Vol 11 No 3, March 2002
1009-1963/2002/11(03)/0298-04

Chinese Physics

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Nucleation of diamond on silicon wafers using C_{60} in the hot filament chemical vapour deposition system*

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(Received 31 August 2001; revised manuscript received 14 November 2001)

Scanning electron microscopy and Raman shifts were used to study the process of diamond nucleation and growth using C_{60} in the hot filament chemical vapour deposition (HFCVD) system. The process of nucleation and growth of diamond films on silicon wafer using C_{60} as intermediate layer in HFCVD system is described. In order to increase the density of diamond nuclei on the wafers, it is not necessary to use negative bias. The UV-light pre-treatment is not beneficial for improving the diamond nucleation. The multi-layers of C_{60} molecules, but not a monolayer, can increase the density of diamond nuclei in the presence of H atoms.

Keywords: diamond thin films, scanning electron microscopy, C_{60}
PACC: 8120V, 6116D, 6148

1. Introduction

Diamond is a remarkable material for innumerable applications because of its unusual combination of physical and chemical properties.[1−3] It has the highest thermal conductivity, highest hardness and lowest compressibility of any known material. It also possesses a high Young's modulus, high electrical resistivity, a wide energy gap, a wide optical transparency band, and can therefore be applied in electronics, opto-electronics, optical and protective coatings. However, there are some difficulties in the direct nucleation of diamond films on non-diamond substrates. It is necessary to pre-treat non-diamond substrates by polishing them with diamond grit,[4] or using a buffer layer such as DLC, β-silicon,[5] iridium[6] etc. These pre-treatments are essential to obtain a high initial nucleation density of diamond crystallites on the substrate in order to form continuous films. Meilunas *et al.*[7] found that fullerene is useful in increasing the density of diamond nucleation. Because fullerene is a new optical and semiconducting material,[8,9] it is important not only in providing the new method for improving diamond nucleation but also in opening a new application field for fullerene.

Meilunas *et al.*[7,9,10] and Sariciftci *et al.*[8] have reported on the results of the growth of continuous diamond films on silicon substrates using fullerene as a buffer layer in microwave chemical vapour deposition (MWCVD) using negative bias. Yang *et al.*[11] found that the density of diamond nuclei was increased by microwave plasma alone, without using negative bias. In this paper, we report on the results of using C_{60} as a buffer layer in hot filament chemical vapour deposition (HFCVD) to nucleate and grow diamond on silicon wafers. Without applying UV-light pre-treatment on Si/C_{60} in our experiment, we obtained good nucleation of diamond on the substrate, even better than that with the UV pre-treatment.

2. Experiment and results

Diamond films were grown in a HFCVD system that has been previously described.[12,13] The reactive gases were mixtures of H_2 and CH_4. Polished silicon (100) was used as the substrate. We obtained C_{60} clusters from C soot by evaporating graphite in

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a He atmosphere. All $7\times10mm^2$ samples were pieced from mirror-polished silicon wafers. They were subsequently ultrasonically cleaned in trichloethylene, acetone and ethanol for 15 min, and then rinsed in deionized water, and finally etched for 1 min in 5% HF solution. The purified C_{60} clusters were sublimated onto silicon (100) substrates as continuous films (about 50 nm thick) at 420°C and the temperature of the substrate was 200°C, with a pressure of 1.33×10^{-3}Pa in the chamber. A HFCVD system was used for the diamond deposition. The substrate temperature was maintained at 800°C, measured by a thermocouple. The tungsten filament operating at 2000°C, measured by an optical pyrometer, was aligned parallel to the silicon substrate. The distance between them was about 4mm. Diamond films were grown with a constant 1.5% methane concentration in hydrogen. The ambient pressure was maintained at 1.5kPa. The deposition was performed for 4–6 h. We carried out three experiments, as described below.

Experiment 1. Put the Si/C_{60} substrates into the chamber of HFCVD system, evacuate the chamber to 10^{-3}Pa, and then pre-treat the substrates by UV-light for 15min. Fill in CH_4/H_2 at once after the pre-treatment and carry out the deposition. The result is shown in Fig.1.

