than 98 vol% Ar.

In this study we have investigated the growth of polycrystalline and nanocrystalline diamond films using HFCVD systems, with inert Ar and He carrier gas dilutions for biomedical applications. One of our major aims of this work is to produce ultrasmooth, adherent uniform NCD films for use in biomedical and microelectromechanical (MEM) applications and aerospace devices. Medically, diamond is a material with potential for use in orthopaedic implantation as it exhibits both haemocompatibility and histocompatibility characteristics; it is also chemically inert, biostable, demonstrates good hardness and does not degrade. The structure, properties and growth of NCD have been studied using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS); in addition the crystallinity and diamond quality have been investigated using Raman and x-ray diffraction (XRD) observations.

2. Experimental details

Deposition of the diamond films was performed using a custom built HFCVD system, previously described in detail [18, 19]. Diamond films were grown on mirror polished silicon of size 5 mm^2. All substrates were mechanically abraded using 1 μm diamond powder and ultrasonically treated for 15 min in an acetone bath. Samples were mounted on a molybdenum substrate holder (50 mm^2) in the HFCVD chamber and deposition was carried out for 6 h. The total gas flow rate was maintained at 100 sccm; the buffer gas dilution (argon or helium) varied between 0 and 99 vol%; in hydrogen, the hydrocarbon gas, methane, was maintained at a constant concentration of 1 vol% through precisely calibrated MFCs. The substrate temperature was varied between 650 and 850 °C, measured with a K-type thermocouple, the filament temperature was verified using a hand-held optical pyrometer and the pressure was maintained constant at 26.6×10^2 Pa (N m^{-1}). The important CVD process parameters are summarized in table 1.

The morphology of the as-grown diamond films was ascertained by the use of a Jeol scanning electron microscope (SEM, model JSM 5600LV). The quality of the polycrystalline
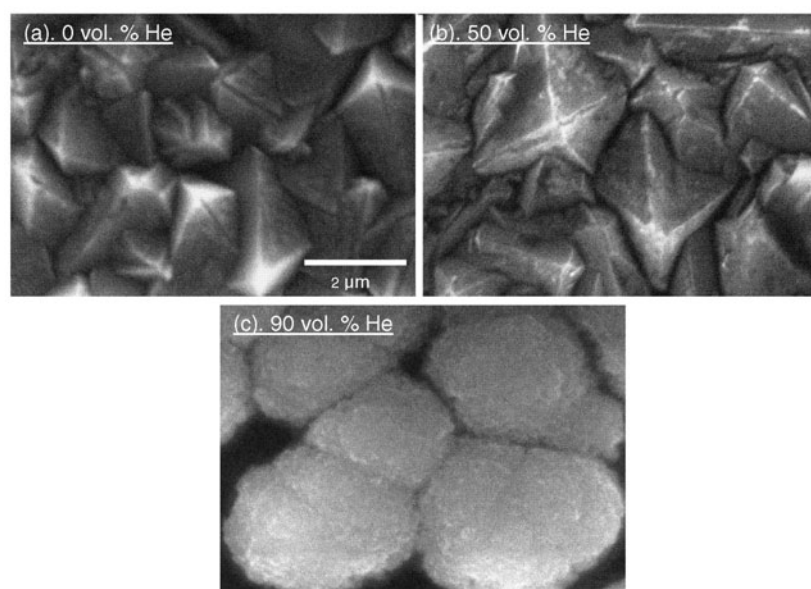
Figure 1. SEM images of diamond films grown on Si for 4 h, in (a) 0 vol% He, (b) 50 vol% He and (c) 90 vol% He; all micrographs are scaled to 2 μm.

diamond films was monitored by using Raman spectroscopy (Kaiser Holoprobe) with a 532 nm Nd:YAG laser as the excitation source. XRD using a Phillips PW170 diffractometer was used for further confirmation of the film quality.

3. Results and discussion

3.1. Effects of helium addition on the structure

The morphological effects of various concentrations of helium to the standard methane/hydrogen growth mixture on the structure of diamond films were investigated. Figure 1(a) shows the SEM image of the as-grown diamond surface deposited for 4 h with 1 vol% CH_4 in H_2 (i.e. without the addition of helium gas). Under these conditions it is observed that the films exhibited large mixed crystal facets and, with crystal sizes averaging $\sim$4 μm, the topography of the film surface is rough because of the large crystals. The crystallites are distinct and well defined.

