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Observations of nanotube and 'celery' structures following diamond CVD on single crystal diamond substrates

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Abstract

Diamond films have been grown onto polished single crystal high-pressure high-temperature diamond substrates using microwave plasma chemical vapour deposition. After deposition, unusual whiskers were observed on the surface of the film originating from growth step edges. Some of these whiskers curled up lengthwise to resemble 'celery'-like structures of length ~20 μm and diameter <1 μm. Electron microscope analyses of these structures revealed the whiskers to be largely amorphous, although some smaller whiskers contained crystalline material embedded within them. A suggestion for their mechanism of formation involving metal-catalysed growth at step edges is presented.

Keywords: Nanotube; Celery; CVD diamond growth

1. Introduction

Following the preparation of macro quantities of C_{60} by Kratschmer et al. [1] a number of different forms of carbon have been synthesised leading to interest in such materials for use in electronics applications. Since Iijima reported the preparation of carbon nanotubes (CNTs) [2], methods such as high pressure arc [3], laser ablation [4] and chemical vapour deposition (CVD) [5–7] have been developed to produce such material. The resulting CNTs have the structure of a rolled up graphite sheet, capped at each end with a carbon dome.

Similarly, carbon nanoparticles (CNPs) have been prepared by microwave plasma CVD, using growth conditions similar to those for CNTs, i.e. ~5% CH_4/H_2, 30 Torr, substrate temperature ~600 °C and growth time of 15 min, with both methods requiring a metal catalyst (usually Ni) for growth. Other techniques, such as hot filament CVD [8] and cathodic arc [9] deposition, have also been used to produce CNPs.

Multichannel carbon tubules have been synthesised by Mukhopadhyay et al. [10]. In their work, camphor was pyrolysed and the soot was vacuum deposited resulting in multichannel–multilayer tubules of the order of 1000 μm long, with diameters of ~10 μm. The structure of these tubules was reported to differ from that of standard CNTs by being neither that of diamond, nor graphite. The same group later produced so-called spongy carbon 'nanobeads' by a method in which Ar was flowed through a camphor/ferrocene mixture at 50 °C, and then into a quartz tube at 1000 °C [11]. The resulting 'beads' were hollow and amorphous in structure, with diameters in the range of 0.2–0.8 μm, and are reported to form chains covered in a graphitic shell with a fibrous outer structure.

We now present observations of whisker formations found on the surface of diamond films that have been grown homoepitaxially by microwave CVD. These structures seem to be of two types, with similarities to both the carbon tubules and nanobeads discussed above, although they have a 'celery-like' structure that has not been hitherto reported.

2. Experimental

Deposition experiments were performed using an ASTeX-style 2.45 GHz microwave plasma CVD reactor. Single crystal (1 0 0) high-pressure high-temperature (HPHT) diamond substrates (Sumitomo) were placed on an alumina plate on a cooled substrate holder. The substrates were thus elevated approximately 1 mm into

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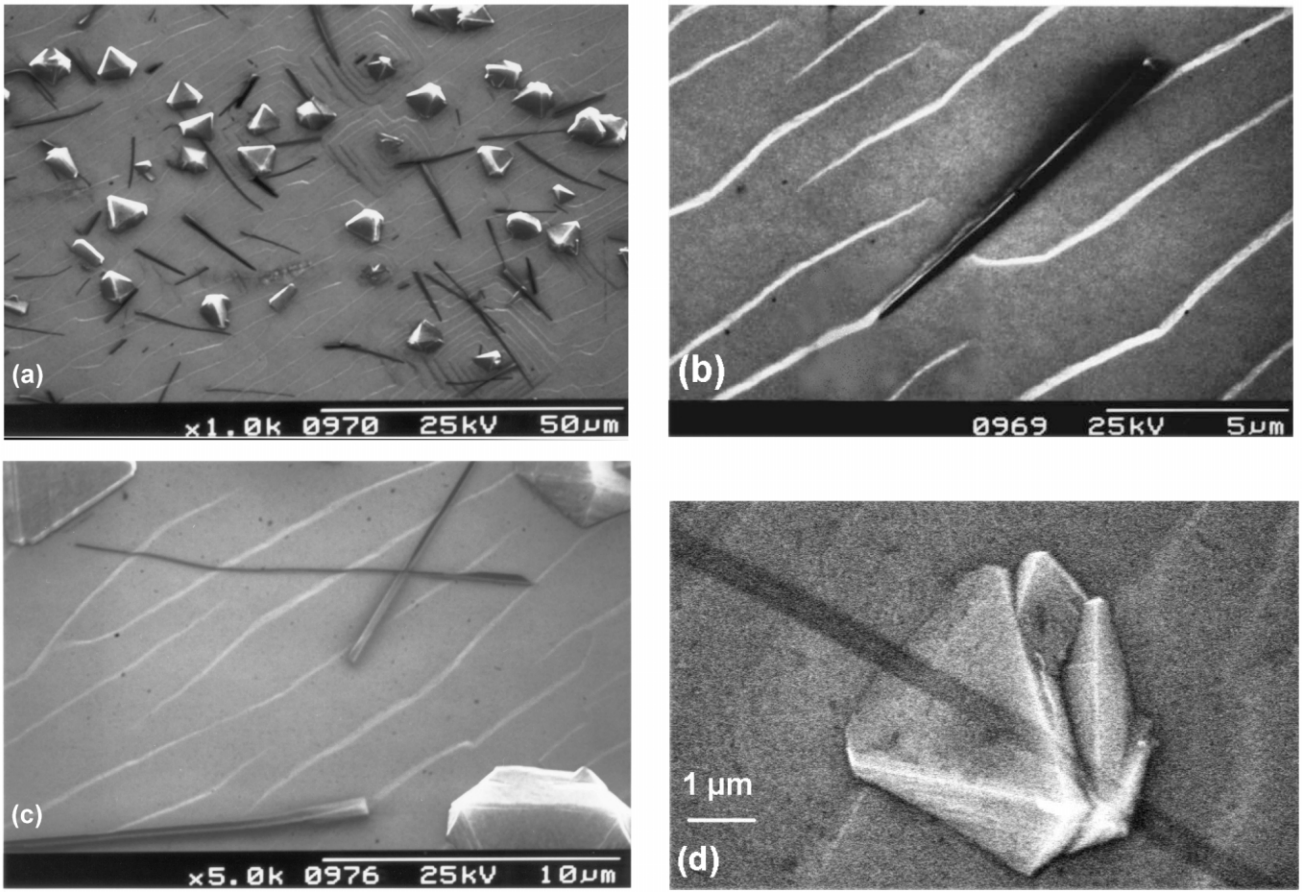

