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Allotropic phase transformations induced by ultraviolet power laser irradiation of graphite

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Optically induced allotropic phase transformations of carbon were studied. Under irradiation with a laser beam of 337.1 nm wavelength, at an energy density of 1.9 mJ per 0.1 mm^2, graphite transformed into α-carbin, and amorphous carbon-film transformed into rhombohedral graphite with no evidence of high-temperature effects. The transformations differ from the changes occurring due to heating alone. We suggest that the results could be explained by the one-photon excitation and recombination of electrons.

1. Introduction

The effect of laser radiation on carbon has so far been studied from the point of view of graphite melting or evaporation. Venkatesan *et al.* [1] and Gold *et al.* [2] report the irradiation of graphite by infrared and visible lasers to produce liquid state carbon. The evaporation of different forms of carbon using an infrared laser and condensation of the carbon vapours on cold substrates made it possible to obtain layers which, in addition to the graphite and amorphous carbon, contained metastable forms, such as carbin and lonsdaleite [3]. The effect of ultraviolet laser irradiation on graphite has not been extensively studied. There have been investigations [4, 5] of the composition of vapours above graphite irradiated by an ultraviolet laser under decreased pressure. It appeared possible to identify the original, primary emission of positive and negative ion-molecule clusters undergoing gradual dissociation. The number of molecular ions was much larger under laser excitation than when other methods were used to produce carbon vapours from graphite.

We can expect that high-energy photons will exert a different influence on the material than do long wavelength photons. This difference applies above all to the excitation of electrons. The purpose of this study was to irradiate carbon with ultraviolet laser light, to find out whether electron excitation has a specific effect on which polymorphous form of carbon will emerge.

It is obvious that the main allotropic carbon forms are associated with various electron configurations of the carbon atom. In the order of increasingly excited state of s and p electrons, there are the following configurations: $\sigma sp\pi Py\pi Pz$ (carbin), $\sigma sp^2\pi Pz$ (graphite) and σsp^3 (diamond). So far we know a means of causing the crystallization of a form with the most excited electron state (diamond) this is the work performed by the external high pressure or electric energy supplied directly to valency electrons. We expect that by forcing a change in the electron configuration we can cause an allotropic carbon transformation.

We undertook this study with the expectation that a concentrated beam of high-energy photons will cause the in-mass transition of the electrons of carbon bonds to higher energy states. This will be accompanied by thermal effects related to recombination and vibration excitation. As a result, irradiation by ultraviolet laser light beam should "force" an allotropic transformation.

2. Experimental details

The irradiation was performed using a pulse, vacuum nitrogen gas laser. The laser generated light with $\lambda = 337.1$ nm (3.68 eV) at a repetition frequency, $\nu_r = 95$ Hz, and pulse width 5 μsec. The energy of a single light pulse was 1.9 mJ. The energy was measured using chemical actionometry. The laser light was focused on a spot of 0.5 mm × 0.2 mm. The irradiated probe was moved perpendicular to the light beam at a velocity of 5 to 6 cm min^{-1}.

Pressed polycrystalline graphite, in the form of a 50 mm × 50 mm × 20 mm block, was used as a material for one of the two samples. The structure of graphite is shown in the electron image and diffraction pattern in Figs 1a and 2a. It can be seen that the material was oriented. A film of amorphous carbon, a few hundred nanometres thick, derived by carbon evaporation from an arc at a pressure of 0.1 Pa, was used as the material for the other sample. The structure of the film is shown by the electron image and diffraction pattern in Fig. 3a. The radial distribution function at atoms of an amorphous carbon film obtained from carbon arc vapours was studied by Kakinoki [6], who showed that there were three-dimensional lattice bonds of the diamond type ($a = 0.155$ nm) and of the graphite type ($a = 0.141$ nm).

