

## $\gamma$ carbon

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An fcc  $\gamma$  phase of carbon with a lattice constant  $a = 3.57 \text{ \AA}$  has been detected experimentally. This phase is formed during the low-temperature annealing of an amorphous carbon film subjected to bombardment by argon ions during its growth. It is suggested on the basis of an analysis of experimental data (found by electron diffraction, Auger spectrometry, etc.) that the  $\gamma$  phase is metallic carbon.

The literature<sup>1-3</sup> reveals descriptions of about 20 actual and hypothesized modifications of carbon: hexagonal, cubic, and rhombohedral graphites; several modifications of diamond [a cubic modification (with the diamond lattice), a hexagonal modification, and a second cubic modification];  $\alpha$ ,  $\beta$ , and several other modifications of carbene; etc. Some of the forms which have been suggested, however, are actually not modifications of pure carbon but chemical compounds or solid solutions containing components other than carbon. They are formed under the influence of all possible impurities, which participate, for example, in the condensation of carbon films by various methods (pyrolytic condensation, plasma condensation, deposition from the gas phase, etc.). At least for the "pure" crystalline modifications of carbon—graphite, diamond, and "carbin"—the structure unavoidably has covalent chemical bonds in four, three, or two directions (respectively the  $sp^3$  bond in diamond, the  $sp^2$  band in graphite, the  $sp^1$  bond in "carbin," etc.).

In this paper we report the experimental observation of a metastable crystalline modification of pure carbon which we call  $\gamma$ -C and which we interpret as metallic carbon (as we will discuss below). This proposed metallic  $\gamma$  modification of carbon arises after a low-temperature annealing of amorphous carbon films which, along with the substrate, have been bombarded with argon ions during their growth.<sup>4</sup>

Carbon with a cubic lattice with a lattice constant  $a$  ranging over a broad interval (from 3.33 to 5.2  $\text{\AA}$ ) has been observed previously in "carbon" films by various investigators<sup>5-9</sup> during condensation of films from ion beams. The high dielectric properties and transparency of such films at certain limited values of the constant of the cubic lattice,  $a = 3.6 \pm 0.05 \text{ \AA}$ , approximately equal to those of diamond ( $a = 3.56 \text{ \AA}$ ), led to the incorrect conclusion that these films are diamond. These investigators did not properly heed the presence on the electron diffraction patterns of (200), (220), and even (100) and (110) lines, which are forbidden for diamond. As we read the descriptions by which these films were prepared,<sup>6-9</sup> we conclude that significant amounts of impurities and contaminants might have entered these films. The appearance of superstructural lines in Refs. 6-9 should thus probably be attributed to the formation of compounds of stoichiometric composition (carbides, for example) or ordered solid solutions with a cubic lattice.

In the present experiments we took special measures to prevent impurities and contaminants from entering the carbon films. All the structural parts of the chamber which were

capable of emitting atoms under the influence of ion bombardment or heating were made of graphite. The impurity concentration in the stock material (graphite) was less than 0.1%. As substrate we used cleaved NaCl crystals at 180 °C after an ion etching. This substrate temperature was chosen because ion bombardment forms a polymer film on this substrate at  $T < 150 \text{ }^\circ\text{C}$ . The carbon films were annealed on tungsten diaphragms which had been annealed beforehand in vacuum. According to Auger spectroscopy, our carbon films contained no metals of any sort (the error was  $\sim 1$  at. %).

We have observed  $\gamma$  carbon for the first time in annealed carbon films whose preparation included bombardment with argon ions at  $E_{Ar^+} = 40 \text{ eV}$ . Before the annealing, the carbon film was amorphous. The electron diffraction pattern in Fig. 1 shows several halos with intensity maxima at  $I_1 = 0.135 \text{ \AA}^{-1}$  (weak),  $I_2 = 0.255 \text{ \AA}^{-1}$  (weak),  $I_3 = 0.310 \text{ \AA}^{-1}$  (very weak), and  $I_4 = 0.465 \text{ \AA}^{-1}$  (strong). The corresponding "interplanar" distances are  $d_1 = 3.7 \text{ \AA}$ ,  $d_2 = 1.94 \text{ \AA}$ ,  $d_3 = 1.61 \text{ \AA}$ , and  $d_4 = 1.075 \text{ \AA}$ . The widths of the diffraction rings are  $\Delta I_1 = 0.2-0.08 \text{ \AA}^{-1}$ ,  $\Delta I_2 = 0.28-0.2 \text{ \AA}^{-1}$ ,  $\Delta I_3 = 0.32-0.28 \text{ \AA}^{-1}$ , and  $\Delta I_4 = 0.55-0.35 \text{ \AA}^{-1}$ , respectively.

