

Attempts to p-Dope Ultrananocrystalline Diamond Films in a Hot Filament Reactor

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ABSTRACT

Ultrananocrystalline diamond (UNCD) films have been deposited using hot filament chemical vapour deposition using Ar/CH₄/H₂ gas mixtures plus additions of B₂H₆ in an attempt to make p-type semiconducting films. With increasing additions of B₂H₆ from 0 to 40,000 ppm with respect to C, the film growth rate was found to decrease substantially, whilst the individual grain sizes increased from nm to μm. With 40,000 ppm of B₂H₆, crystals of boric oxide were found on the substrate surface, which slowly hydrolysed to boric acid on exposure to air. These results are rationalised using a model for UNCD growth based on competition for surface radical sites between CH₃ and C atoms.

INTRODUCTION

Recently, so-called ultrananocrystalline diamond (UNCD) films have become a topic of great interest, since they offer the possibility of making smooth, hard coatings at relatively low deposition temperatures, which can be patterned to nm resolution [1,2]. These differ from nanocrystalline diamond (NCD) films [3], since they have much smaller grain sizes (~2-5 nm), and have little or no graphitic impurities at the grain boundaries. Most reports of the deposition of these films describe using a microwave (MW) plasma chemical vapour deposition (CVD) reactor and gas mixture of 1%CH₄ in Ar, usually with addition of 1-3% H₂ [1].

Addition of N₂ to the gas feed mixture has a profound impact on the conductivity, field emission, and electrochemical behaviour. It is believed that the nitrogen preferentially accumulates in the grain boundaries, since both the grain size and grain-boundary widths increase with the addition of N₂, but the overall bonding structure in both regions remains mostly unchanged [4]. This is not doping in the conventional sense, and conductivity is related to mid-gap states in the diamond film. Nevertheless these 'nitrogen-doped' UNCD films exhibit overall n-type semiconducting behaviour which shows great promise for electronic devices [5].

Standard microcrystalline diamond (MCD) [6] and nanocrystalline diamond (NCD) [7] films can be readily doped with boron to give p-type conductivity. This gives an activation energy of 0.37 eV, and conductivity can be controlled from intrinsic to near metallic. This is achieved by addition to the gas mixture of boron (usually in the form of gaseous B₂H₆ or B(CH₃)₃) during CVD. However, to date, surprisingly, there are no reports in the literature of p-type UNCD being deposited by a similar method, despite the obvious benefits that this would bring in terms of potential UNCD p-n devices.

We have previously reported the use of Ar/CH₄/H₂ gas mixtures to deposit UNCD in a hot filament (HF) reactor [8,9,10], with the compositional diagram for mixtures of Ar, CH₄ and H₂ being mapped out corresponding to the type of film grown. The gas mixture required for UNCD deposition in a HF reactor is different from the 1%CH₄/Ar/H₂ used in a MW reactor, due to the different heat and species distributions within the two types of system. For the majority of the HF-growth composition diagram, diamond films are deposited only in a very narrow region around $[\text{CH}_4]/([\text{CH}_4]+[\text{H}_2]) \sim 0.5\text{-}6\%$, with UNCD films being deposited only in the region of the MCD/‘no-growth’ boundary. UNCD deposition in HF reactors, therefore, is not ideal, since the process window is very small and even small changes in gas flow rates from any of the 3 process gases can be enough to shift the process out of the UNCD-growth region into the MCD or no-growth regions. The growth rate for UNCD under these conditions is small, around $0.05\text{-}0.1 \mu\text{m h}^{-1}$.

In this paper we shall present results concerning attempts to p-dope UNCD using B₂H₆ additions to the gas mixture in a HF reactor.