Figures 1(b) and (c) show diamond film growth with the addition of 50 and 90 vol% He, respectively. For the 50 vol% helium mixture the average crystallite sizes have increased to approximately 7 μm. The crystals are well faceted and there is evidence of secondary nuclei on the surface of the film. There is a large variation in crystal size as compared to films deposited with no helium introduction as the amount of helium gas is increased. Significant changes in the crystal structure are apparent at helium concentrations above 50 vol% (figure 1(c)); the crystals show round and polyfaceted grains, a distinguishing feature of NCD growth. It is apparent that the addition of helium is affecting the crystal structure of the films. With the addition of 90 vol% helium the crystallite size is reduced, with the films exhibiting a greater degree of amorphous character (figure 1(c)). The films are nanocrystalline; similar structural changes have been observed with the addition of nitrogen to the methane/hydrogen mixture [21]. However, the concentration at which the inert gas influences the structure is
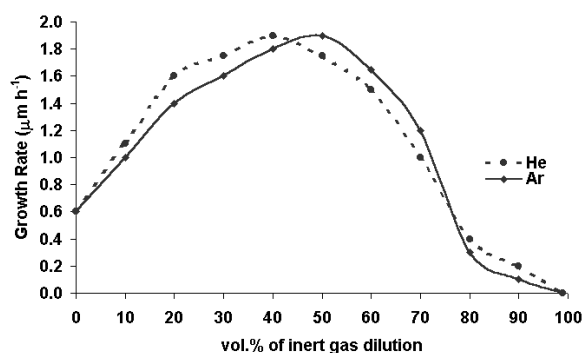
Figure 2. Diamond growth rate as a function of helium and argon concentration.

much lower with nitrogen in comparison to helium [18]. This may be due to the effects on the filament and the effect on the growing diamond lattice [19]. High levels of helium may affect the filament temperature and reduce the carbon concentration at the growth surface. It is probably the reactivity of nitrogen that affects growth, as He is inert. In addition, nitrogen is a reactive species and is known to incorporate into the film altering significantly not only the structure but also the electrical characteristics of the diamond film [18].

The rate was calculated from the thickness of the films and from the deposition time (figure 2). Initially the growth rate increases with increasing He dilution. A maximum growth rate of 1.9 μm h^{-1}, is reached at a concentration of 40 vol%. Above this concentration the deposition rate significantly decreases to <0.3 μm h^{-1}, at dilutions of 85 vol% He.

3.2. The effect of helium on the diamond film quality

Typical Raman spectra of the diamond films deposited with helium concentrations (diluted in H$_2$) up to 90 vol% are shown in figure 3. These spectra show the predominant diamond peak centred around 1332 cm^{-1}, indicative of high quality diamond. There is a slight deviation in the wavenumber from standard CVD diamond (figure 3(a)), which is typical for diamond films deposited by CVD [12]; however, the deviation is very small ($\sim$1.5 cm^{-1}), indicating compressive stress incorporated in the film. It has been previously calculated [19] that for every 1 cm^{-1} shift in the diamond peak the film exhibits compressive stress of −2 GPa. Therefore, a 1.5 cm^{-1} shift represents an increase in compressive stress of 3 GPa. Additionally, the samples exhibit broad peaks centred around $\sim$1500 cm^{-1}, which are associated with graphitic and amorphous phases. The width of the broad band (figures 3(b)–(d)) increases accordingly as the concentration of helium increases. Figure 3(e) shows the D- and G-bands of microcrystalline graphite centred on 1350 and 1580 cm^{-1}, respectively. At dilutions of 90 vol% He (figure 3(e)) the diamond film quality has decreased significantly with NCD films being deposited; this spectrum does not indicate the presence of any diamond phases due to the low Raman detection efficiency for diamond compared to graphite at this excitation wavelength.

