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A new hard allotropic form of carbon: Dream or reality?

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Abstract

An unusual phase of carbon with the fcc crystal structure, the lattice constant of which is very close to that of diamond, was reported before in a number of publications. In all the published works, the existence of fcc carbon could not be unambiguously established, as only insignificant amounts of fcc carbon in mixture with other carbon modifications were obtained so far. The present work provides for the first time clear evidence for the existence of the carbon modification with the fcc crystal structure. Thin films consisting exceptionally of fcc carbon were obtained by various methods, namely by hot-filament CVD, plasma-assisted CVD and treatment of the diamond surface in hydrogen plasmas. Results of electron diffraction, Raman spectroscopy, AES, XPS, EELS and HRTEM of the films consisting of fcc carbon clearly indicate its unique crystal and electron structure. The micro-hardness of the films of fcc carbon was found to be equal to $HV_{0.01} = 250$ which is quite different from the hardness of all the known carbon modifications.

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1. Introduction

In spite of the fact that carbon is presumably the best ever investigated chemical element, it reserves many surprises and riddles for scientists. Among others, one crystal form of carbon, namely carbon with the face-centred cubic (fcc) crystal structure, has been a mystery for a long time. The question of the existence of fcc carbon appears to be extremely important, as it would represent the fourth basic form of carbon with delocalised and unhybridised electrons in addition to diamond with sp^3 -, graphite with sp^2 - and carbyne with sp^1 -hybridisa-

tion of electron orbitals. Indeed, each carbon atom in the face-centred cubic crystal lattice has a coordination number of 12, which cannot be obtained on the basis of hybridisation of the carbon four valence electrons. Thus, when assuming that the nature of electron bonds in fcc carbon is close to that in metals, it is expected to have a high electrical conductivity and hardness similar to that of fcc metals, i.e. roughly between $HV = 100$ and $HV = 300$.

There are some publications predicting the existence of a carbon allotrope with the fcc crystal structure [1–4], however, fcc carbon is thought would be less stable than diamond.

The first experimental evidence for the existence of fcc carbon was obtained over 40 years ago. An unusual crystal modification of carbon present in synthetic diamond, which was at that time a new and exciting

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material, was reported by Lonsdale et al. in the late fifties [5]. XRD studies of synthetic diamond grits showed the normal diamond pattern, but, in addition, strong reflections in the 200, 222 and 420 positions that would not be expected for diamond. Beside these additional reflections, there were satellite spots on the high-angle side of all the diamond reflections. These satellite and additional reflections were found to form the pattern of a face-centred cubic structure having a lattice constant of 3.539 Å as compared with 3.567 Å for diamond. Although the crystal lattice constant of the fcc carbon phase was very close to that of diamond the difference between them was still significantly larger than the experimental error ($\pm 0.1\%$). Another unusual feature of the diamond grit examined by Lonsdale et al. was that some particles had presumably a density significantly lower than that of diamond.

The next reference about the carbon allotrope with the fcc crystal structure was the paper of Palatnik et al. [6] published in 1984. In this work carbon films were obtained by ion-stimulated condensation of carbon. The films were consequently annealed at various temperatures, which led to the formation of carbon nano-particles with the fcc crystal structure. It was for the first time suggested that the carbon allotrope with the fcc crystal lattice can be metallic carbon, i.e. formed as a result of the presence of unhybridised s- and p-electrons in its electron structure. This supposition was made on the basis of the calculated value of the carbon atomic radius in fcc carbon. It was equal to 1.26 Å, which is significantly higher than the carbon covalent radius (0.77 Å) and close to the values of atomic radii for typical fcc metals (1.24–1.49 Å).

Since 1984 a number of works indicating the formation of fcc carbon were published [7–16]. In all these publications fcc carbon with the strong diffraction reflexes forbidden for the diamond crystal lattice and the lattice constant close to that of diamond was obtained. Fcc carbon was synthesised by various methods, namely: high-temperature high-pressure treatments of carbon precursors [7,8], shock compression of carbon [9–11], plasma-assisted chemical vapor deposition from various hydrocarbons [12–15] and carbon ion implantation [16]. In spite of the large number of publications on fcc carbon, its existence could not be unambiguously established, as only insignificant amounts of fcc carbon in mixture with other carbon modifications were obtained so far. Recently nano-particles of carbon with the fcc crystal lattice were found in Mexican crude oil [17], providing evidence that fcc carbon might not be as exotic as it can be expected. In addition to the publications mentioned above, there are some works in the literature where a carbon phase with the electron diffraction pattern similar to that of diamond, but comprising strong forbidden for diamond reflexes was synthesised. In fact, the electron diffraction from such a phase is very

similar to that from fcc carbon. For example, such a carbon phase was designated as “diamond-structured carbon” in Refs. [18,19].

