

Diamond deposition in a hot-filament reactor using different hydrocarbon precursor gases

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A hot-filament reactor was used to deposit polycrystalline diamond films upon single-crystal Si substrates using hydrocarbon/H₂ gas mixtures. We studied the effect upon the deposition process and resulting film properties by varying the hydrocarbon gas from C₁H_x to C₄H_x alkanes. This was done maintaining a constant carbon-to-hydrogen ratio, but using a substantially lower-than-normal filament temperature (1500°C) in order to highlight differences in activation barriers and in the chemistry of the diamond-forming step. It was found that with increasing hydrocarbon chain length the deposition rate decreased, from a value of about 0.4 μm h⁻¹ for methane/H₂ mixtures to less than 0.07 μm h⁻¹ for butane/H₂. This was accompanied by an increase in the relative proportion of amorphous carbon to diamond present in the films. After one hour deposition the diamond grain size remained constant at about 20 nm, irrespective of the precursor gas. The measured Knoop hardness of the films also decreased when using process gases other than methane. We also studied the effect of changing the bond order in C₂H_x precursor gases (ethane, ethene, ethyne) but found that this had no effect on either the deposition rate or the film quality.

1. Introduction

The production of diamond films by chemical vapour deposition (CVD) is now a major field of research throughout the world [1–4]. Despite this intensive effort there is still some controversy over the actual mechanism whereby diamond, rather than graphite, nucleates and then grows on the substrate surface. Indeed, it is still not certain which species within the gaseous reaction mixture are responsible for the diamond-forming step. The most likely candidate is the methyl radical [1,5], although carbon atoms and acetylene [1,5] have also been suggested. Various spectroscopic studies [1,7–11] of the gaseous plasma region directly above the substrate surface show that a large number of different stable and unstable hydrocarbon species are present, produced by dissociation and recombination reactions. However, the role played by these species is still not

clearly understood, and it is for this reason that we have undertaken the present study.

2. Experiment

The deposition chamber was a standard hot-filament CVD (HFCVD) reactor using a Ta filament as the means by which the gas mixture was energised. The filament temperature was measured using a two-colour optical pyrometer, whilst the substrate temperature was monitored with a thermocouple clamped to the face of the substrate. Substrates were single-crystal {100} Si, pre-abraded with 1–3 μm diamond powder, and then cleaned with methanol. Deposition conditions are given in table 1. Note that the filament and substrate temperatures used here are substantially lower than is normal for optimum, high-rate diamond growth. Most groups use fila-

Table 1
The deposition conditions used in the HFCVD reactor

Pressure	30 Torr
Gases	H ₂ /hydrocarbon
Total gas flow rate	200 sccm
H ₂ -to-carbon ratio	100:1
Substrate temperature	750°C
Filament temperature	1500°C
Deposition time	6–13 h

Hydrocarbons: (a) Alkane series – methane, ethane, propane, butane; (b) Bond-order series – ethane, ethene, ethyne.

ment temperatures of at least 2000°C and substrate temperatures higher than 900°C for HFCVD, yielding reported growth rates of a few $\mu\text{m h}^{-1}$ or better [12]. We found that using these higher temperature conditions in our system resulted in films contaminated with Ta from the filament, and also gave very little variation in film properties with deposition gas. Since the aim of this work is to study the role of the process gas from a chemical point of view, it was necessary to reduce the reaction rates to values that allowed easier study of the process; hence the “gentler” process conditions and slower deposition rates.

In our studies we replaced methane, the most widely used carbon-containing precursor gas, with

different hydrocarbons, while maintaining a constant total carbon-to-hydrogen ratio in the gas mixture. We studied the effects of two sets of hydrocarbon gases: (a) *alkanes*, increasing the number of carbon atoms per molecule from 1 to 4 by using the series methane, ethane, propane and butane, and (b) *bond order*, increasing the degree of unsaturation of the C–C bond in the C₂H_x species by using ethane, ethene (ethylene) and ethyne (acetylene).

The deposited films were analysed by energy-dispersive X-ray analysis (EDX), electron microscopy, laser Raman spectroscopy (LRS) and electron energy-loss spectroscopy (EELS). Microhardness measurements were made on a Matsuzawa machine with a Knoop diamond micro-indenter, at loads ranging from 10 to 500 g [13]. Film thickness and hence deposition rates were obtained by scanning electron microscope (SEM) analysis of film cross-sections.

