

STRUCTURES OF THE VAPOR PHASE GROWN CARBON NANOCRYSTALS

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Based on the hybridization of carbon, it is known to exist in two forms: diamond or graphite. However, a few unexplainable crystalline forms of carbon such as n-diamond, i-carbon, and hexagonal diamond have been reported during synthesis of diamond by high-pressure high-temperature or CVD. The structures of these forms or the path of their existence is largely unknown.

We devised a unique mechanism for capturing large density of carbon nanocrystals by immersing platinum wire substrates into the dense zone of a microwave plasma under diamond growing conditions [1]. We studied the structure of the synthesized 2-5 nm carbon crystals by using single-crystal electron nanodiffraction. In this specialized technique, an electron beam 0.7 nm in diameter is converged on the sample, to obtain near atomic crystallographic information at the exact location of interest on the sample. Our studies indicated that nearly 80% of the crystals did not have the diamond-cubic or graphite structure, instead showed carbon with the face-centered cubic (fcc) structure, and also body-centered cubic (bcc) structure.

For the fcc phase, also known as n-diamond, the cell parameter obtained through diffraction studies was $a = 0.36$ nm. This structure shows the (200) reflection forbidden for diamond. In order to understand the structure of this new phase, we used simulations of electron diffraction from clusters of carbon atoms with stacking faults, or vacancies or mixture of sp^2 and sp^3 bonding. The diffraction from these clusters however did not provide an explanation for the appearance of forbidden reflections such as (002) and hence were clearly not responsible for the n-diamond structure.

Prior studies reporting the n-diamond phase have ruled out the possibility of any contamination detectable within the resolution of an electron microscope. Our study on the relative intensity of diffraction spots for a large number of crystals at different zone axes indicated that the structure may include hydrogen atoms. Hydrogen atoms cannot be detected by an electron microscope; however, they do change the intensity of diffraction spots from a crystal, when they are present within the smallest repeating unit. We used density functional theory to support this possibility.

We also saw evidence for a body-centered cubic phase with $a = 0.31$ nm in the diffraction patterns. This phase has never been reported previously for carbon. Our theoretical analysis also supports the incorporation of

hydrogen in this new carbon phase. The models proposed for the fcc and bcc phase are indicated in Fig. 1.

To date, there has been no direct experimental determination of the structure of nuclei responsible for diamond synthesis using CVD methods. Nevertheless, the currently known hypotheses on the nucleation of diamond involve a significant step of hydrogen mediation to create diamond nuclei [2,3]. In this regard, the current observations on several different crystalline CH_x phases at nanoscale are significant, i.e., these phases might act as intermediate phases prior to diamond nucleation.

References:

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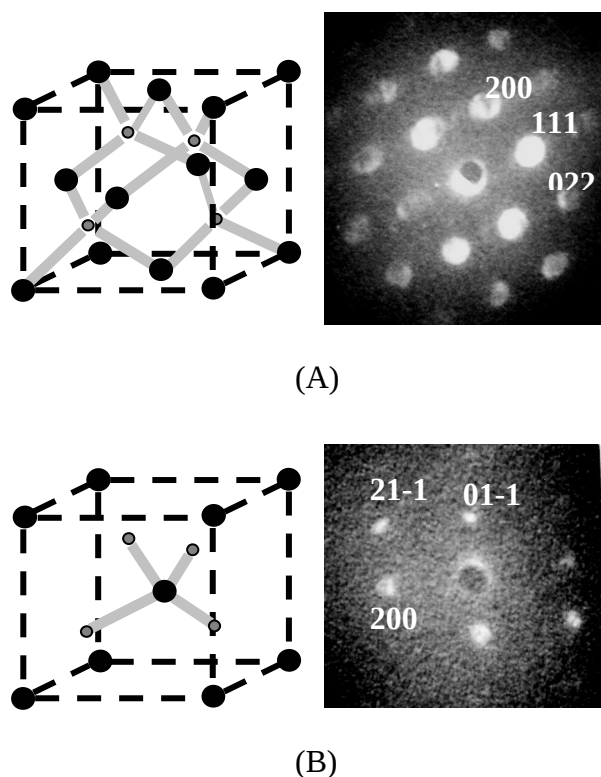


Figure 1: The proposed structures for (A) n-diamond (fcc carbon) and (B) bcc-carbon. In both these structures, the dark atoms indicate carbon, light gray small atoms indicate hydrogen. The images on the right indicate the observed diffraction patterns.