We reported results on the formation of films comprising fcc carbon as a result of transformation of the diamond surface in hydrogen plasmas in Refs. [20,21]. It was clearly shown that the crystal structure of the films was completely different from that of diamond. However, we were unable to examine the electron structure and properties of these films before because of their low thickness.

The present work presents new results on the synthesis and investigation of thin films of several microns in thickness composed exceptionally of fcc carbon.

2. Experimental details

Thin films of fcc carbon were deposited on Ni substrates by hot-filament CVD (HFCVD) and plasma-assisted CVD (PACVD) as well as by treatment of the surface of diamond single-crystals in a hydrogen plasma.

Deposition on thin films of fcc carbon by hot-filament CVD was performed at the substrate temperature of roughly 500 °C. The substrate, that was a Ni-wire, was placed near a Ta hot-filament heated at a temperature of 2000 °C in a hydrogen flow. After the temperature of the Ni wire reached 500 °C 1% methane was added to hydrogen and the deposition process was carried out for 5 min.

Deposition of fcc carbon by arc-discharge PACVD was performed using the unit described in Ref. [22] at a substrate temperature of 700 °C from an Ar-CH₄-H₂ mixture. The unit comprises a water-cooled ring anode, a needle graphite cathode and a substrate holder. A bell-shaped plasma is formed between the needle cathode and the ring anode. The substrate is placed on the holder in the middle of the plasma bell.

The technique employed for obtaining films of fcc carbon on the diamond surface as a result of its treatment in hydrogen plasmas was described in detail elsewhere [20,21]. The commercially available bulk diamond CVD samples produced by the ASTeX company were employed. A conventional downstream microwave plasma reactor was used for etching the diamond substrates in hydrogen plasmas at a substrate temperature of nearly 800 °C, power of 300 W and pressure of 1.6 mbar for 4 h.

The films of fcc carbon were examined by optical microscopy, SEM, XPS, AES and Raman spectroscopy with the 514.5 nm excitation wavelength. The JEOL JSM-35CF, JEOL-4000EX, JEM-100C, Riber UNI-150A with a high-resolution double retarding electron spectrometer and ESCALAB-5 instruments were used in this work. The micro-hardness of films of fcc carbon on Ni substrates was measured on tapered cross-sections

by use of a Leitz 7862 instrument at a load of 10 g. Each micro-hardness value was obtained on at least 10 different positions of the film.

3. Results and discussion

Ni appears to be an ideal substrate for growing fcc carbon from the gas phase, as it possesses a crystal structure very similar to that reported for fcc carbon. Another important advantage of Ni as a substrate for deposition of fcc carbon is related to the fact that the formation of quality diamond from the gas phase on Fe, Co or Ni is very unlikely [23,24].

Fig. 1 shows a typical electron diffraction pattern of fcc carbon. It can be seen that the diffraction pattern comprises three reflexes that are forbidden for the diamond crystal lattice. The crystal lattice parameter of fcc carbon is found to vary from 0.354 to 0.356 nm from sample to sample. Some variations in the crystal lattice parameters of fcc carbon can be related to the relatively low exactness of the electron diffraction method, which is equal to roughly ± 0.001 nm. The obtained results on

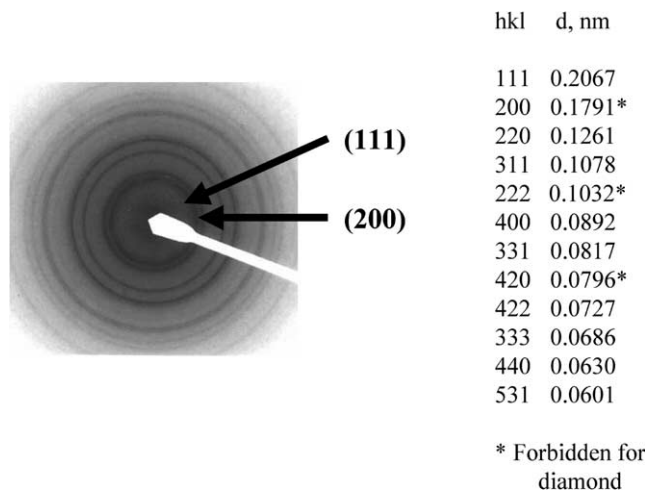


Fig. 1. Electron diffraction from fcc carbon.

the crystal lattice parameter of fcc carbon are very close to those reported in the literature.