3. Results

Before examining the results for films grown using different hydrocarbon gases, we first show

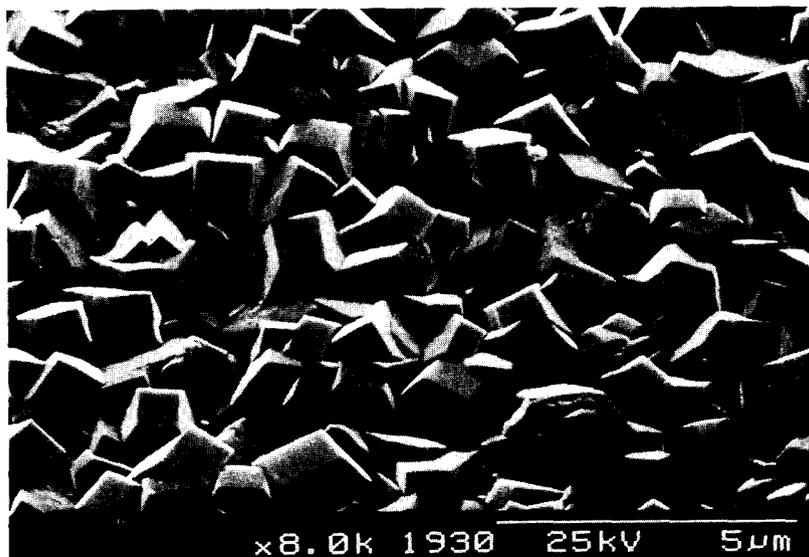


Fig. 1. Scanning electron micrograph of a 6.7 μm film produced using methane/H₂ mixture. The film is continuous and polycrystalline.

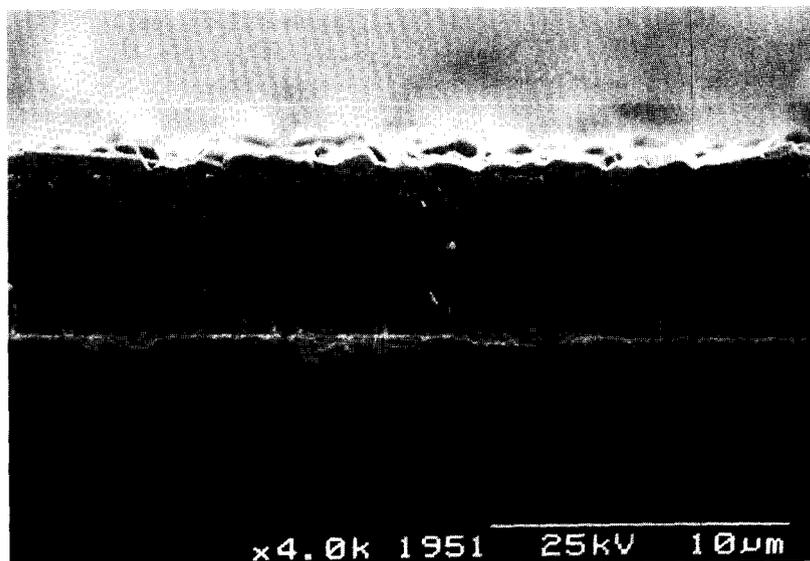


Fig. 2. SEM cross-section of the film in fig. 1 showing columnar growth structure.

the results using methane. Fig. 1 is an SEM photograph of a film grown using a methane/ H_2 mixture, and fig. 2 shows a cross-section of this film. The film is polycrystalline and is about $6.7 \mu\text{m}$ thick. LRS of this film gives the 1332 cm^{-1} peak characteristic of diamond, with no corresponding graphite peak at about 1550 cm^{-1} (see fig. 3). Transmission electron microscope (TEM) studies using EDX and EELS showed no measurable contamination from either filament or non-diamond material. The film was also shown to be

diamond by both electron diffraction and EELS. Film hardness was comparable to that of natural diamond (80 GPa) since no indentations could be seen until an indenter load of 1 kg was used, at which loads the diamond tip of the indenter rapidly eroded. The highest hardness recorded was 50 GPa for a $1.3 \mu\text{m}$ film at 100 g load.