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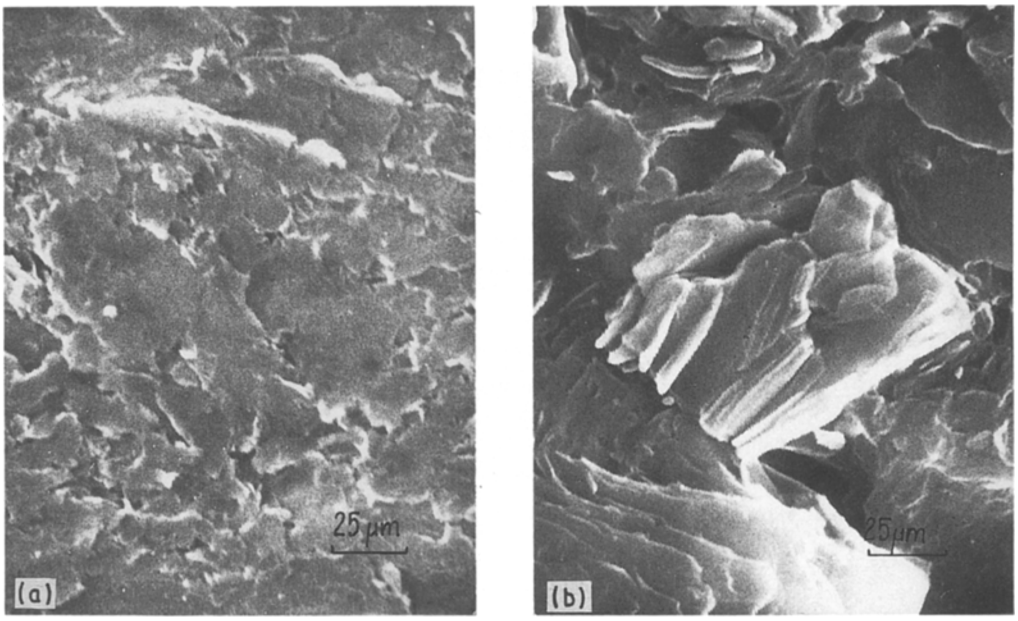


Figure 1 Scanning electronmicrographs of graphite surface: (a) unirradiated; (b) irradiated.

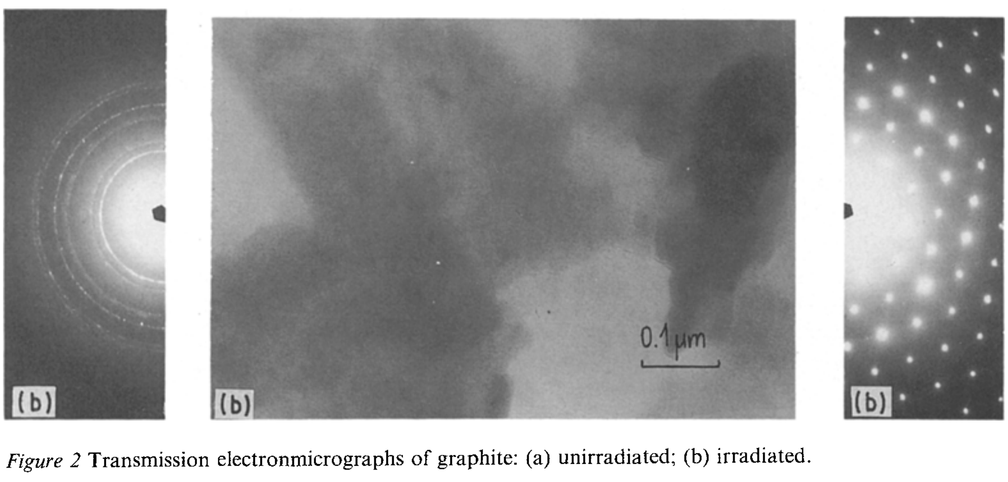
Samples were irradiated through a quartz plate 20 mm thick under normal pressure in air. The irradiation time necessary for distinct changes in the material was ~1 min.

3. Results

We found no manifestation of the effects of high temperature on the irradiated substrates. There was no evaporation on the cold walls of quartz, silicon or a polished nickel plate situated opposite to or in contact with the irradiated surface. No luminescence of any kind was observed during irradiation, and the substrate morphology did not show features indicating a transition through a liquid state. Moreover no evidence was found for the emergence of an amorphous phase.