Fig. 1. SEM micrographs of the 'celery-stick' whiskers on the surface of the diamond film after CVD. (a) A low magnification picture showing the large number of whiskers, secondary nucleated diamond crystallites and the step edges. (b) A higher magnification picture showing a single whisker originating from and running along a step edge. (c) Whiskers that have fully peeled away from the surface and curled up lengthwise to form celery-sticks. (d) The 'shadow' of a whisker that had masked an area of the surface during growth.

the plasma, enabling automatic heating of the substrate to ~900 °C (as measured by a two-colour optical pyrometer). The chamber pressure was 40 Torr with an applied microwave power of 1 kW, with deposition lasting 8 h. All of the films were exposed to a hydrogen plasma (10 min) after growth, and were then cooled back to room temperature in flowing H_2. The feedstock gases used were H_2 (99.999% purity), CH_4 (99.999% purity), with a total gas flow of 200 sccm and gas mixing ratio of 1% CH_4/H_2.

Films and whiskers were examined by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). TEM samples were prepared by placing the substrate face down onto a mesh grid with filter paper underneath. Using a pipette, a few drops of ethanol were gently added. The ethanol was drawn into the filter paper causing some of the whiskers to become lodged on the grid. After allowing the components to dry, the substrate was removed, and a second grid attached on top of the first, effectively sandwiching material between them. Selected area diffraction was also utilised to investigate the crystallinity of the whiskers. The whiskers were also analysed by energy dispersive X-ray analysis (EDX).

3. Results and discussion

Initial investigation of the diamond film growth surface by SEM (Fig. 1a) showed that the (1 0 0) surface did not grow at a uniform rate over the whole substrate area. Differential growth rates in different areas of the surface created various levels of terraces separated by vertical growth steps. In addition, some isolated crystals formed via secondary nucleation, showing that the deposition conditions were not perfectly optimised for homoepitaxy. Both these features were not unexpected, however, an unusual feature of the film surface was the presence of growth features with a 'whisker-like' morphology. These whiskers were mostly straight and appeared to taper to a point, with one end located at the growth step edges on the diamond film surface (Fig. 1b). The whiskers had a width of <1 μm with an

average length of ~20 μm, although some were as long as 50 μm. Some of the whiskers were observed to have peeled away from the surface and had begun to curl up lengthwise (as if tending to a tubular structure), resulting in an appearance reminiscent of a 'celery-stick', see Fig. 1c. EDX analysis showed these whiskers to be composed solely of carbon, with no metal content observed above the detection limit of the machine. After the whiskers had been removed from the surface by washing with ethanol (ready for TEM analysis), 'shadows' remained behind indicating where the whiskers had lain. These shadows suggest that the whiskers had grown and peeled away from the surface at some point *during* the deposition process. They had then lain on top of the surface in such a way as to mask areas of the surface from the plasma, thus preventing growth underneath them. An example of this shadowing is shown in Fig. 1d, where the 'ghost' of a whisker can be seen both on the surface and crossing a secondary-nucleated diamond crystallite.