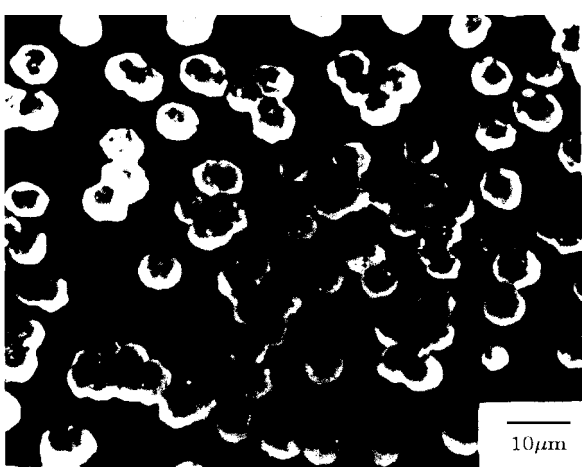


Fig.1. SEM micrograph of the diamond nuclei on the Si/C_{60} substrates prepared with UV-light pre-treatment in experiment 1.

Experiment 2. The conditions and procedure are almost the same as experiment 1 except omitting the pre-treatment by UV-light. The result is shown in Fig.2.

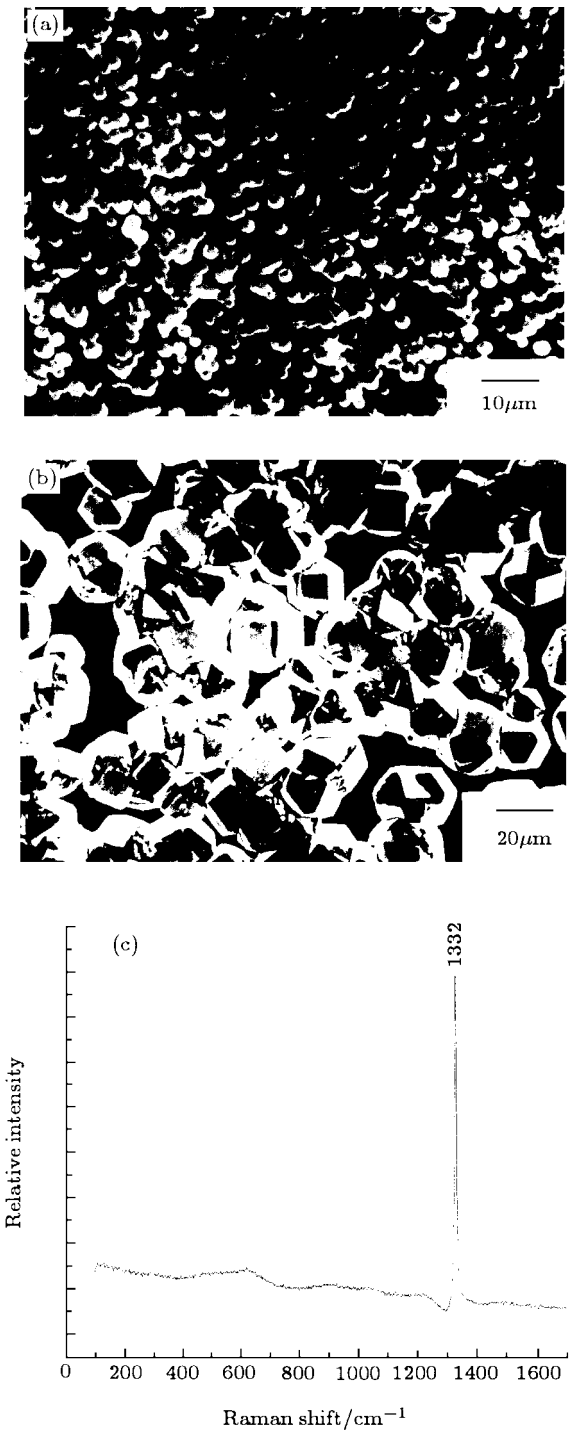


Fig.2. SEM micrographs of (a) the diamond nuclei and (b) diamond particles grown for 4–6 h on the Si/C_{60} substrates without UV-light pre-treatment in experiment 2. (c) The Raman shift of the diamond particles in experiment 2.

Experiment 3. Put the Si/C_{60} substrates into the chamber of the HFCVD system. Fill H_2 into the chamber at first for 30min after evacuating it, and then fill CH_4 into the chamber (the proportion of H_2/CH_4 is the same as in the experiments 1 and 2). No UV-light pre-treatment was used in the process. The result is shown in Fig.3.