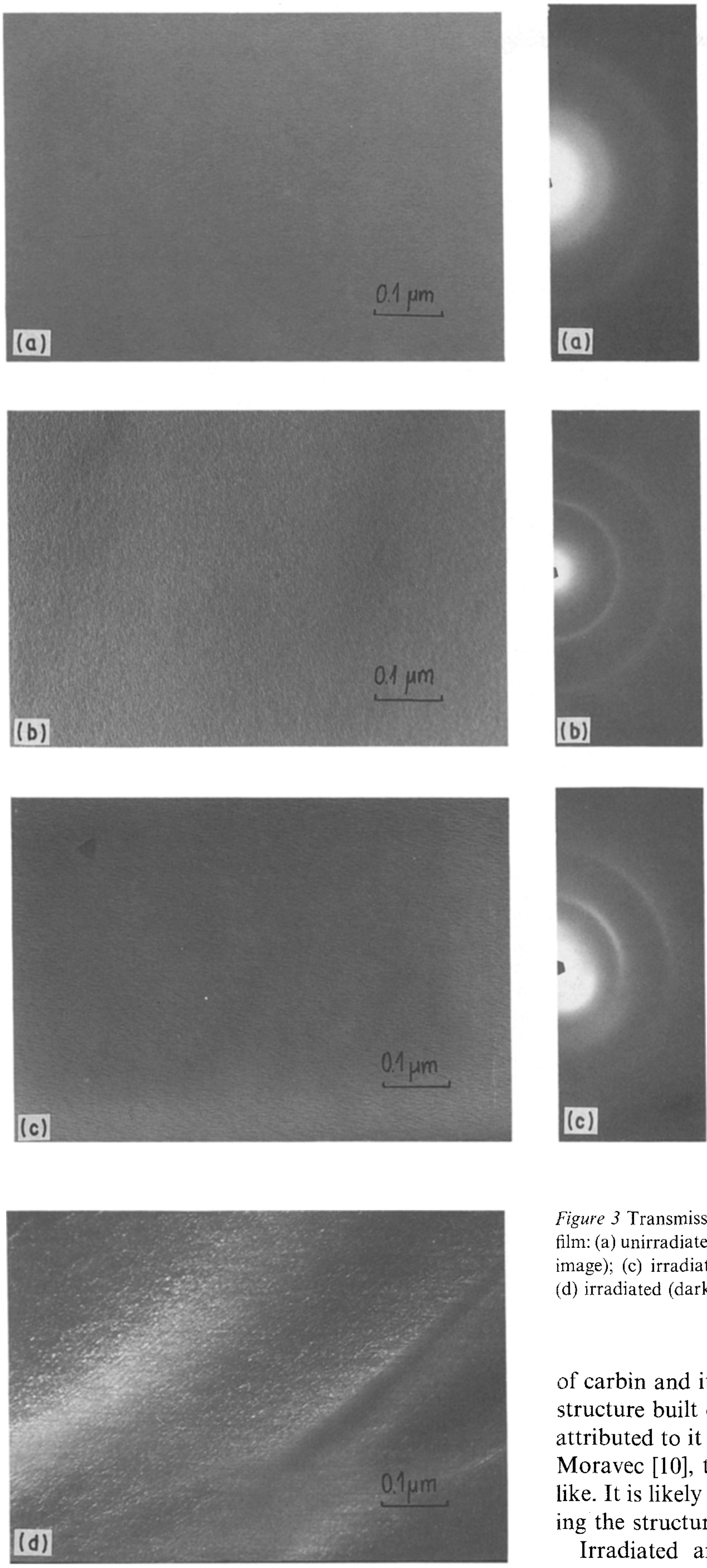
Characteristic allotropic transformations were found in the irradiated substrates. Irradiated graphite transformed into α-carbin. The surfaces of α-carbin monocrystal plates were larger than the grains of irradiated graphite. Graphite transformations are shown in Figs 1b and 2b. α-Carbin is an allotropic form of carbon,

Exp. *d* (nm)	Graphite *d* (nm)
0.098	0.099
0.106	–
0.112	0.112
0.121	0.123
0.168	0.168
0.207	0.205
0.338	0.336



Exp. *d* (nm)	α-Carbin *d* (nm)
0.123	0.124
0.128	0.129
0.148	0.148
0.168	0.169
0.220	0.223
0.261	0.257
0.441	0.440

Figure 2 Transmission electronmicrographs of graphite: (a) unirradiated; (b) irradiated.