EXPERIMENT

Films were deposited using a standard HF CVD reactor operating at a pressure of 100 Torr using high purity Ar, CH₄ and H₂ as source gases. Mass flow controllers were used to control the ratios of the gases. $[\text{Ar}]/([\text{Ar}]+[\text{H}_2])$ was kept constant at 80% (*i.e.* 200 sccm Ar and 50 sccm H₂), and that of $[\text{CH}_4]/([\text{H}_2]+[\text{CH}_4])$ at 1% (0.5 sccm CH₄), which means the deposition is in the UNCD growth region of the Ar/CH₄/H₂ composition diagram [8,9]. For doping experiments, B₂H₆ was metered into the gas mixture at concentrations of 0, 300, 2000 and 40000 ppm with respect to CH₄. Although adding B₂H₆ also adds 6 hydrogens to the gas mixture, the extremely low flow rates of B₂H₆ (even when doping at 40000 ppm this is only 0.02 sccm) compared to that of H₂ (~50 sccm) ensure that the effect of these additional H’s on the overall gas mixture is negligible. The filament was made from 0.25 mm-diameter rhenium metal, wound around a 3 mm-diameter core to produce a 2 cm-long coil that was positioned 5.5 mm from the substrate surface. Rhenium was used for the filament material rather than tantalum since Re does not act as a sink for carbon or boron species, unlike Ta which can absorb significant amounts of boron for many hours into the deposition run [11]. The filament temperature was kept constant at 2400°C and monitored using a 2-colour optical pyrometer. The substrate was single crystal Si (100) which had been manually abraded prior to deposition using 1-3 μm diamond grit, and then ultrasonically cleaned with propan-2-ol. The substrate sat on a separate heater to give additional uniform heating and to maintain it at a temperature of ~850-900°C (also measured using the optical pyrometer). Typical deposition times were 15 h. After deposition the films were analyzed by laser Raman spectroscopy (325 nm excitation), and both scanning and transmission electron microscopy (SEM and TEM). A simple 2-point probe test (5 mm separation) was used to gauge the electrical conductivity of the film, although this will only be an approximate figure due to inaccuracies associated with contact resistance or surface conductivity effects.

RESULTS

The results for film deposition are presented as a function of increasing B_2H_6 concentration in the gas phase, while maintaining a constant ratio of $Ar:H_2:CH_4$.

$B_2H_6:CH_4 = 0$

This was an undoped control sample, and produced UNCD films at a growth rate of $\sim 0.05 \mu m h^{-1}$. In the SEM, the films showed no evidence of facets, even at very high magnification (see Figure 1, inset). TEM analysis revealed the films to be composed of randomly-oriented crystals with grains < 10 nm in size, and with lattice spacings consistent with that of diamond. The Raman spectrum (Figure 1) showed the presence of the feature at 1150-1190 cm^{-1} , which has been attributed [12] to sp^2 carbon in *trans*-polyacetylene-like molecules trapped at the nanograin boundaries. This peak is often considered as being a signature for UNCD, despite its origin being sp^2 carbon. The electrical conductivity was $\sim 1 M\Omega$.

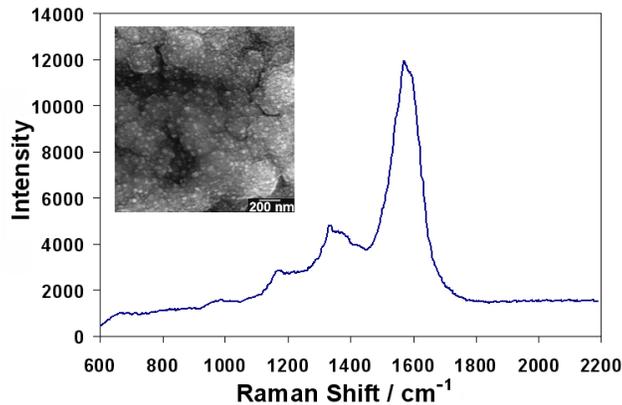


Figure 1. Raman spectrum and SEM image (inset, scale bar 200 nm) from a UNCD film grown with no B_2H_6 addition, showing a very small diamond line at $1332 cm^{-1}$, a large G band and the $1170 cm^{-1}$ feature.

$B_2H_6:CH_4 = 0.0003$ (300 ppm)

For this film, the growth rate dropped to $\sim 0.02 \mu m h^{-1}$, and the grain size increased to 100-500 nm, making the film NCD (Figure 2, inset). The Raman spectrum (Figure 2) shows that the $1332 cm^{-1}$ diamond peak is now dominant, while the $1170 cm^{-1}$ peak has almost vanished. The conductivity was, again, $\sim 1 M\Omega$.

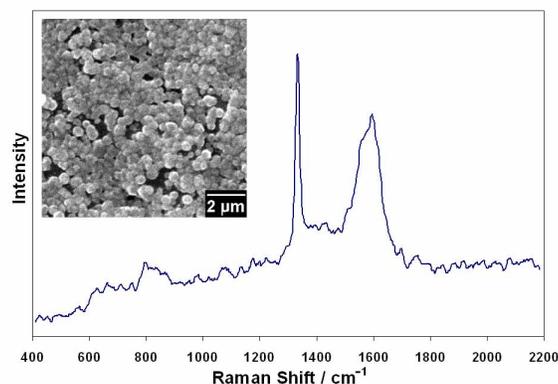


Figure 2. Raman spectrum and SEM image (inset, scale bar 2 μm) from the film grown with 300 ppm B_2H_6 addition, showing an increased diamond line, and decreasing G band and 1170 cm^{-1} feature.

