Diamond growth on turbostratic carbon by hot filament chemical vapor deposition

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Diamond films were grown on turbostratic carbon (TC) pregrown on Cu substrates by hot filament chemical vapor deposition. Auger electron spectroscopy, Raman spectroscopy, x-ray diffraction, infrared absorption spectroscopy, and scanning electron microscopy were used to characterize both the TC and the diamond films. It was shown that the TC films could form on Cu at low temperatures ($\approx 650\,^\circ\mathrm{C}$) with the catalysis of Mo and that diamond crystallites rapidly formed on TC in less than 10 min at higher temperature ($\approx 1000\,^\circ\mathrm{C}$). The sp^3 bonds were found to coexist with sp^2 bonds in TC. The sp^3 bonds in TC provide nucleation sites for diamond crystals and improve the nucleation rate at the early stage of deposition of diamond on TC.

INTRODUCTION

Chemical vapor deposition (CVD) is a successful method of synthesizing diamond from the gas phase, in spite of the fact that diamond is metastable relative to graphite under CVD conditions.[1–4] During deposition, molecules which contain carbon and hydrogen are excited. Some excited carbon species condense on the substrate surface and combine to form combinations of sp^2 and sp^3 bonds,[5–7] i.e., to form thermodynamically stable graphitic, amorphous carbon and metastable diamond structures.[8] The excitation can be accomplished by many methods. Among them, the hot filament chemical vapor deposition (HFCVD) is known to be both effective and very simple.[3,9]

Nucleation of diamond at subatmospheric pressure has been a subject of argument since diamond growth at reasonable growth rates from the vapor phase was discovered.[10] It is well known, based on experimental observations, that the diamond nucleation density on a substrate surface can be increased by surface pretreatments prior to diamond deposition, such as scratching with diamond powders[11–13] and nondiamond abrasives.[14,15] Furthermore, the nucleation density can also be increased by nonscratching surface pretreatments such as predeposition of carbonaceous layers of a-C:H[16,17] or even oil residue.[18] Another technique for nucleation enhancement is simply to bias the substrate negatively while immersed in a methane-hydrogen plasma.[19,20]

It is important to understand the nucleation mechanism of diamond from the vapor phase onto foreign substrates which have undergone different pretreatments. Several hypotheses concerning diamond-nucleation enhancement by scratching the substrate surface with diamond and nondiamond abrasives have been made. One of them is that residual diamond particles left on the surface from scratching act as diamond nucleation sites, since diamond preferentially nucleate on the diamond seeds. Iijima *et al.*[11,12] observed that the diamond nucleated on "diamond seeds" left from the scratching process by high-resolution transmission electron microscopy (HRTEM). Park and Lee[13,21] suggested that scratching created new, strong binding energy, nucleation sites.

Carbide carbonaceous nucleation promoters have also been postulated. Williams *et al.*[22] observed a β-SiC layer between the Si substrate and diamond film in cross-section TEM studies. Stoner *et al.*[20] found an interlayer of amorphous carbon between the diamond and silicon substrate in high HRTEM studies. However, they observed that growing diamond on untreated bulk SiC did not yield a high nucleation density, thus suggesting that the carbide formation during the deposition only plays an intermediate role and that some type of carbonaceous precursor may be involved.[20] Belton and co-workers[23] found disordered graphite formed on a nickel substrate prior to diamond nucleation. Ravi *et al.*[16] observed that depositing diamond on an initial thin diamondlike carbon (DLC) layer, which deposited on a molybdenum substrate prior to diamond growth, increase nucleation density by up to an order magnitude as compared to performing the deposition on the same substrate but no DLC layer. However, the nature of the DLC layer was never well characterized.

Recently, it was reported that diamond could be formed rapidly on a highly disordered carbon film by HFCVD in less than 1 min,[24] and it has since been proven that this carbon film was turbostratic carbon (TC).[25] In order to better understand the process of TC growth and diamond formation on the TC, Auger electron spectroscopy (AES), Raman spectroscopy, x-ray diffraction (XRD), infrared absorption spectroscopy (IR), and scanning electron microscopy (SEM) have been used to characterize the TC and the diamond films grown on TC. In this paper, it will be shown, using the results from AES, Raman spectroscopy and IR spectroscopy, that the TC contains a mixture of sp^2 and sp^3 bonds. The details of early steps of diamond nucleation and growth on the TC will also be discussed.