The fcc carbon films deposited on Ni are found to have a milky-white colour. Fig. 2 and Fig. 3 show the surface morphology of the films deposited on the Ni-wire by hot HFCVD and on the Ni-sheet by PACVD. The film deposited on the Ni-wire is continuous and has a nano-grain structure with a grain size of some 100 nm. The film deposited on the Ni-sheet by PACVD is also very fine-grained but characterised by the presence of a network of cracks.

Fig. 4 shows Auger spectra from the film of fcc carbon deposited on the Ni-sheet. It can be seen that before Ar etching the surface comprises some oxygen. After 20 min of etching the near-surface layer of the film consists only of carbon with traces of Ar. After etching for 120 min some Ni from the substrate appears in the film.

Spectroscopic studies of the films of fcc carbon were carried out in order to obtain information about its atomic and electronic structure.

The Raman spectrum from the fcc carbon film shown in Fig. 5 consists of very weak broad peaks corresponding to the phonon density of state. Note that there are no optical phonons in fcc carbon that has only one atom per primitive cell. That is why we did not see the strong sharp peak at nearly 1330 cm^{-1} typical for the Γ -point of the optical phonon dispersion in diamond. The weak Raman feature at 1585 cm^{-1} is due to the maximum in the phonon density of states at the edge of the acoustic phonon branches and it is close to the peak typical for sp^2 -hybridised carbon. The weakness of the Raman signal can be explained by the destructive interference between the exciting and reflecting photons on metallic surfaces in the backscattering Raman configuration. A peak at about 1600 cm^{-1} from sp^2 -hybridised carbon is usually present in the Raman spectra of almost all carbon polycrystalline materials, for example diamond films [25,26], as sp^2 -hybridised carbon usually forms along partially amorphous grain boundaries.

Fig. 6 shows integrated Auger spectra of the four carbon allotropes mentioned above. As one can see the

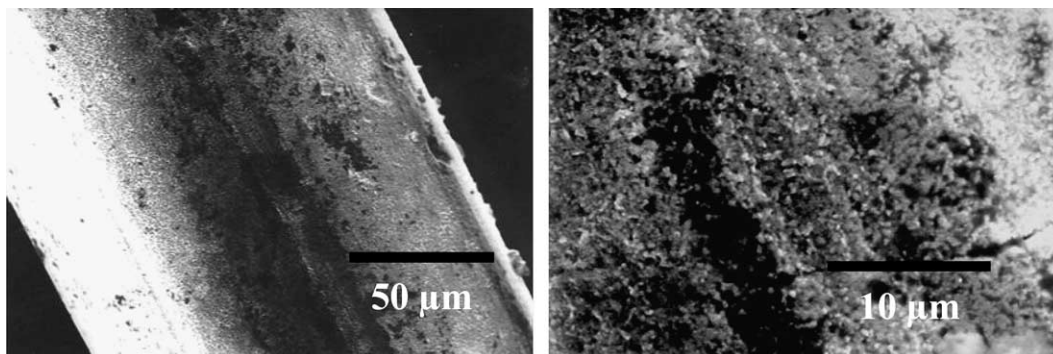


Fig. 2. Surface morphology of a film of fcc carbon deposited on a Ni-wire by HFCVD.

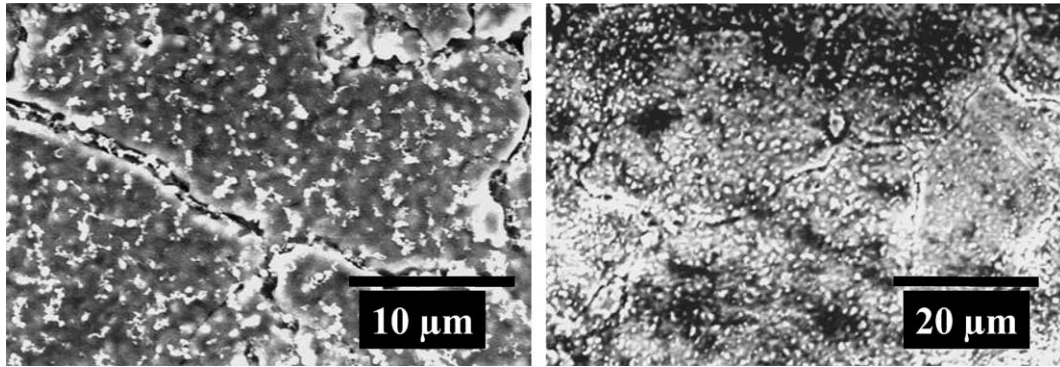


Fig. 3. Surface morphology of a film of fcc carbon deposited on a Ni-sheet by PACVD.