These results show that the films produced in our experimental HFCVD reactor using methane/ H_2 are good quality pure diamond, with no graphitic or amorphous carbon (a-C) phases pres-

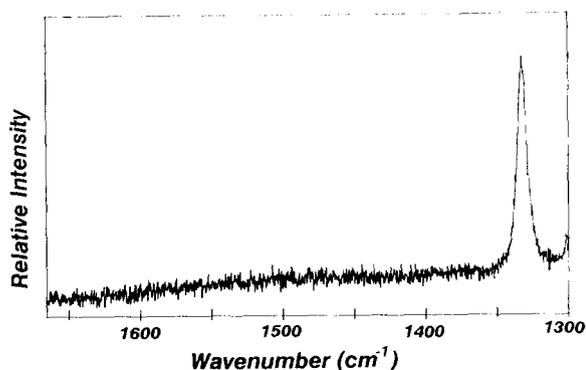


Fig. 3. Laser Raman spectrum from the film shown in fig. 1, showing the 1332 cm^{-1} peak characteristic of diamond and no amorphous carbon peak at 1550 cm^{-1} .

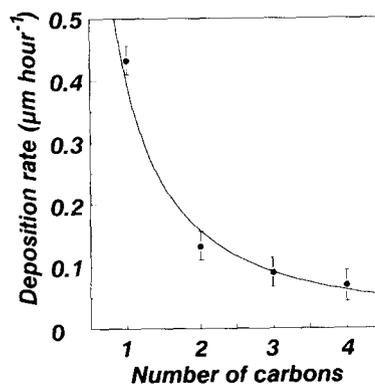


Fig. 4. Film deposition rate versus number of carbon atoms in the hydrocarbon/ H_2 precursor gas mixture.

ent. We now turn our attention to the way in which these properties alter when methane is replaced by other hydrocarbons in the process gas mixture.

3.1. Alkane series

Fig. 4 shows that with *increasing* number of carbon atoms in the hydrocarbon component of the process gas (i.e. as we go from methane to butane), the deposition rate *decreases* rapidly. EELS analysis of films deposited using hydrocarbons other than methane shows that a peak characteristic of amorphous carbon appears, the relative importance of which increases with increasing hydrocarbon molecular weight (see fig. 5). For films deposited using butane/ H_2 , only isolated diamond crystals were observed in a background "sea" of a-C (see figs. 6a and 6b). Further evidence for this decline in film quality is given in fig. 7, which shows the LRS spectrum for a film grown using propane which exhibits a much reduced diamond peak with a strongly developed graphitic and a-C peak. This change in film com-

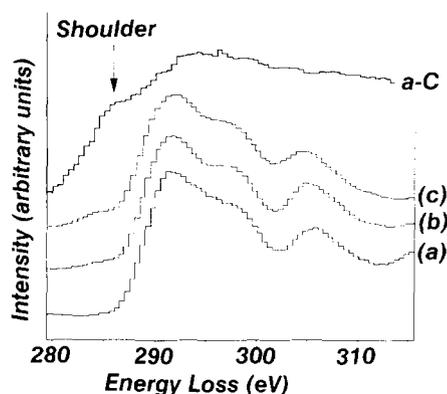


Fig. 5. EELS spectra from films deposited using different hydrocarbon/ H_2 gas mixtures: (a) methane, (b) ethane, and (c) butane. The spectra have been deliberately offset along the vertical axis for clarity. The sharp carbon K-edge starting at about 287 eV shows that the films are diamond. The shoulder at about 285 eV is characteristic of amorphous carbon, as can be seen from the topmost trace which is from a standard a-C sample. With increasing molecular weight of the hydrocarbon process gas this shoulder increases in height relative to the diamond K-edge, showing that the proportion of a-C to diamond present in the films is increasing.

position with increasing alkane molecular weight is also reflected in the measured Knoop hardness values, which decrease rapidly from a value of about 18.7 GPa for methane/ H_2 to 11.8 GPa for butane/ H_2 (both results for a 50 g load on a 0.5 μm film). However, irrespective of precursor gas, TEM analysis of individual diamond grains within the films after 1 h growth revealed the same grain size of about 20 nm.