EXPERIMENT

The TC and diamond films were deposited in a hot filament assisted chemical vapor deposition system as de-

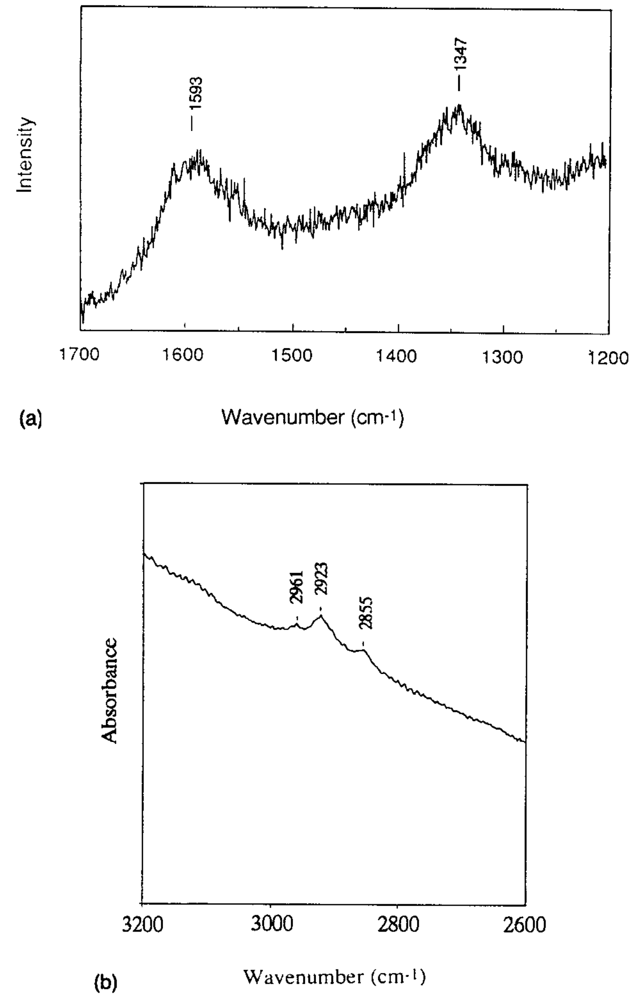

FIG. 1. Raman spectrum (a) and IR absorption spectrum (b) for TC.

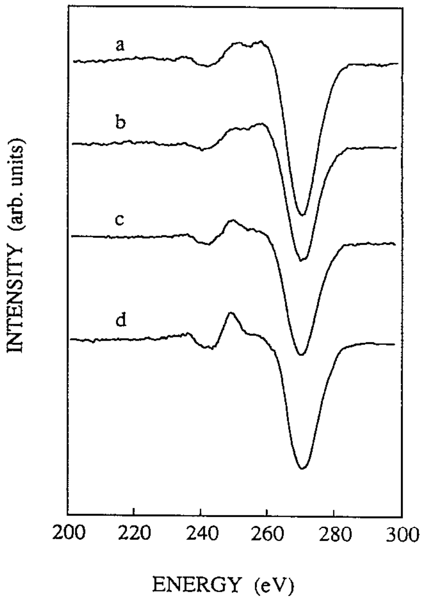

FIG. 2. The carbon *KLL* Auger spectra for (a) the diamond film deposited on Si for 20 hours with H_2:CH_4=100:0.5; (b) the sample S1, upper side of free-standing film; (c) the sample S2, under side of the free-standing film; (d) the high pure graphite. (a) and (d) are inserted for calibration.

scribed elsewhere.[24] The temperature of the filament (T_f) was measured by an optical pyrometer and was set around 2000 °C. The temperature of the substrate surface (T_s) was controlled by the T_f and the filament to substrate distance. The T_s was measured with a thermocouple and set to approximately 650 and 1000 °C for growing TC and diamond, respectively. The H_2 flow rate was set at 100 sccm and the CH_4 flow rates were set at 0.7 and 2.0 sccm for TC film growth and for the subsequent diamond film growth, respectively. The TC films grew on a polycrystalline OFHC-Cu surface which was facing a Mo sheet for 200 min. After growing the TC film, the coated surface of the Cu substrates were placed reverse facing the filament for following diamond growth process for 1, 10, and 100 min, respectively.