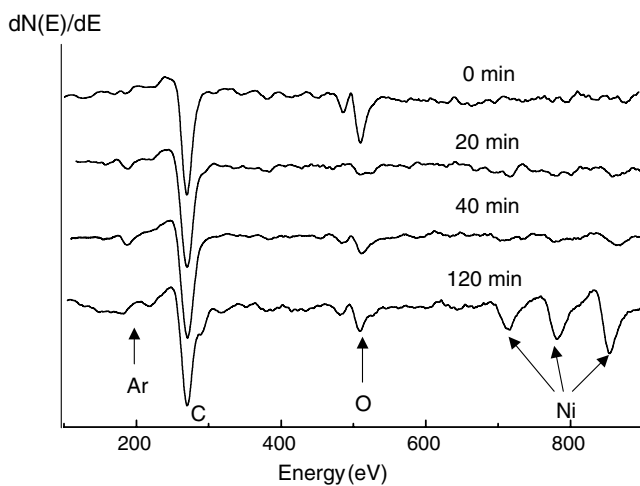


Fig. 4. Auger spectra from the film of fcc carbon deposited by PACVD after various time of Ar etching.

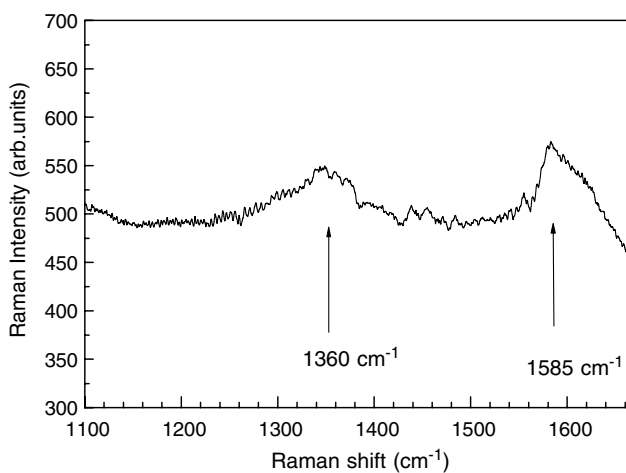


Fig. 5. Raman spectrum from fcc carbon.

high-energy part of the Auger spectrum of fcc carbon is shifted by 7 eV towards low energies compared to graphite.

The structure of the valence band and the bond type can be established from self-deconvoluted Auger spectra, which indicate the density of electron states in the valence band. Fig. 7 shows the distribution of density of electron states in the valence band of fcc carbon, diamond and graphite. The bond energy was calculated from the vacuum level and the spectra shown were normalised by the total number of electrons. The region of high energies (over 15 eV) in the spectra corresponds to s-electrons, and that of low energies corresponds to p-electrons. The presence of a peak in the state densities of fcc carbon at energies of 25–30 eV is a special feature of the valence zone of this carbon allotrope. This feature presumably indicates a low rate of hybridisation of electron orbitals in the valence zone.

One of the most important properties distinguishing fcc carbon from other carbon allotrope is its density. Fcc carbon according to its crystal structure and crystal lattice period should have a density of roughly 1.7 g/cm³, which is considerably lower than that of diamond and graphite with densities of correspondingly 3.51 g/cm³ and 2.26 g/cm³. Relative density of various substances can be calculated on the basis of results of electron-energy loss spectroscopy (EELS) by means of the well-known relationship between the density of electron states (n) and plasmon energies (E):

$$n_2/n_1 = (E_2/E_1)^2,$$

where n_2 and n_1 are densities of electron states of the substances 2 and 1, and E_2 and E_1 are energy losses in the EELS spectra of the substances 2 and 1. If it is a matter of two allotropes of one chemical element, the ratio between the values of densities of electron states are directly proportional to the ratio between the densities of the two allotropes. Thus, if the density of one allotrope is known, one can calculate the density of the other one comparing the positions of peaks in the EELS spectra. Fig. 8 shows the EELS spectrum of fcc carbon compared to that of diamond and graphite. Diamond and graphite have peaks at energies of roughly 34 eV

