Formation of a new cubic form of carbon from carbyne

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The transformation of carbyne into a new diamond-like form of carbon under normal pressure at a temperature of 360—400 °C was observed.

Key words: carbon, carbyne, diamond, allotropic forms of carbon.

Previously[1] we reported the synthesis of ultradisperse diamond (UDD) from amorphous carbyne in the presence of small amounts of UDD.

In the present work we report new data concerning the transformation of amorphous carbyne obtained by low-temperature carbonization of polyvinylidene chloride (PVDC), into UDD in the absence of added UDD.

Experimental

Samples of carbyne were obtained by dehydrochlorination of PVDC according to the procedure described previously.[1] The amorphous carbyne powder was heated in a quartz tube in air at 360—400 °C for 40 h. During heating the black powder turned into a white product, whose yield was no more than 15 % of the starting carbyne. IR spectra of the samples were recorded on a UK-20 two-beam spectrophotometer.

Results and Discussion

Figure 1 shows the X-ray diffraction pattern of white carbon, which indicates that the new carbon formed from amorphous carbyne is partially crystallized, and the interplanar distances in its structure are typical of the cubic lattice of Si rather than of a diamond phase:

d/Å	I
3.028	61.5
1.870	100.0
1.583	6.4
1.910	7.7

Figure 2 presents the IR absorption spectra of the new carbon (curve *2*) and of the starting carbyne powder (curve *1*). The cumulene structure of carbyne is characterized by absorption bands at 1950 and 1070 cm^{-1}. In the 1600 cm^{-1} region, an absorption band corresponding to β-carbyne is also recorded.[2] As carbyne is heated, a new absorption band at 1300—1400 cm^{-1} with a shoulder in the 1330 cm^{-1} region arises in the IR spectrum (curve *2*), which is typical of diamond-like carbon. A similar IR spectrum (curve *3*) was presented in a previous paper[3] devoted to the preparation of thin carbyne films by ionic sputtering of graphite on a silicon support. In this case, as in our study, no diamond phase was detected by X-ray phase analysis.

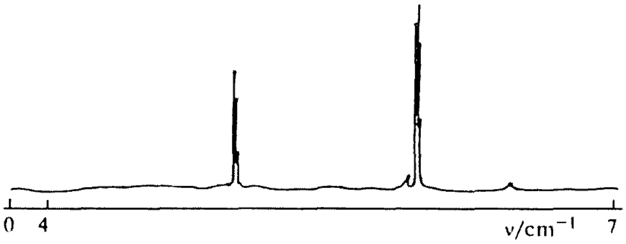

Fig. 1. X-Ray diffraction pattern of white carbyne.

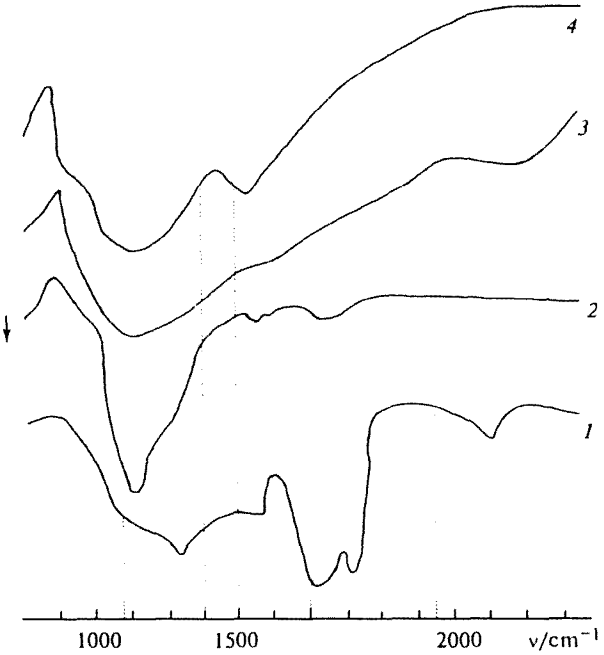

Fig. 2. IR spectra: (*1*) initial carbyne; (*2*) new carbon; (*3*) the spectrum described in Ref. 3; and (*4*) pure SiO_2.

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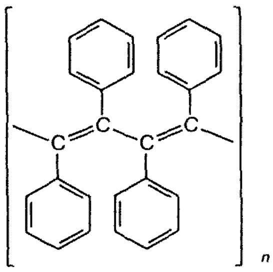
Previously, in a study[4] dealing with the preparation of oriented crystalline films with a carbyne structure, the crucial role of the support in the formation of ordered carbyne chains was noted. Heating an amorphous carbyne film on a Si support at 150—250 °C leads to its crystallization, with the chains always perpendicular to the basis plane of the support. Increasing the temperature to 400 °C results in regular crosslinking accompanied by heat evolution, which promotes the transformation of carbyne into cubic carbon. It was of interest to consider the role of the support and of the air oxygen in more detail.

In a previously published study,[5] chemical reactions of organic radicals stabilized on a SiO_2 surface that was activated by heating in a flow of oxygen were studied. This treatment yields tricoordinated ≡Si silicon atoms in the SiO_2 lattice. The interaction of organic radicals with this surface at elevated temperatures affords carbon deposits consisting of coordinatively unsaturated carbon atoms, $^\cdot$C≡ or :C=. The most probable precursors of tricoordinated silicon (carbon) atoms are peroxide groups ≡SiOOSi≡ (or ≡COOC≡). The O—O bond is readily cleaved on heating, and the chains containing the nonbridging oxygen atoms ≡SiO$^\cdot$ (≡CO$^\cdot$) thus formed are subsequently stabilized by the rotation of the tetrahedron containing one of these O atoms. Apparently, similar reactions also occur in our experiment when a sample of carbyne is heated in air in a quartz tube.

Diamond-like carbon was obtained by the pyrolysis of poly(phenylcarbyne) under atmospheric pressure.[6]



The Raman spectrum of this carbon exhibits peaks at 1336 and 1582 cm^{-1}, indicating the presence of sp^3-hybridized diamond-like carbon atoms. The authors regard the material obtained as a diamond-like intermediate formed during the transformation of graphite into diamond.

Based on the data of IR spectroscopy and X-ray phase analysis we conclude that the product of heating amorphous carbyne, obtained by low-temperature carbonization of PVDC at 360—400 °C in air in a quartz tube, is a new form of diamond-like carbon, the lattice of which is similar to the cubic lattice of silicon.

Thus, carbyne exhibits the remarkable capability of reproducing the structure of the support. Whereas in the experiment with UDD, the role of the support was played by the UDD particles themselves, the use of Si as the support leads to the formation of cubic carbon with a Si type lattice.

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