The TC and diamond films were usually kept on the substrates and exposed to the atmosphere prior to analysis. Sample S1 is the upper side of a free-standing diamond film which faced the filament during deposition and sample S2 is the corresponding under side which was in contact with the substrate during deposition. For the IR measurements, the TC and diamond films were scraped off from the substrates and mixed with KBr crystals, then ground down to powders. The IR sample was then obtained by pressing the powder mixture of TC and KBr onto a dish using a special die. A pure KBr dish was also made as a reference for the IR measurements. The AES experiments were performed using a commercial AES spectrometer (Perkin-Elmer Physical Electronics). The samples were put into an UHV chamber with a base pressure of 7×10^{-10} Torr. The spectra were taken in the differentiated mode with a 2 eV peak to peak modulation amplitude. The exciting electron beam voltage was set at 2.5 kV. The XRD experiments were carried out using a Siemens D5000 diffractometer, with a monochromatized Cu *Kα* radiation of 40 kV and 20 mA. The Raman spectra were measured with a cw argon laser source with a 514.5 nm wavelength. Laser power was set from 100 to 500 mW.

RESULTS AND DISCUSSION

Figure 1(a) displays a Raman spectrum of the TC film. The spectrum consists of two broad peaks around 1347 and 1593 cm^{-1}, respectively, proving that the TC film is highly disordered carbon which consists of shapeless particles whose structure is between amorphous carbon and graphite with a low degree of graphitization.[26,27]

Infrared absorption spectrum in the C-H vibrational region for the TC film, from 2600 to 3200 cm^{-1} is shown in Fig. 1(b). Two main absorption features at 2855 and 2923 cm^{-1} were found. Similar absorption spectra have been reported for diamond film grown by CVD on Si and on natural diamond.[8,28-30] In *a*-C:H films, the most prominent feature is the C-H stretch vibration band at around 2900 cm^{-1}.[31] Kobashi *et al.* have interpreted the peak at

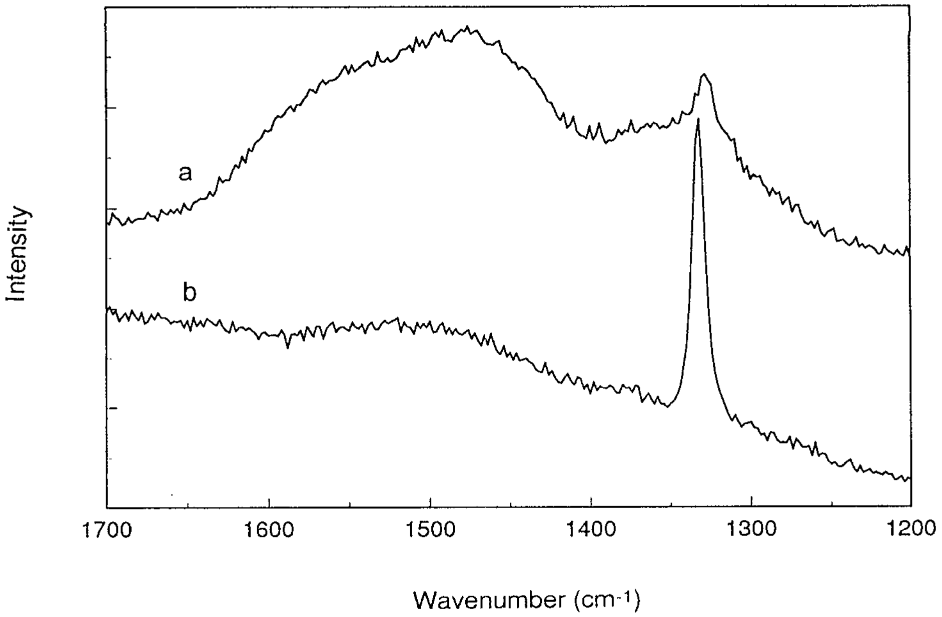

FIG. 3. Raman spectra for (a) under side of free-standing film (S2); (b) upper side of free-standing film (S1).