3.3. Effects of argon addition on the structure

Argon is an inert gas and ten times heavier than helium with a much lower ionization energy; its effect on the structure and growth has also been investigated. Figure 4(a) shows a diamond film deposited for 4 h, without the presence of argon, in a HFCVD system. The crystals are
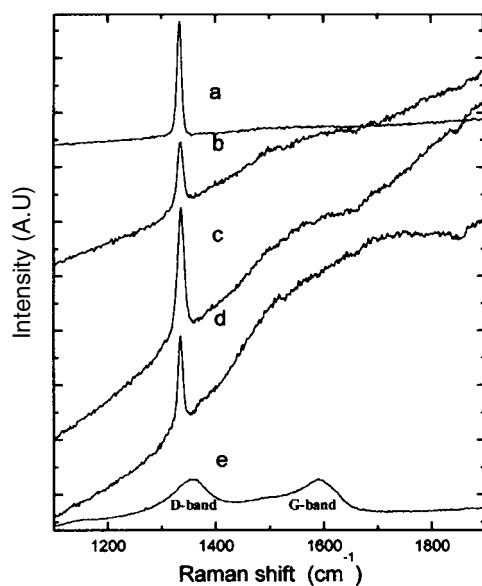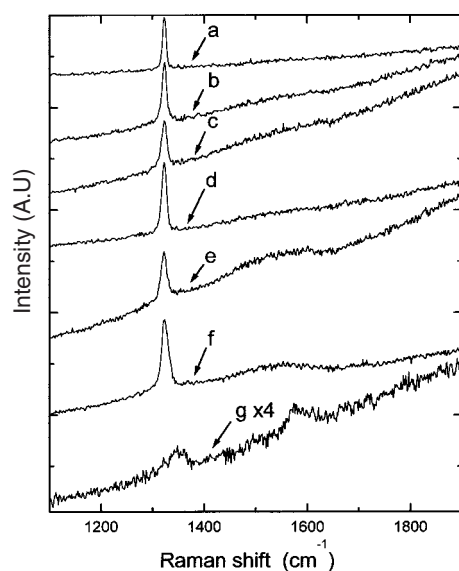
Figure 3. Raman spectra of diamond films deposited at He concentrations (a) 0 vol%, (b) 10 vol%, (c) 20 vol%, (d) 50 vol% and (e) 90 vol%, deposited under standard conditions on Si.
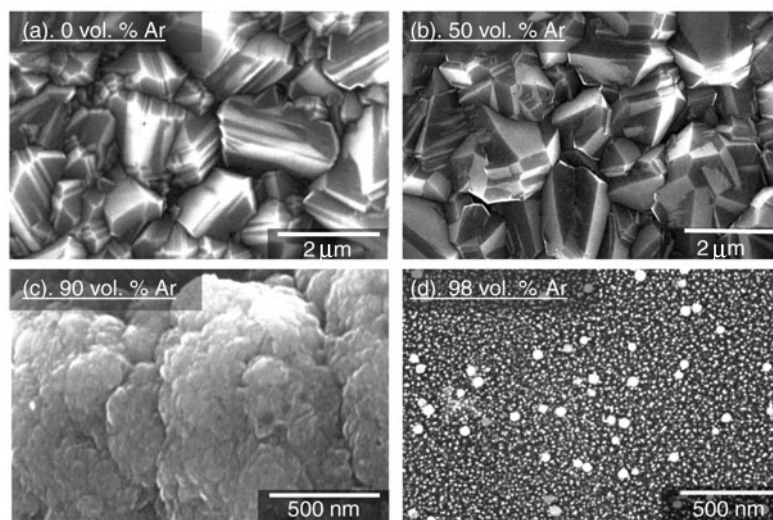
Figure 4. SEM images of diamond films grown on Si for 4 h, in (a) 0 vol% Ar, (b) 50 vol% Ar, (c) 90 vol% Ar and (d) 98 vol%.

well faceted and pyramid shaped, the average crystallite size is ∼2 μm and the morphology is rough. Initially, when argon is added there are notable changes in the crystallinity of the films with a significant change in the average crystallite size. Figure 4(b) demonstrates the effect of argon addition for samples deposited with 50 vol% dilution. The crystals are still well faceted indicating good quality diamond. The average grain size has increased from about 2 μm to approximately 5–8 μm (figure 2). This result is in agreement with research done on argon dilution in MWCVD systems except that these systems gave smaller crystallite sizes than the

Figure 5. Raman spectra of diamond films deposited at argon concentrations of (a) 0 vol%, (b) 10 vol%, (c) 20 vol%, (d) 30 vol%, (e) 60 vol%, (f) 70 vol% and (g) 90 vol%.

HFCVD system used in this study [10]. At very high argon concentrations, >90 vol%, there is a transition in crystallinity from microcrystalline through to nanocrystalline, as exemplified in figures 4(c) and (d). The crystals show voids and the absence of intergranular deposits. The effects of argon dilution are therefore similar to those observed for helium.

Raman spectra for samples grown with the addition of argon to the methane/hydrogen mixture are shown in figure 5. The characteristic diamond peak appears at 1332 cm^{-1} for all the samples up to a level of 50 vol% dilution with argon. The film quality for all the samples is comparable. Therefore, good quality films can be grown in this range. However, at very high levels of argon dilution the Raman spectrum for the sample is very similar to that observed for DLC films. The peaks for DLC have been reported at 1345–1355 and 1574–1590 cm^{-1}, i.e. the D- and G-bands mentioned earlier [22, 23]. These results support the observations for the SEM analysis and are indicative of NCD growth.

4. Conclusions

In this paper, it has been demonstrated that good quality nanocrystalline films may be deposited using up to 90 vol% helium or 98 vol% argon in the gas mixtures. The helium in the gas phase profoundly influences the film structure. Higher concentrations of helium in the gas mixture led to variation in the film uniformity and morphology. The trend for argon dilution is similar to that for helium. By varying the helium and argon concentrations it is possible to control the crystallite sizes and thus produce NCD films.

Acknowledgments

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