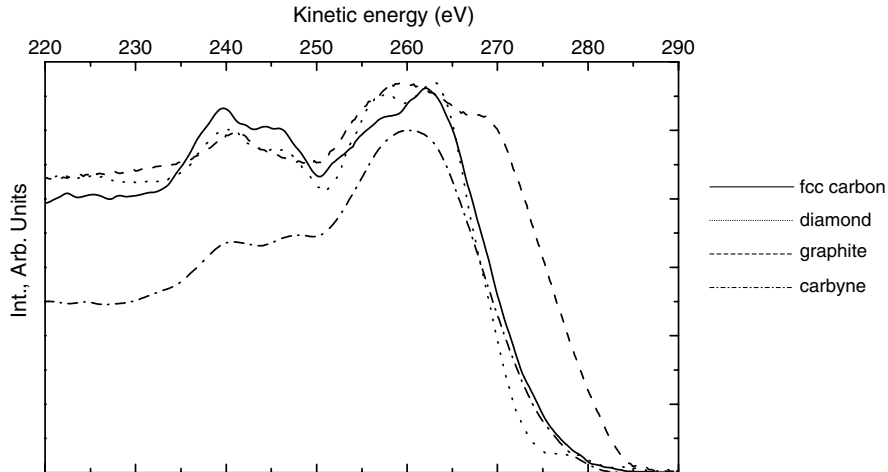


Fig. 6. Carbon peak in the Auger spectra from fcc carbon compared to that from different carbon allotropes.

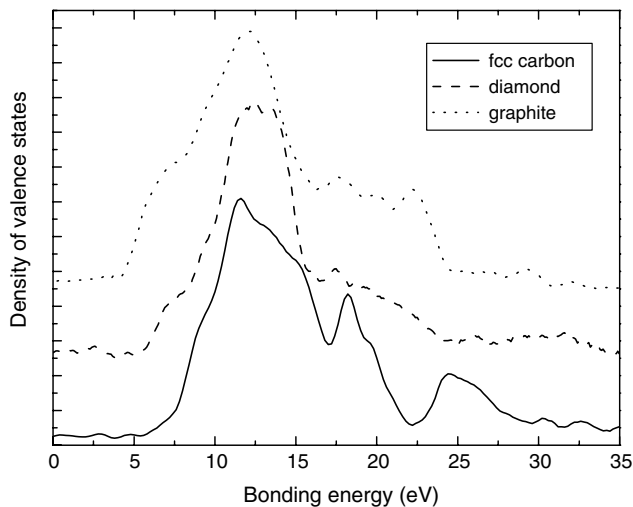


Fig. 7. Density of electron states in fcc carbon compared to that in different carbon allotropes.

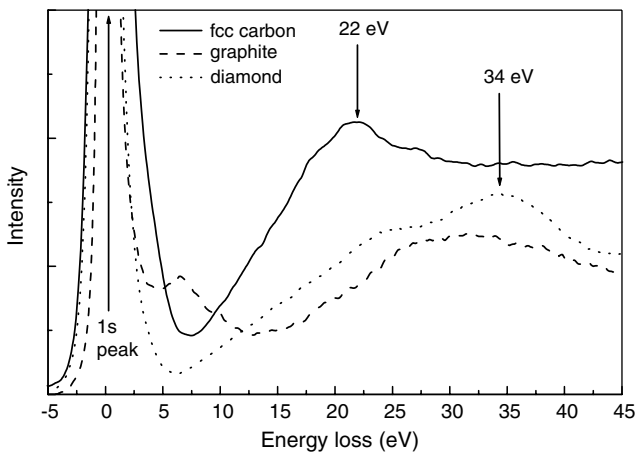


Fig. 8. Electron-energy loss spectrum from fcc carbon compared to that from different carbon allotropes.

and 27 eV. In the EELS spectrum of fcc carbon there is the only one peak at 22–23 eV. The density of fcc carbon calculated on the basis of the EELS spectra is equal to roughly 1.6 g/cm^3 , which is very close to the theoretical density of fcc carbon calculated on the basis of the electron diffraction data. It should be noted that the EELS spectrum of graphite consists of two peaks: one at 25 eV and the other one at 7 eV; the latter one corresponds to unhybridised π -electrons. The EELS spectrum of fcc carbon consists of the only one peak similar to that of diamond, which is evident that all the electron bonds in fcc carbon are equivalent, i.e. they are presumably based on unhybridised electrons.