2854 cm^{-1} as originating from CH_2 vibrations where the carbon atoms are sp^3 bonded with the adjacent carbon atoms, whereas the peak at 2923 cm^{-1} originates from CH and CH_2 vibrations also with the carbon atoms being sp^3 bonded.[8] The weak peak at 2961 cm^{-1} is believed to come from the monohydrogen atoms bonded to olefinic sp^2 carbon.[29]

Turbostratic carbon is known as a highly disordered carbon structure. It has been extensively studied by x-ray diffraction[32] and by transmission electron microscopy.[25,33] In the bulk form, the TC consists of Basic Structure Units (BSUs).[33] Like graphite, the BSU also consists of hexagonal planes of carbon bonded to each other by sp^2 bonds. The difference with respect to graphite is in the stacking of the basal planes. In the TC, the basal planes are rotated in a random manner around the *c* axis. The mean diameter of the BSUs (L_a) is in the order of 100–150 Å, and their mean height (L_c) is $L_c < L_a < 2L_c$.[34] Neighboring BSUs are tilted with respect to one another.

Figure 2 shows the differentiated carbon *KLL* Auger spectra of the diamond film that grown on the TC. For calibration, the spectra of the diamond deposited on Si [Fig. 2(a)] and the high purity graphite [Fig. 2(d)] which were measured in the same AES chamber have been inserted into the figure. Figure 2(b) is the Auger fine structure for the upper side (S1) of the free-standing film. It indicates a pure diamond structure containing only sp^3 bonds. The shape and energies are similar to those reported previously.[35] In Fig. 2(c) the Auger fine structure for the under side (S2) of the film has obviously changed character from diamond to graphite and shows that there are not only sp^3 bonds but also sp^2 bonds.

The Raman spectrum for this film [Fig. 3(a)] further verifies the coexistence of diamond and turbostratic carbon on the under side. It displays a relatively sharp peak at 1328 cm^{-1} and a broad peak around 1500 cm^{-1}. The former is the characteristic wave number of diamond crystallites[36] and the latter arises from amorphous carbon.[37] In addition, Fig. 3(b), which is the Raman spectrum of the upper side of the free-standing film only shows the sharp feature at 1332 cm^{-1}. This peak is the diagnostic feature for diamond[6,26,27] and therefore reveals that the upper side of the film has a pure diamond structure.

X-ray diffraction measurements were carried out for samples S1 and S2. The values of the interlayer spacing of the two sides, upper and under, are in agreement with the values for natural diamond[8] as given in Table I. For the upper side (S1) the ratio of intensities between the (111) line and the (220) line is larger than for the under side (S2), which implies that the synthesized film for the upper

TABLE I. Interlayer spacing of the diamond films.

	ASTM		Upper side (S1)		Under side (S2)	
(*hkl*)	*d* (Å)	Intensity	*d* (Å)	Intensity	*d* (Å)	Intensity
111	2.06	100	2.08	100	2.04	100
220	1.261	25	1.28	38	1.26	64
311	1.075	16	1.09	64	1.07	94
331	0.818	16	0.81	35	0.82	44

