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Investigating the role of hydrogen in ultra-nanocrystalline diamond thin film growth

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Abstract

Hydrogen has long been known to be critical for the growth of high-quality microcrystalline diamond thin films as well as homoepitaxial single-crystal diamond. A hydrogen-poor growth process that results in ultra-nanocrystalline diamond thin films has also been developed, and it has been theorized that diamond growth with this gas chemistry can occur in the absence of hydrogen. This study investigates the role of hydrogen in the growth of ultra-nanocrystalline diamond thin films in two different regimes. First, we add hydrogen to the gas phase during growth, and observe that there seems to be a competitive growth process occurring between microcrystalline diamond and ultra-nanocrystalline diamond, rather than a simple increase in the grain size of ultra-nanocrystalline diamond. Second, we remove hydrogen from the plasma by changing the hydrocarbon precursor from methane to acetylene and observe that there does seem to be some sort of lower limit to the amount of hydrogen that can sustain ultra-nanocrystalline diamond growth. We speculate that this is due to the amount of hydrogen needed to stabilize the surface of the growing diamond nanocrystals.

1. Introduction

Hydrogen has long been considered to be a vital component of any gas mixture used for the chemical vapour deposition of diamond. It is key in a number of vital steps in diamond deposition, from etching away any growing sp^2 -bonded nuclei, stabilizing the surface of the growing diamond nuclei, and abstracting the surface hydrogen to provide a reactive site for methyl radical absorption [1]. However, diamond films with fine grain sizes can be grown in hydrogen-poor conditions. One route to growing ultra-nanocrystalline diamond (UNCD) thin films, which are diamond thin films with extremely fine grain sizes, has been to remove the excess hydrogen in the plasma in favour of argon [2–4]. This gas mixture results in a film with a unique nanostructure, and it has long been known that the transition between microcrystalline diamond and UNCD can be controlled just by varying the amount of hydrogen in the plasma [5]. The nature of this transition has not been studied extensively and is thus poorly understood.

This current study focuses on understanding better the role that hydrogen plays in UNCD growth. This is done by replacing methane with acetylene as the hydrogen precursor; this acts to form gas chemistry rich in the carbon dimer (C_2) which is associated with the production of nanocrystalline diamond and UNCD thin films. One pathway toward forming C_2 in the plasma is the thermal decomposition of methane into acetylene, which results in the remaining hydrogen being dissociated in the plasma [6]. By using acetylene, the overall amount of hydrogen in the plasma should be reduced by eliminating the thermal decomposition of methane. We look at the nanostructure of the films as hydrogen is reduced to determine the effect on UNCD thin films.

2. Experiment

UNCD films were deposited in a microwave plasma enhanced chemical vapour deposition (MPCVD) system (iPlas Cyrranus Mark 1) on Si wafers, where they were ultrasonically seeded in a suspension of methanol and nanometre-sized diamond powder (of 4 nm average diameter). The conditions used to deposit the films were gas flows between 98 and 99 sccm Ar and 0.5 sccm CH_4 , and between 0.5 and 1.5 sccm H_2 ; the total pressure was maintained at 200 mbar, the substrate temperature was 800 °C, as monitored with a thermocouple inside the substrate holder, and the microwave power was 850 W. As hydrogen was added, the flow of Ar was reduced so that, for the '0.5% H_2 ' sample, 0.5 sccm of H was added, and the flow of Ar was reduced to 99 sccm to maintain a constant flow rate of 100 sccm.

Scanning electron microscopy (SEM) was performed in a Hitachi S-4500 field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 5 kV and a beam current of 10 μA . High-resolution transmission electron microscopy was performed using a JEOL 4000EX microscope at 400 kV. The low-resolution images were taken with an objective aperture placed just after the sample to maximize the contrast in the image. The micrographs were recorded using a 1024 \times 1024 Gatan CCD camera, while the diffraction patterns were recorded photographically. The samples used for the TEM studies were prepared using Ar ion milling of the film at 5 kV after polishing away the Si substrate material to obtain sufficient sample thickness for electron transparency.

3. Results

The surface morphology of the acetylene-grown UNCD films can be seen in figure 1. It should be noted here that the growth plasma was not stable when all the hydrogen was removed, so the lowest hydrogen concentration achievable was 0.5%. Figure 2 illustrates a sharp change in the film growth as hydrogen is taken out of the plasma. At H_2 concentrations of 1% and 1.5%, the film looks to be UNCD. However, there is a sharp transition between 1% and 0.5% H_2 , where not only diamond was grown, but also a non-crystalline carbonaceous structure. Growth rate data taken from these films (not shown) indicates that the growth rate was reduced from 0.25 to 0.15 $\mu m h^{-1}$ as hydrogen was removed from the plasma. Further details as to the structure of this non-diamond carbon are shown below.