These results, taken together, suggest that growth of the diamond phase formed with all the process gases may have a common mechanism or chemical precursor but that, at the prevailing temperature, the bulk deposition is sensitively dependent upon the hydrocarbon precursor and its fragmentation probability. This is in marked contrast to the results obtained at much higher filament temperatures by ourselves and other workers [4] where, because of the extensive fragmentation, growth rates and film quality are found to be relatively independent of the precursor hydrocarbon gas.

3.2. Bond-order series

Fig. 8 shows the variation of film deposition rate with increasing unsaturation of the C-C bond, as the hydrocarbon gas is varied from ethane to ethyne. It can be seen that there is very little dependence of deposition rate upon bond order. EELS, SEM and LRS analysis of all three films also shows virtually indistinguishable results, namely that all the C_2H_x hydrocarbons produce continuous diamond films containing a small amount of a-C. Hardness values were all similar, as were the diamond grain sizes measured by TEM, which were again about 20 nm.

4. Discussion

It is clear that under the experimental conditions used in our reactor (low filament temperature), the crucial factor determining diamond deposition is the chain length of the hydrocarbon precursor gas, and its dissociation probability, not the specific details of the bonding within the molecule. For the alkane series the results can be

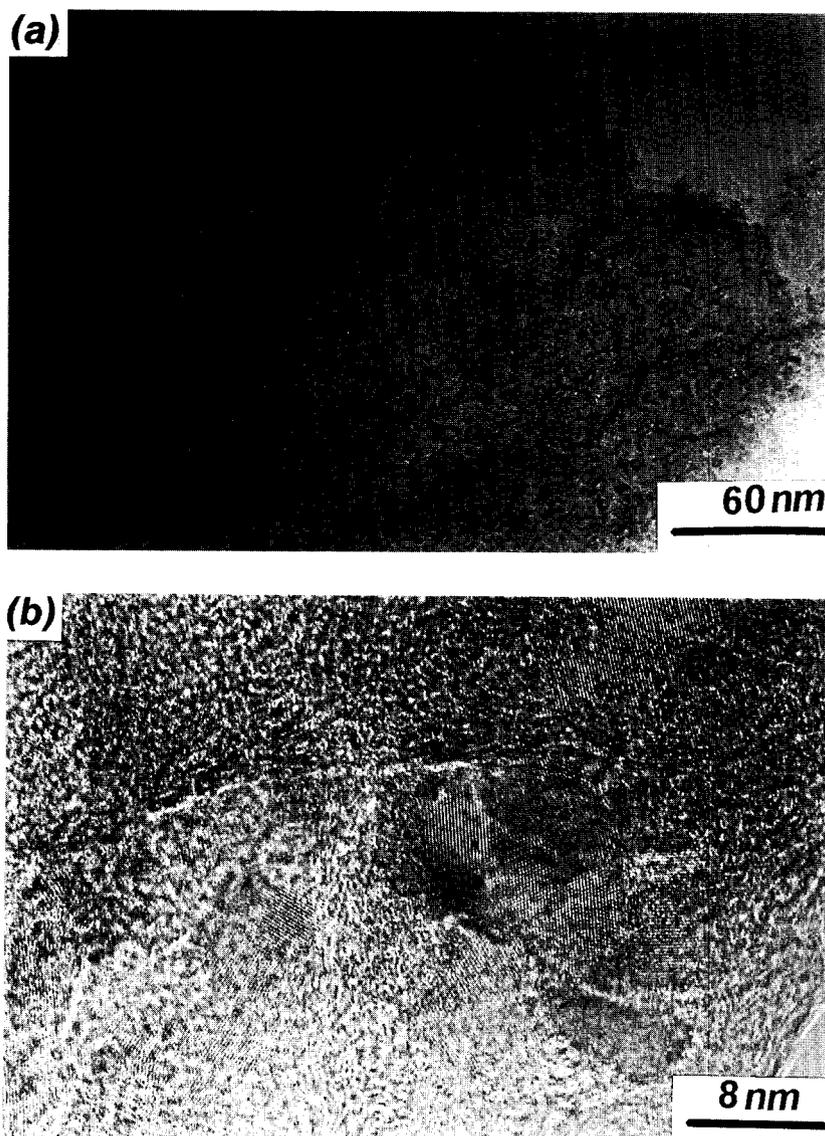


Fig. 6. TEM images of a film grown for 1 h in butane/ H_2 . (a) This shows the amorphous carbon background, against which the isolated diamond grains show up as small, darker regions. (b) Close-up of an individual diamond grain. The crystal planes can be clearly seen, as well as twinning and the a-C background.