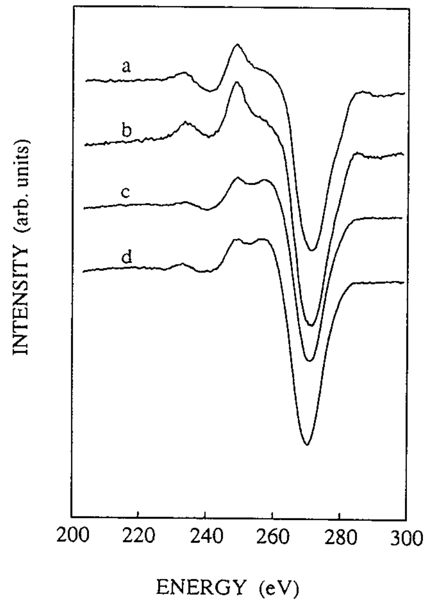

FIG. 4. The carbon *KLL* Auger spectra for (a) the TC film; (b) the diamond deposited on the TC for 1 min; (c) the diamond deposited on the TC for 10 min; (d) the diamond deposited on the TC for 100 min.

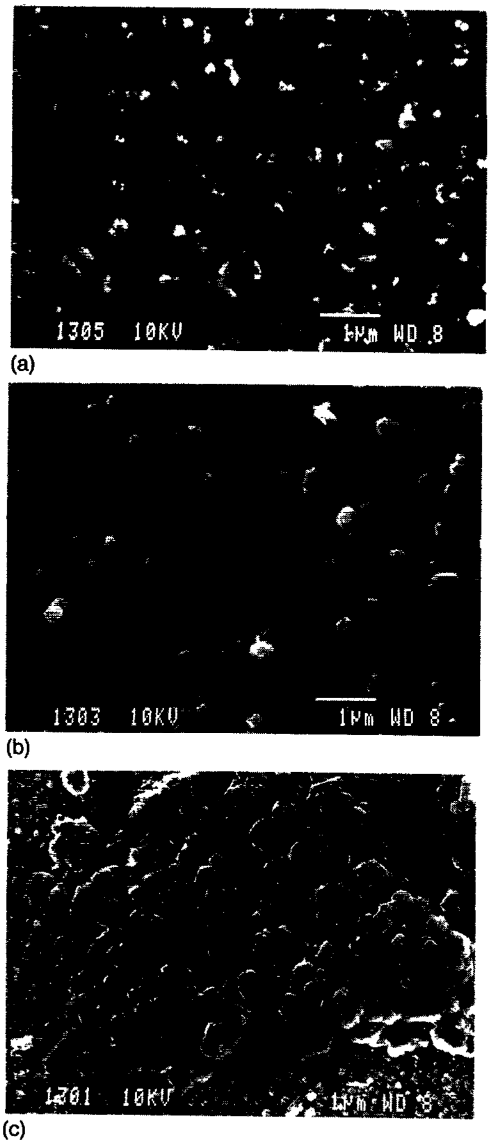

FIG. 5. SEM micrographs of diamond grown on the TC with deposition time of (a) $t=1$ min; (b) $t=10$ min; (c) $t=100$ min.

side has a greater diamond component than for the under side.

Data of AES, Raman spectroscopy and XRD, obtained from the free-standing diamond film, confirm that a diamond film can form on TC film under the conventional CVD conditions.

Furthermore, the AES fine structures and the SEM micrographs from a time-series samples for diamond formation, 1, 10, and 100 min, have been performed, to see that the process of diamond formation on the TC. The Auger fine structures of the C *KLL* (Fig. 4) from the time-series indicate the transition from graphite to diamond with increasing of formation time. The SEM micrographs (Fig. 5) from the same time-series samples verify this change also.

For 1 min deposition time, many regions with dimensions around 0.01–0.3 μm [Fig. 5(a)] can be observed. For some of them, the appearance is already of well faceted diamond. These regions are believed to consist of sp^3 bonded clusters. However, the Auger fine structure [Fig. 4(b)] shows that the film is graphitic on the surface. This is attributed to residues of sp^2 bonds around the cluster since the heating time is too short. Quantitative analysis of the AES data indicates that the surface composition is around 25% Cu for 1 min deposition time, whereas no trace of copper was found in the AES spectrum from the TC film, indicating that the etching rate of the sp^2 bonded carbon is very fast and that the sp^3 bonded clusters collect on the substrate surface. For 10 min deposition time, very well faceted diamond particles are observed [Fig. 5(b)]. The Auger fine structure [Fig. 4(c)] also shows almost pure diamond on the surface. This proves that the nondiamond carbonaceous component has been etched away almost completely and that diamond has already formed and grown. For 100 min deposition time, the initial diamond particles grow and other small diamond particles are nucleated [Fig. 5(c)]. These new small diamond particles come out of continued normal nucleation.