Figure 2 shows the low-resolution TEM images from the diamond films. Globally, the trend shows what was observed in the SEM images—that the films grown with additional hydrogen are diamond up to a critical point, below which large quantities of sp^2 -bonded carbon are nucleated. Closer examination of the films indicates that, as the overall hydrogen content is lowered in the films, the size and overall concentration of the microcrystalline diamond inclusions decreases. These microcrystalline diamond inclusions have been studied elsewhere [9]. They occur in all UNCD thin films, and are larger heavily faulted diamond

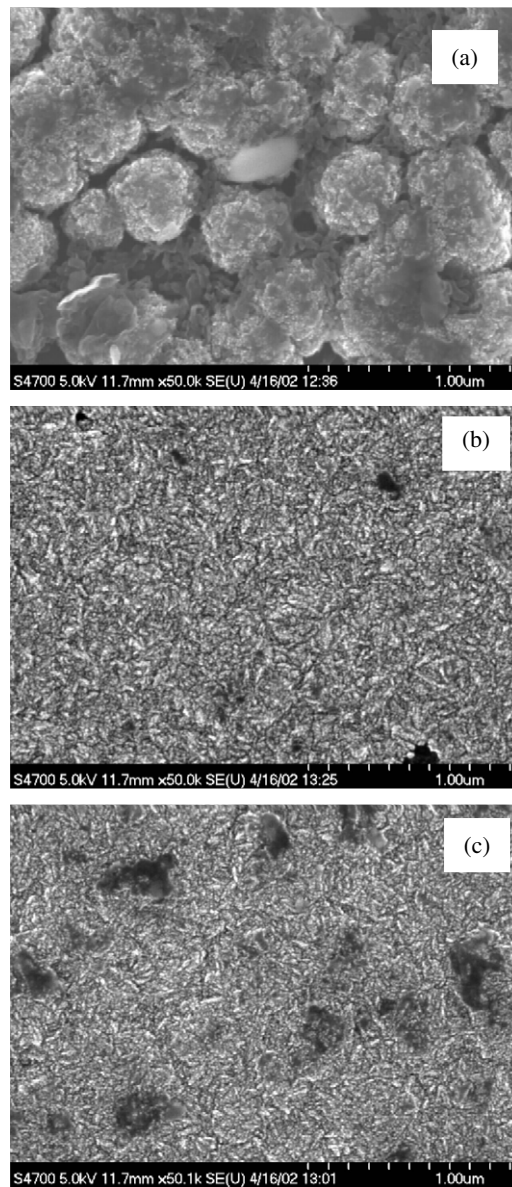


Figure 1. Scanning electron microscopy images of the surface topology of acetylene-grown UNCD with (a) 0.5%, (b) 1%, (c) 1.5% additional H_2 in the plasma.

crystallites. In the observed images, these diamond crystallites show up as the darker areas observed in the nanocrystalline diamond film.

Figure 3 shows high-resolution TEM images of the acetylene-grown UNCD films. What can be seen in 3(a) (the 0.5% H_2 acetylene film) is that, even as the hydrogen is decreased in the samples, the overall grain size does not decrease; in fact, it remains roughly constant with hydrogen concentration, even when a great deal of graphitic carbon is nucleated during growth. The inset diffraction patterns also show the rise of a significant amount of ordered graphitic material in figure 3(a).