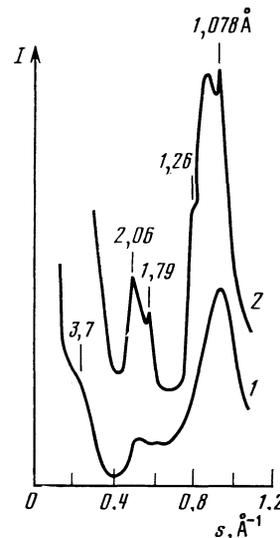


FIG. 1. Interference functions of a carbon film ( $E_{Ar^+} = 40 \text{ eV}$ ). 1—Before annealing; 2—after annealing at  $T = 400 \text{ }^\circ\text{C}$  for  $t = 30 \text{ min}$  [ $I$  is the diffraction intensity, and  $s = (2 \sin \theta) / \lambda$ , where  $\theta$  is the diffraction angle, and  $\lambda$  is the wavelength of the electron].

After an amorphous carbon film is annealed at  $T = 400^\circ\text{C}$  for 30 min, single-crystal inclusions  $\sim 100 \text{ \AA}$  in size appear in the originally structureless matrix (curve 2 in Fig. 1). Against the background of the halos, we find clearly defined (111), (200), (220), and (311) Debye rings and several other lines, weak, which belong to an fcc carbon lattice with a period  $a = 3.57 \text{ \AA}$ , approximately equal to the period of the diamond lattice. The crystalline  $\gamma$ -C phase which we observe, however, is not diamond: The electron diffraction pattern has intense (200), (220), etc., lines which are forbidden for the diamond lattice. On the corresponding electron micrographs we see precipitates of crystalline carbon  $\sim 100 \text{ \AA}$  in size.

It should be noted that amorphous carbon films prepared by bombardment at  $E_{Ar^+} = 40 \text{ eV}$  have an electrical conductivity two orders of magnitude higher than that of films prepared without ion bombardment ( $E_{Ar^+} = 0$ ).

Raising the annealing temperature to  $450^\circ\text{C}$  (30 min) leads to the disappearance of the  $\gamma$  phase, whose place is taken by microscopic crystalline inclusions of graphite, which occupy a smaller area on the electron micrographs, in a  $\gamma$ -C  $\rightarrow$  graphite phase transition (the reason is that the density of graphite is higher than that of  $\gamma$ -C, and there may be a thickening of crystalline inclusions which convert into graphite).

The  $\gamma$ -fcc lattice which we observe cannot be attributed to any phase, whether or not it contains carbon, other than pure carbon. As noted above, the total impurity concentration in the amorphous carbon films was  $< 1\%$  before and after their annealing, while the concentration of the  $\gamma$  phase reached  $\sim 10$ – $20\%$  in the various samples, i.e., was at least an order of magnitude above the possible error in the determination of the purity of the carbon film.

With regard to the possible nature of the  $\gamma$  phase we could invoke the following considerations (which rule out the formation of cubic diamond).

1. The  $\gamma$  phase is an ionic compound with a NaCl lattice. Its density would then be  $\rho_C^i = 3.18 \text{ g/cm}^3$ ; the number of carbon ions in the unit cell would be  $n^i = 8$ ; and the coordination number would be  $z^i = 6$ . At the closest packing of the anions and cations, their atomic radii would be

$$r^- = \frac{a\sqrt{2}}{4} = 1.26 \text{ \AA}, \quad r^+ = \frac{a-2r^-}{2} = 0.52 \text{ \AA}.$$

2. The  $\gamma$  phase is metallic carbon. In this case its density would be lower,  $\rho_C^m = 1.59 \text{ g/cm}^3$ ; the number of carbon atoms in the unit cell would be  $n^m = 4$ ; the coordination

number would be  $z^m = 12$ ; and the atomic radius would be

$$r^m = \frac{a\sqrt{2}}{4} = 1.26 \text{ \AA}.$$

In either case we can completely rule out the possible existence in the  $\gamma$  phase of any of the three types of covalent binding which correspond to small coordination numbers:  $sp^3$  ( $z = 4$ ),  $sp^2$  ( $z = 3$ ), and  $sp^1$  ( $z = 2$ ).