explained if we assume that the hydrocarbon is not completely dissociated by the action of the filament or reaction with H atoms. This is feasible in our system due to the unusually low filament temperature. It can be envisaged that if a large hydrocarbon is only partially dissociated,

fragments composed of C_2H_x or C_3H_x species may attach themselves to the growing diamond surface. Such long-chained species bonded to the diamond surface will block neighbouring sites from subsequent attack, so reducing the overall growth rate. Furthermore, unlike the smaller

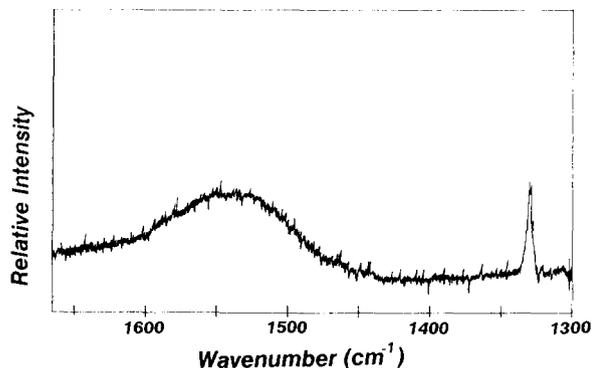


Fig. 7. Laser Raman spectrum for a film grown using propane/ H_2 . The diamond peak is reduced and there is now a significant amorphous carbon feature centred around 1550 cm^{-1} .

chemisorbed methyl groups, these larger hydrocarbon fragments will not necessarily propagate the diamond structure, since there will also be a tendency for them to cross-link on the surface forming amorphous phases. The formation of a-C phases is normally suppressed by the presence of reactive H atoms, which either etch away these phases [3,14], or convert them to diamond by providing a set of local conditions in which diamond is thermodynamically more stable than graphitic phases [15,16]. However, for larger hydrocarbon fragments the rate of formation of a-C on the surface may be faster than the rate of

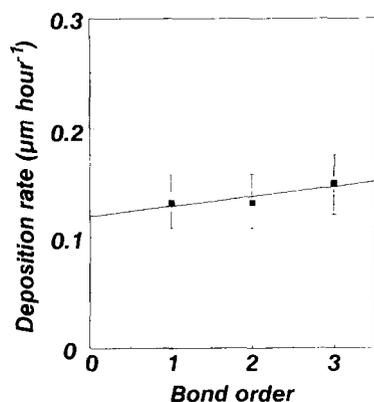


Fig. 8. Film deposition rate versus C-C bond order: 1 = ethane, 2 = ethene and 3 = ethyne.

removal by H atom reactions. Therefore, as the hydrocarbon chain length increases, we see an increase in the proportion of a-C to diamond in the films, with an accompanying deterioration in film properties. Further support for this model is provided by the observation that when a hotter filament (2000°C) is used, the dependence of deposition rate and film properties upon process gas virtually disappears [4]. This would be consistent with almost total decomposition of the hydrocarbon (either by direct pyrolysis on the filament or by chemical reaction with an increased concentration of energetic H atoms) and the fact that larger hydrocarbon fragments will no longer be present in significant concentrations near the substrate surface.

The similarity of the results for the bond-order series – ethane, ethene and ethyne – suggest that H atoms near the filament rapidly react with the original process gas to produce an equilibrium distribution of saturated and unsaturated C_2H_x species. Since H atoms are in such vast excess, the equilibrium concentration of each C_2H_x species will be approximately independent of precursor gas. This implies that even under our low filament temperature conditions, rapid C-H bond-making and -breaking occurs, even though the alkane series data suggest C-C bond-breaking is far from complete.

Another important point to note is the much reduced deposition rate using ethyne as compared with methane as a process gas. This provides further evidence against ethyne being an important species in the diamond-forming mechanism (at least under our process conditions) and reinforces the suggestion that methyl radicals are the key species determining diamond growth.

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