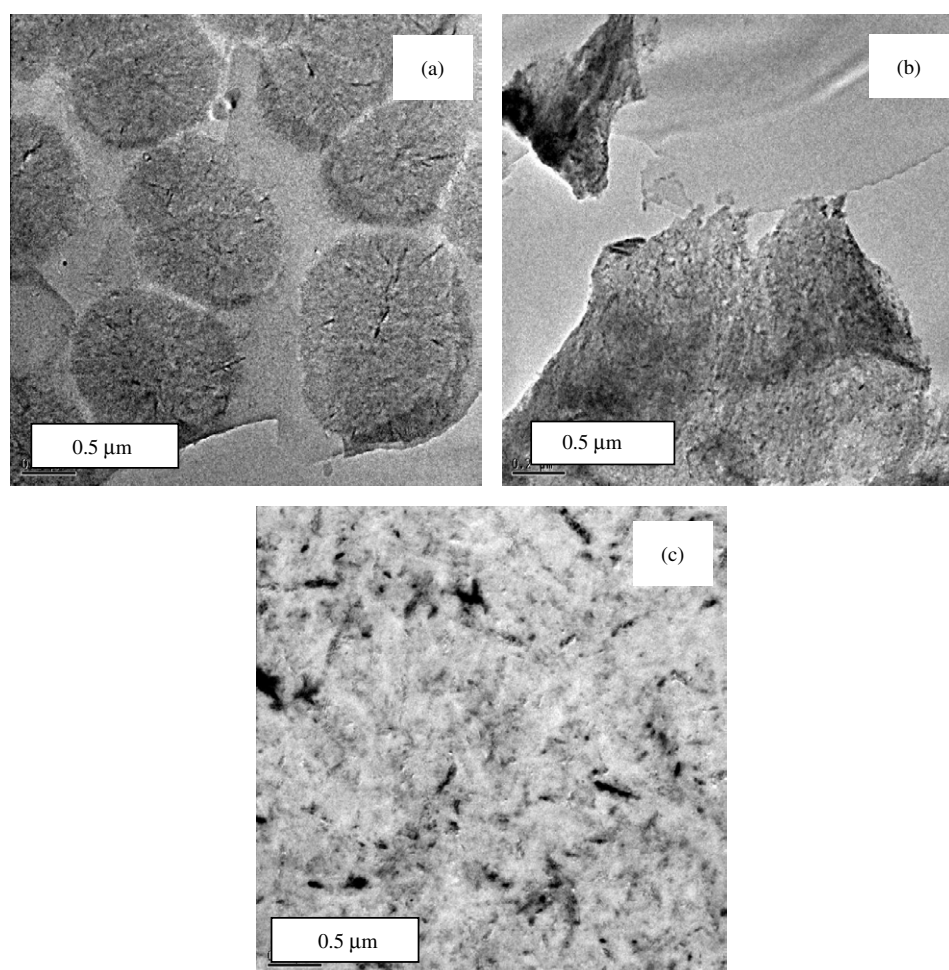


Figure 2. Low-resolution transmission electron microscopy images of the structure and topology of acetylene-grown UNCD with (a) 0.5%, (b) 1%, (c) 1.5% additional H₂ in the plasma.

4. Discussion

In order to determine the effect of removing hydrogen from the plasma during UNCD growth, we replaced methane gas with acetylene. As discussed elsewhere, C₂ thought to originate as CH₄ is thermally decomposed in the plasma to methane, while dissociative recombination of acetylene produces the carbon dimer. Both the thermal decomposition of the methane and the dissociation of the acetylene results in the addition of extra hydrogen in the plasma. If the hypothesis that the presence of hydrogen and methyl radicals is tied to the occurrence of the larger diamond crystallites, then these crystallites should be reduced in size and frequency with the replacement of methane with acetylene in the gas phase during growth. Additionally, if the C₂ dimer is the main driver for UNCD thin film deposition, the overall film growth rate and structure should not change dramatically upon replacing methane with acetylene. What was observed in the previous section implies that this is not the case.

The experimental data shown above illustrate two trends as hydrogen is reduced in the Ar/C₂H₂/H₂ plasma. First, the size of the larger diamond crystallites does decrease, while the