It is observed that diamond nucleation occurs in less than 10 min from the data of AES and SEM for time-series samples. To explain the rapid nucleation of diamond, it is reasonable to postulate that certain carbonaceous clusters, which have the correct crystal structure and bonding configuration to promote the formation of diamond, i.e., to provide the preferential sites for diamond nucleation, may form in the TC. From Raman and infrared absorption results, it can be deduced that there are sp^3 tetrahedral bonds coexisting with the sp^2 trigonal bonds in the TC film. The authors propose that the sp^3 bond cluster in bulk TC may provide the site for diamond nucleation. The main question concerning the structure of TC is how the tetrahedral bonds exist in the main trigonal bonds within the TC. In general terms, it was considered that the sp^2 clusters were interconnected by sp^3 carbon in the *a*-C:H.[17,37] Robertson *et al.* have shown this by discussing the bulk electron states of the *a*-C:H.[38] Using high resolution transmission electron microscopy, Iijima has detected that polycrystalline graphite also contained a small number of regions where sp^3 bonds were formed by bending the basal plane of graphite.[39] Here, the authors suggest two possible ways for the coexistence of sp^3 and sp^2 bonds in TC. In both of them, the local sp^3 bond clusters have the diamond structure. One would be that the sp^3 tetrahedral bonds are located between the BSUs of turbostratic carbon, i.e., lie at the boundary of the BSUs. In this case, if three basal planes in three adjacent BSUs are linked together, some carbon atoms in the corner can belong to the three basal planes, as shown in Fig. 6(A). The tetrahedral bonds are therefore formed around these atoms when the basal planes are at an angle of 120° with respect to one another. Another way to understand the coexistence of sp^3 and sp^2 bonds is to consider that the sp^3 bonds are located within the BSU. The tetrahedral bonds can form within the BSU in the following manner: (1) a basal plane is rotated 60° around the *c*-axis relative to its adjacent basal plane; (2) the central atoms in hexagonal cell are moved from the original plane and come closer [Fig. 6(B)].

The process of nucleation and growth of diamond on the TC can be revealed from these results. At the initial stage of deposition, atomic hydrogen preferentially etches the nondiamond carbonaceous component, i.e., the regions containing sp^2 trigonal bonds[8,40,41] since the reaction rate of hydrogen with sp^2 bonded carbon is much faster than hydrogen with sp^3 bonded carbon.[8,25] Simultaneously, the sp^3 tetrahedral bonded clusters distributing in the bulk of the TC film remain on the surface. The etching of nondiamond carbon enhances the hydrocarbon radical concentration above the growth surface, which improves the sp^3 clusters growth. As the deposition time increasing, the sp^3 bonded clusters grow up to be nuclei for diamond crystallites and become isolated and collect on the Cu substrate, whereas some residues of TC are left around these sp^3 clusters and finally TC only remains between the Cu substrate and the sp^3 clusters. These sp^3 clusters provide nuclei for diamond crystallites which after the rapid nucleation continue to grow at the normal rate for CVD diamond growth. A consequence of the process is that the use of TC films on the copper as substrates for CVD diamond growth results in very rapid nucleation of the diamond film.

CONCLUSIONS

The turbostratic carbon can be catalytically synthesized on Cu at 650 °C. Diamond crystallites can then form on the TC within less than 10 min at 1000 °C.