$\text{B}_2\text{H}_6:\text{CH}_4 = 0.002$ (2000 ppm)

For this film, the growth rate dropped further, to $\sim 0.01 \mu\text{m h}^{-1}$, and the morphology became microcrystalline, with faceted crystals averaging $\sim 1 \mu\text{m}$ in size (Figure 3, inset). Conductivity was 50 Ω .

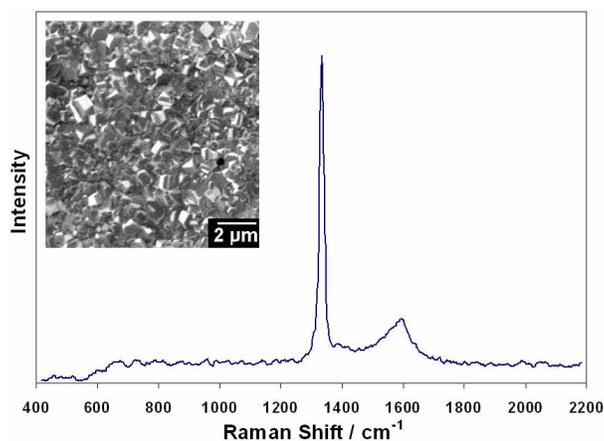


Figure 3. Raman spectrum and SEM image (inset, scale bar 2 μm) of the film grown with 2000 ppm B_2H_6 addition, showing the dominant diamond line, small G band, and absence of 1170 cm^{-1} feature.

$\text{B}_2\text{H}_6:\text{CH}_4 = 0.04$ (40,000 ppm)

These films no longer resembled diamond, and were composed of isolated larger (10-20 μm) crystallites on a clean surface (Figure 4, inset). The diamond peak was still visible in the Raman spectrum (Figure 4), but 2 smaller peaks at 808 and 878 cm^{-1} appeared which are assigned to boric oxide (B_2O_3) and boric acid (H_3BO_3), respectively [13].

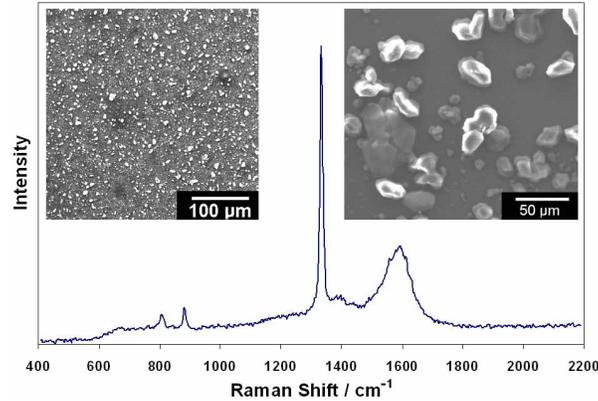


Figure 4. Raman spectrum and SEM image (inset, left) of the film grown with 40,000 ppm B_2H_6 addition taken 4 h after removal from the CVD reactor. There is some diamond deposition, however the surface is covered in isolated amorphous particles (probably B_2O_3). Inset right is the SEM image after the sample was left exposed to laboratory air for 1 week, showing that large crystals of boric acid have grown on the surface.

When the samples were left exposed to laboratory air for extended periods of time, the 878 cm^{-1} peak was seen to increase in intensity relative to the diamond peak on a timescale of a few hours, while the 808 cm^{-1} peak became smaller and eventually disappeared. SEM analysis revealed the presence of 20-30 μm crystals of boric acid on the substrate surface (Figure 4, inset, right).