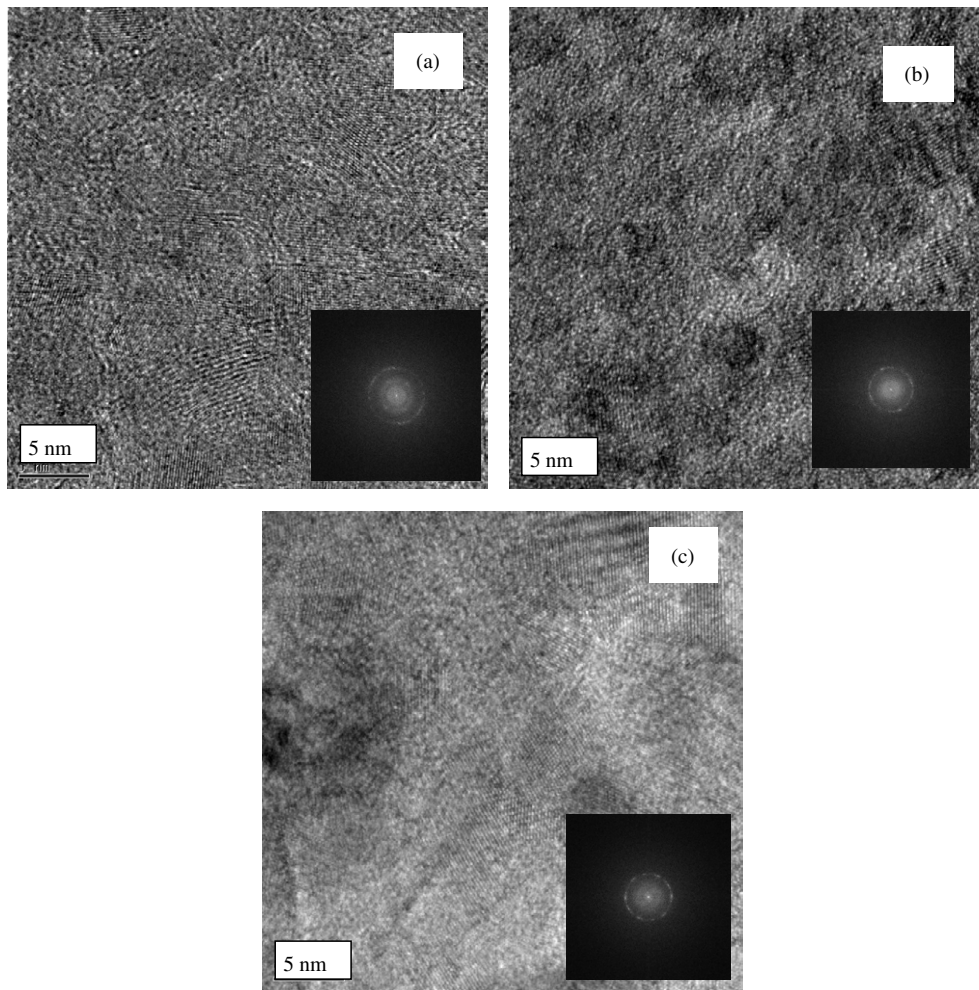


Figure 3. High-resolution images showing the difference between the nanoscale structure between acetylene-grown UNCD with (a) 0.5%, (b) 1%, (c) 1.5% additional H₂ in the plasma. Electron diffraction patterns are inset with the images.

diamond nanocrystals remain constant in size. Second, once the hydrogen in the plasma is decreased below a certain point, the film degenerates quickly into a composite of UNCD and heavily sp^2 -bonded amorphous carbon. The first trend in the film morphology can be explained using the hypothesis stated above to explain the transition between microcrystalline and UNCD thin films, which was detailed in an earlier study [7]. Here, it was found that as hydrogen was added to the base gas chemistry for UNCD deposition (99% Ar, 1% CH₄), the overall size of the nanoscale diamond crystallites did not change, but rather there is a competitive growth mechanism between the nanocrystalline diamond component of the film and some larger, heavily faulted, microcrystalline diamond inclusions found in UNCD thin films. Here, we see a similar trend: as hydrogen is removed from the gas phase of the plasma during deposition, the size and frequency of these microcrystalline diamond inclusions decreases.

The appearance of amorphous carbon is a bit of an anomaly. Conventionally, it has been held that UNCD growth was possible even in the absence of hydrogen, and that the presence of

C₂ alone was sufficient for diamond growth in the absence of hydrogen [8–10]. However, this seems to show just the opposite—that there is a minimum amount of hydrogen necessary for the growth of any diamond thin films, even UNCD. One possible explanation for this could be that hydrogen does play a role in the growth of UNCD thin films by etching away graphitic nuclei formed during growth, which is commonly known for diamond films grown using hydrogen/methane plasmas. Recent work done on diamond nanopowder in the same size range of the UNCD nanodiamond grains shows that hydrogen is necessary to stabilize the surface of diamond nanoparticles and, when removed, the surface reconstructs into a fullerene-like sp² bonded configuration [11]. A similar process may be occurring during the growth of UNCD, where hydrogen stabilizes the growing diamond nanocrystals initially. When a sufficient amount of hydrogen is removed from the system, the surfaces of the growing nanocrystals reconfigure to a sp²-like configuration, and results in the growth of graphitic carbon. However, this result does indeed point to the fact that hydrogen is a crucial component for the deposition of UNCD thin films.

5. Conclusion

In this paper, the role of hydrogen in the growth and morphology of UNCD thin films has been investigated. By replacing methane with acetylene and using an Ar/C₂H₂/H₂ gas chemistry to remove a portion of the hydrogen in the plasma that is inherent in UNCD growth plasmas, we find that there is a minimum level of hydrogen necessary to sustain diamond growth, below which a significant amount of graphitic carbon is nucleated. We suggest in this paper that hydrogen is a necessary component to stabilize the growing diamond nanocrystals, but that the presence of hydrogen also results in the nucleation of some microcrystalline diamond inclusions.

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