Using the AES, Raman spectra and IR results, it has been qualitatively reported that the sp^3 bond clusters coexist with dominant sp^2 bonds in TC. A suggested explanation to understand this coexistence is that the excited carbon species can condense on a Cu surface to form the sp^3 and sp^2 bonds during the TC film synthesization where sp^3 bond clusters lie between or inside the BSUs of TC. During the deposition of diamond on the TC, with the assistance of

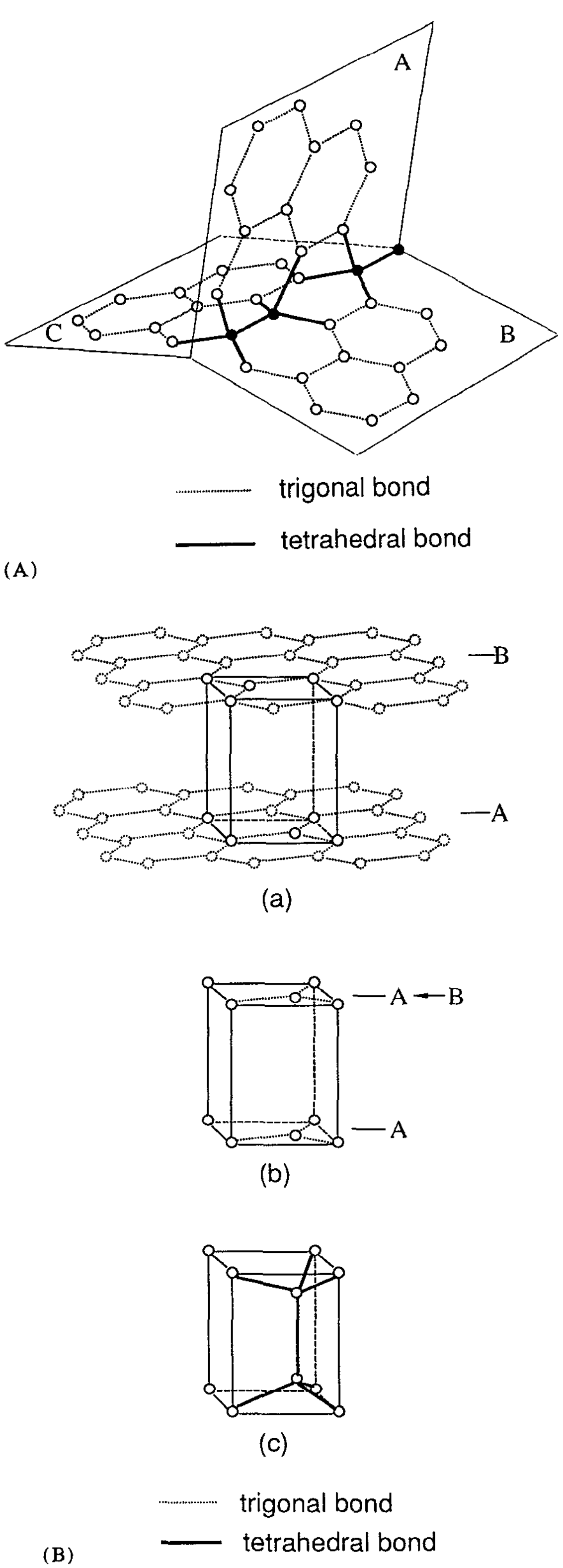

FIG. 6. (A) An idealized model for tetrahedral linkage of carbon atoms at the boundary of three TC basic structure units. The basal planes *A*, *B*, and *C* belong to the BSUs *a*, *b* and *c*. Corner atoms (black) are tetrahedrally bonded when the basal planes are at an angle of 120° with respect to one another. (B) A crystallographic structure relationship of trigonal bonds in graphite, turbostratic carbon and tetrahedral bonds for diamond. (a) A graphite unit cell which contains two carbon atoms; (b) a possible arrangement of two TC basal planes, accomplished by a graphite basal plane *B* being rotated 60° around the *c* axis to be plane *A*; (c) tetrahedral bonds formed by the central atoms in the hexagonal cell moving closer to one another.

atomic hydrogen, sp^2 regions were etched away and sp^3 clusters provided the nuclei rapidly to form diamond crystallites. In further growth, these diamond crystallites have a normal growth rate.

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