If possibility 1 is correct (the NaCl lattice), the electron diffraction pattern should have contained lines which would be superstructural for an fcc lattice: (100), (110), (210), (211), etc. A particularly strong effect—intense superstructural lines—should have been found in the case of highly charged carbon ions:  $C^{4-}$ , ten electrons per atom;  $C^{4+}$ , two electrons per atom;  $C^{2-}$ , eight electrons per atom; and  $C^{2+}$ , four electrons per atom. Such effects result from the presence of two carbon ion species in the NaCl lattice, with scattering power differing by a factor of several units. A less favorable case for the observation of superstructural lines is that of ions of low charge:  $C^{1-}$ , with seven electrons per atoms, and  $C^{1+}$ , with five, because their intensities are lower than in the three other cases, which correspond to higher values of the structure factors for the superstructural lines.

Possibility 2 thus appears to us to be the more likely; i.e., the  $\gamma$  phase detected here appears to be metallic carbon. Metallic carbon can be expected to have its share of unique properties (superconductivity, etc.) and will thus attract some interest.

Evidence in favor of metallic carbon comes from our calculation of the atomic radius of the carbon:  $r_C^m = 1.26 \text{ \AA}$ . This radius is far larger than the covalent radius  $r_C^c = 0.77 \text{ \AA}$  and is markedly different from the ionic radii of carbon:  $r_C^{4+} = 0.15 \text{ \AA}$  and  $r_C^{4-} = 2.6 \text{ \AA}$  (Ref. 10). On the other hand,  $r_C^m = 1.26 \text{ \AA}$  falls in the rather narrow interval ( $r = 1.24$ – $1.49 \text{ \AA}$ ) of atomic radii for several typical metals: groups VIII, VIIB, VIB, VB, and IB of the periodic table.<sup>10</sup>

Further evidence for possibility 2 comes from the Auger spectroscopy of the annealed films containing particles of  $\gamma$  carbon. Near the carbon peak in the Auger spectrum of these films (Fig. 2) there is a satellite peak,  $S$ , due to electrons from an energy interval of width  $5 \text{ eV}$  (the width of the satellite Auger peak is  $10 \text{ eV}$ ) near the vacuum level. It is here, however, that we find the electron states of the conduction band of all possible modifications of carbon. The presence of  $\gamma$  carbon is thus accompanied by a filling of the conduction band with electrons.

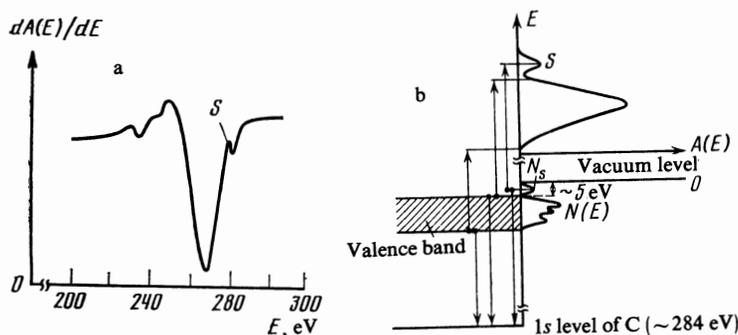


FIG. 2. Emergence of a satellite  $S$  in the Auger spectrum of an amorphous carbon film containing  $\gamma$  carbon. a—Auger spectrum b—energy distribution of the Auger electrons,  $A(E)$ , and electron state density  $N(E)$  in the valence band ( $N_S$  is the additional peak in the state density).

We also observed the  $\gamma$  phase when we annealed amorphous carbon films whose preparation involved bombardment by ions of other energies  $E_{Ar^+} = 150$  eV and 90 eV during layer-by-layer deposition (each carbon monolayer was bombarded by ions in a calculated dose of 1 ion/atom). In this case the  $\gamma$  phase particles appeared as a result of annealing for half an hour at  $T = 300$  °C. During a subsequent additional annealing, with the temperature raised in 50° steps at 30-min intervals to 600 °C, the size of the  $\gamma$ -phase particles increased to 800 Å. The  $\gamma$  phase persisted in the film up to  $T = 800$  °C; i.e., the stability of  $\gamma$  carbon improves with increasing particle size.

In summary, the phase transitions which we have observed during the low-temperature annealing of amorphous carbon films conform to the following order:

amorphous carbon  $\rightarrow$  fcc  $\gamma$ -C  $\rightarrow$  graphite.

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Translated by Dave Parsons