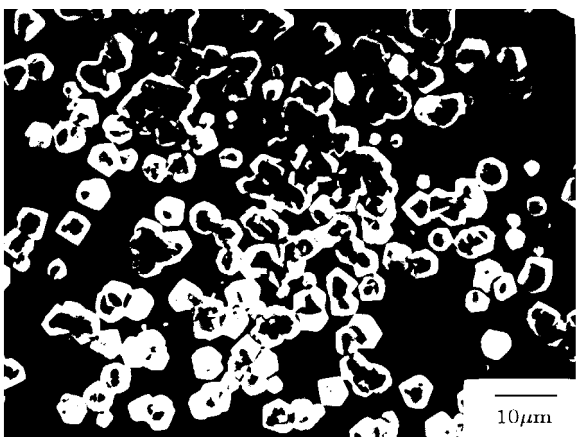


Fig.3. SEM micrograph of the diamond nuclei on the Si/C_{60} substrates in experiment 3.

3. Discussion and conclusion

Many researchers have used negative bias in the process of diamond nucleation on non-diamond substrates.[14] The negative bias has also been used when they nucleated diamond films on silicon wafers using C_{60} clusters in a MW-CVD system.[7–9] But the negative bias itself can enhance the density of diamond nuclei on the silicon substrates ($10^{10}\,cm^{-2}$ at most). In this case, we cannot know definitely what contributes to the enhancement of diamond nucleation on the silicon wafers: negative bias, C_{60}, or both? We have found that there were sparse diamond nuclei formed on the silicon substrates if we did not add C_{60} to the surface, while there were dense nuclei if we added C_{60} without negative bias, as shown in Fig.2. This indicates that, in order to increase the density of diamond nuclei on the wafers, it is not necessary to use negative bias. It also shows the significance of C_{60} in the process of diamond nucleation, as pointed out by Meilunas *et al.*

It is well known that the pre-treatment by UV-light can cause C_{60} molecules to congregate and stabilize on substrates.[5] We also found this in experiment 1, similar to others.[10] Additionally, the pre-treatment may bring about dangling bonds, which can be the base for diamond nucleation. However, from Figs.1 and 2(a), we can see that the density of diamond nuclei with UV-light pre-treatment is not higher than that without it. SEM and the Raman shift of the diamond particles grown for 4–6 h without UV-light pre-treatment prove that the quality of the diamond films is good, as shown in Figs.2(b) and 2(c). We believe that, in the H-rich environment, the bonds of C_{60} molecules could be opened and the electric structure of C_{60} molecules could be more easily translated from sp^2 to sp^3 hybridization, in favour of forming the diamond structure. Also, the bonds of silicon atoms on the surface could also be opened by H atoms. The effect of H atoms was the same as that of UV-light. Therefore the UV-light pre-treatment is not needed for opening the bonds of C_{60} in the H environment. But C_{60} molecules can vaporize at 400–500°C, much lower than the substrate temperature 800°C in our experiments. The diamond nucleation in this case probably occurred before the C_{60} molecules completely vaporized from the silicon substrates so that C_{60} with the dangling bonds opened by H atoms could be connected to the bonds of CH_3. The time of nucleation, 5–10 min, should be longer than that of complete vaporization. So the UV-light pre-treatment is not more beneficial than without it for stabilizing the C_{60} molecules on the substrates. Furthermore, UV-light certainly makes the C_{60} molecules congregate into polymers $(C_{60})_n$ (n up to 20), decreasing the density of the clusters nucleating diamond, which contributes to the difference of the results between experiments 1 and 2.

In Fig.3, we can see that the density of diamond nuclei is much lower than that in Fig.2(a). During the period after H atoms were fed into the chamber and before CH_4 was introduced into it, because the interactive force between the C_{60} molecules was van der Waals force, most of them vaporized from the substrates, leaving a C_{60} monolayer on it. These C_{60} molecules in the monolayer were firmly connected to the substrates by chemical bonds.[15,16] The time lapse of the process was 30min, long enough for most of the C_{60} molecules to vaporize. It can be seen from Fig.3 that a monolayer of C_{60} cannot effectively enhance the density of diamond nuclei. Combining these three experiments, we can reasonably conclude that multilayers, but not a monolayer, of C_{60}, can improve the diamond nucleation in H atom atmosphere without UV-light. Further work about the effect of C_{60} on the heteroepitaxy of diamond is presently in progress.

In summary, high-quality diamond thin films were deposited on Si/C_{60} wafers. In order to increase the

density of diamond nuclei on the wafers, it is not necessary to use negative bias. The UV-light pre-treatment is not beneficial for improving the diamond nucleation. The multi-layers of C_{60} molecules, but not a monolayer, can increase the density of diamond nuclei in the presence of H atoms.

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