Fig. 2 shows bright field TEM micrographs of some of the smaller 'celery-like' whiskers. The wide variation in the size of such whiskers is illustrated in Fig. 2a, in which the larger structure appears to be tubular or semi-tubular (with darker contrast at edges than centre), whereas those at the top and bottom of the micrograph appear solid and cylindrical or flat. Further examples of such growth are presented in Fig. 2b. Here some of the whiskers are filled with material (labelled as 'A') with a different appearance to that comprising the walls. Selected area diffraction was carried out on this section of the whisker and identified the material to be crystalline, although it also showed that it was not graphite. Similar investigations of areas (labelled as 'B' and 'C') that did not contain embedded material showed the whiskers to have an amorphous structure. Due to their size, the larger celery structures seen previously in the SEM were difficult to analyse using TEM, but we believe that the smaller tube-like structures seen in Fig. 2 may be 'immature' versions of the larger whiskers at an earlier stage in their growth. These smaller tubes are noticeably not as straight as the longer celery sticks, but this may be as a result of the TEM preparation method. It is also worth noting that the structures were stable under a 250 kV focused electron beam.

The small structures visible in Fig. 2a and b have similar diameters (0.2–0.8 μm) to the carbon nanobeads reported previously [11], as discussed above. They also seem to have a bobbled structure reminiscent of a string of beads. The previous work also reports the presence of a metal catalyst (Fe) during the synthesis of the material, which has similarities to the present work in which the HPHT diamond substrate contained metallic impurities.

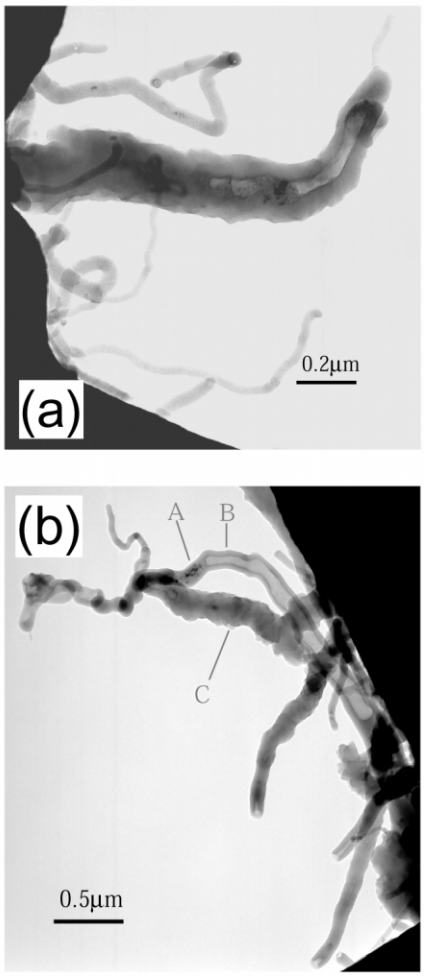

Fig. 2. Bright field TEM micrographs of some of the smaller whiskers. (a) A tubular or semi-tubular whisker (centre), with some solid and cylindrical or flat whiskers (top and bottom). (b) Example of whiskers filled with crystalline material (labelled 'A'). The walls and bulk of the whiskers (labelled as 'B' and 'C') are amorphous.

4. Conclusions

There are many similarities between the small tubular and larger celery structures presented here, and the previously reported Fe-catalysed carbon nanobeads and tubular growth. Along with the fact that the larger celery structures seem to be associated with growth step edges on the diamond surface, this seems to indicate that the growth reported here is due in some way to catalytic activity of metals present in the HPHT single crystal diamond substrate, although, if present, they were at too low a concentration to detect by EDX. Another important contributing factor may be the relative flatness of the growing diamond surface, as this allows extended growth of the features observed.

We can, therefore, construct a growth sequence that is consistent with these observations. Uneven growth of the diamond surface during CVD produces vertical step

edges, which act as nucleation sites for fast lateral diamond growth. However, since the CVD conditions are not optimum for epitaxial growth, defects may form on the step as a result of secondary nucleation, leading to a distortion in the lattice at these points. Alternatively, metallic impurities within the HPHT substrate may diffuse to the surface due to the high deposition temperature, and act as a catalytic centre (remnants of which were possibly observed as the unidentified crystalline material embedded within the smaller tubes). In either case, subsequent growth that originates from the defect sites no longer follows the template of the diamond lattice. Instead, it results initially in many small tube-like amorphous carbonaceous growths, but eventually forms a single long, thin coating that grows along and coats the edge of the step. As the coating grows longer, stresses may develop that eventually cause it to partially peel away from the step edge. These same internal stresses may then cause the whisker to curl up lengthwise into celery-stick structures.

Further work, including more high resolution TEM and electron diffraction analysis, needs to be done to ascertain the exact composition of the celery-sticks and to determine if the unidentified crystalline component inside the whiskers are, indeed, remnants of the metallic impurity that catalysed the growth.

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