Fig. 9 shows high-resolution transmission electron microscopy (HRTEM) images from the (100) crystal plane of fcc carbon. The crystal lattice of fcc carbon together with its projection on the (100) crystal plane according to the electron diffraction results are also schematically shown in Fig. 4 as well as those of diamond. It can be seen that the carbon atoms in the HRTEM image form a tetragon with one atom in the centre, which is typical for both the fcc and diamond crystal lattices. The distance between the two neighbouring atomic planes in the HRTEM image of fcc carbon is equal to roughly 0.18 nm, which is very close to that of fcc carbon obtained on the basis of the electron diffraction results (0.178 nm). The distance between the two neighbouring atomic planes in the projection of the diamond crystal lattice on the (100) plane is equal to 0.126 nm, which is significantly lower than that in the HRTEM image. This provides clear evidence that the crystal lattice of fcc carbon is completely different from that of diamond.

Micro-hardness of the films composed of fcc carbon on Ni substrates is found to be equal to $\text{HV}_{0.01} = 250$ which is close to that of fcc metals. This is not surprising when taking into account the relatively large

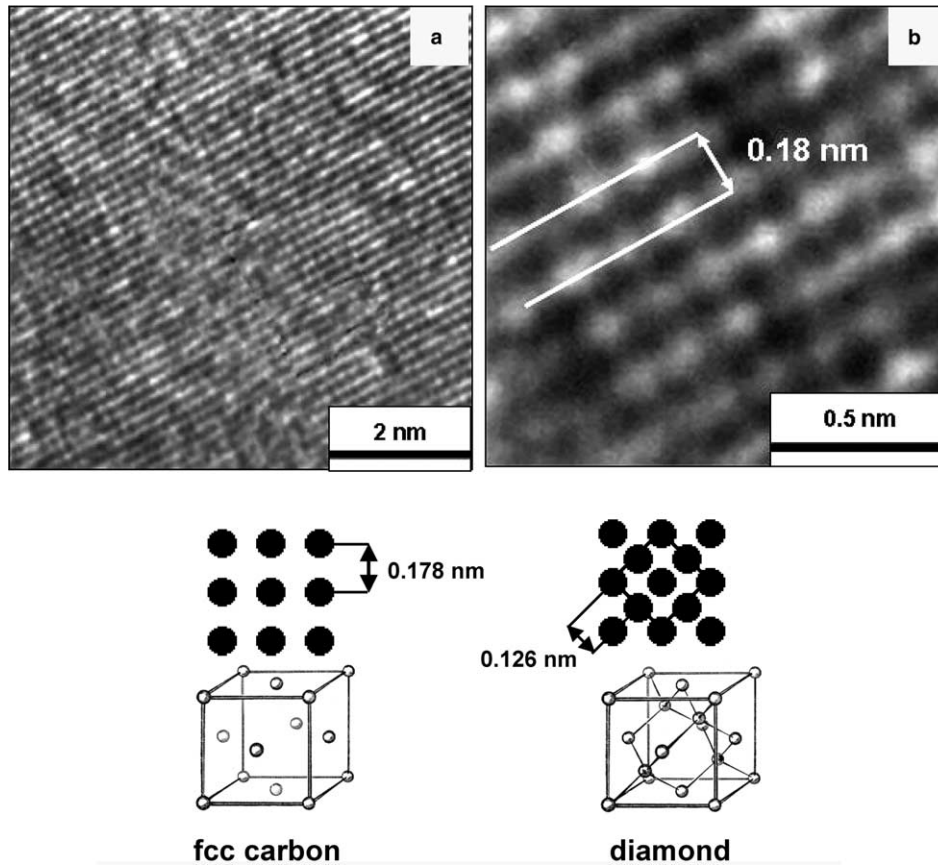


Fig. 9. HRTEM image of the (100) crystal plane of fcc carbon: (a) and (b) the same region of the film at different magnifications; schematic drawings illustrating the crystal lattice of fcc carbon and diamond.

inter-atomic distance and presumably the presence of metallic bonds in fcc carbon.

4. Conclusions

1. Numerous publications provide evidence for the existence of the new carbon form with the face-centered cubic crystal lattice.
2. Thin films composed exceptionally of fcc carbon were for the first time obtained by HFCVD and PACVD on Ni substrates.
3. Fcc carbon has a unique crystal, atomic and electronic structure, which distinguishes it from all the known carbon modifications.

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