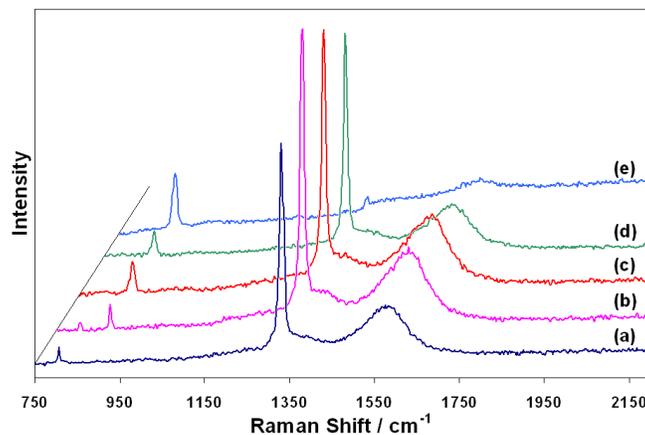


Figure 5. Raman spectra of the sample prepared using $B_2H_6:CH_4 = 0.04$ as a function of air exposure time, for times of (a) 0, (b) 12, (c) 21, (d) 100 and (e) 168 h. The spectra have been offset vertically and horizontally by 50 cm^{-1} for clarity. The peak at 878 cm^{-1} increases with time as the 808 cm^{-1} peak decreases, and then remains constant after a time of about 168 h (1 week). Spectrum (a) corresponds to the SEM image in Figure 4 top-left inset, while (e) corresponds to that of the Figure 4 right inset. In (e) it can be seen that the diamond peak has almost vanished, and the dominant feature is now the 878 cm^{-1} boric acid peak.

DISCUSSION

We found that even small amounts of B_2H_6 added to the gas mixture caused significant changes to the growth rate and morphology of the deposited films. With increasing B_2H_6 content, the growth rate dropped while the films changed from UNCD to NCD to MCD. With higher levels of B_2H_6 addition, the diamond growth rate became vanishingly small, and was accompanied by a Raman peak assigned to boric acid, which increased in intensity upon exposure to air.

These observations may be explained if the B_2H_6 were scavenging selected hydrocarbon radicals. Previously, we developed a model based on computer modelling and experimental measurements for UNCD growth in HF reactors [10]. The model retains CH_3 as the main growth species for diamond, however the overall growth process is also affected by addition to the growing surface of C_1 radical species, in particular C atoms. The C atoms can add to surface radical sites to form reactive adducts, with effectively 3 ‘dangling bonds’. The most likely fate for such reactive surface adduct sites, considering that they are surrounded by a gas mixture containing a high concentration of H atoms, is that they are rapidly hydrogenated to CH_3 . If so, the subsequent reactions will be indistinguishable from attachment and growth by methyl. However, other possible fates for the reactive surface adducts are reaction with other gas-phase hydrocarbon radicals CH_x or restructuring of the surface. We proposed that this would create a disruption in the symmetry of the lattice, and thus provide the surface defect necessary for renucleation. Therefore, depending upon the gas mixture and reaction conditions used, the relative concentrations of each of the important species close to the growing diamond surface (*e.g.* $[H]/[CH_3]$, $[C]/[CH_3]$) determine the probability of a renucleation event occurring and thereby the average crystal sizes, and hence the morphology of the subsequent film, be it MCD, NCD or UNCD.

We now propose that the presence of B_2H_6 perturbs the gas phase hydrocarbon equilibrium in such a way that it selectively scavenges the C_1 radical species (except CH_3) from the vicinity of the growing diamond. If the concentrations of atomic C, (and less importantly CH and CH_2) were to decrease, while that of CH_3 were to remain approximately constant, our model [10] would predict both a decrease in overall growth rate, and a gradual increase in grain size, *i.e.* UNCD→NCD→MCD, as observed in experiment. B_2H_6 is known to dissociate into BH_3 in HF reactors, and BH_3 undergoes ‘H-shifting’ reactions to produce BH_2 , BH and B atoms [11,14]. It is likely that these B-containing radicals can react with the C_1 radicals to form relatively stable species such as CH_2BH , which effectively ‘lock-up’ the C and prevent it adding to the surface. Such reactions may need a third body to dissipate excess energy, and this could be provided by the Ar atom background which are present at reasonably high number densities at 100 Torr.

With larger additions of B_2H_6 , we suggest that the concentration of CH_3 also begins to decrease, leading to a further decrease in growth rate. In this case, it is feasible that the gas phase B:C ratio may become sufficiently high that B atoms can aggregate together on the substrate surface to form islands of solid boron. On exposure to air, these would immediately oxidise to B_2O_3 . Indirect evidence for this is the observation of a white powder (consistent with B_2O_3) on the chamber walls after deposition using these gas mixtures. With long term exposure to water vapour in the air, B_2O_3 is known [13] to slowly hydrolyze to boric acid, as seen in Figure 4.

This explanation remains speculative however, and experimental evidence during UNCD deposition, in the form of direct measurements of the concentrations of B and C radicals by laser

spectroscopic or other techniques, are urgently needed. Since these experiments were performed in a HF reactor, the obvious extension is to repeat them using the standard 1%CH₄/Ar chemistry used for UNCD growth in a MW reactor. However, if the explanation proposed here proves correct, this would imply that B doping of UNCD is not straightforward, and may require significant changes to the gas mixtures and process conditions in order to achieve p-type UNCD.

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