Exp. d (nm)	Graphite rhomb. d (nm)
0.105	0.101
0.119	0.123
0.205	0.211
0.340	0.338

Figure 3 Transmission electronmicrographs of amorphous carbon film: (a) unirradiated (bright-field image); (b) irradiated (bright-field image); (c) irradiated probe inclined by 30° (bright-field image); (d) irradiated (dark-field image d = 0.34 nm).

which emerges from graphite at a lowered pressure, at a temperature of 2700 K [7]. It is noteworthy that it is also obtained in infrared-laser-irradiated graphite [8, 9], during the processes of hydrocarbon cracking with ion participation [10] and of polyacetylene heating at 1300 K [11]. On the basis of chemical synthesis of carbin and its absorption in the infrared, a microstructure built of $=C=C=C=$ or $-C\equiv C-$ chains is attributed to it [12]. However, according to Vora and Moravec [10], the carbin microstructure is diamond-like. It is likely that there is some controversy regarding the structure and the bonds in carbin.

Irradiated amorphous carbon films were transformed into highly oriented rhombohedral graphite. A transformed film is shown in Figs 3b, c and d. The emergence of the 0 0 3 plane only makes it possible to incline the probe at TEM by 30° (Fig. 3c). The irradiated film consists of fine-grain plates (with grain diameter ≈ 1.5 nm) of σsp^2 bond planes, separated by 0.387 nm. The film transformation involves strong stresses causing it to crease and break away from the substrate. Rhombohedral graphite is a polytype of graphite which often appears close to hexagonal graphite. Graphite was not observed exclusively in the rhombohedral form.

In order to complement studies on the transformation of the amorphous carbon film, the film itself and an irradiated film were heated. When the film was heated at a rate of $4\,K\,sec^{-1}$ to 1000 K in the TEM, no structural changes occurred. Heating at $0.4\,K\,sec^{-1}$ in argon at normal pressure caused, even at 673 K, transformation of the non-irradiated film into cubic carbon. (Cubic carbon is an allotropic form of carbon which arises from graphite at a pressure of 15 GPa and a temperature of 180 K [13]). Heating of the irradiated film caused only an increase in grain size of rhombohedral graphite. These transformations are illustrated in Figs 4a and b.

4. Discussion

Absorption of photons of energy $h\nu = 3.6\,eV$ may cause the excitation of the π-electrons in graphite, because the π-band in the band model of graphite is half-filled (parametallic nature of π-electrons), and its width reaches 13 eV. Thus under the influence of light the structure specific for the carbon with double bonds (π) becomes stabilized.

It seems that carbin crystallization, which we observed at irradiated spots, points to this one-photon process. If the experiments were carried out in a high vacuum, in keeping with the above interpretation, then sublimation of ion-molecular-clusters of carbon with π bonds should occur. The observations reported by Kasuya and Nishina [4] seem to provide preliminary confirmation of our explanation.

Another possible interpretation of the formation of carbin at places where graphite was irradiated by an ultraviolet laser beam is to accept the following sequence of events: (1) sublimation of carbon in the form of giant ion-molecules, (2) diffusion of ion-molecules over distances larger than the free path of a molecule under normal pressure, and (3) resublimation on graphite with crystallization of α-carbin. This interpretation is in agreement with existing observations of carbin formation and with the results of studies on the evaporation of graphite irradiated by lasers. An argument against this interpretation is the fact that carbon in the form of an amorphous film was not covered with carbin but rather crystallized into graphite.

Studies on the phase transformation of amorphous carbon in the form of a thin film irradiated by an ultraviolet laser have shown, compared with studies of changes induced by heating only, that crystallization of amorphous material occurs in one direction when irradiated by a laser, and a different direction when heated, irrespective of the heating rate. In this case, the specific nature of the process, involving electron excitation, is also manifested.

In summary, changes in the electron configuration of carbon, which occur under the effect of an ultraviolet laser, can be written as follows

$$\text{graphite } (\sigma sp^2 \pi Pz) \rightarrow \text{carbin } (\sigma sp \pi Pz \pi Py)$$

$$\text{a-carbon } (\sigma sp^3 + \sigma sp^2 \pi Pz) \rightarrow \text{graphite } (\sigma sp^2 \pi Pz)$$

It seems that the optical excitation of carbon electrons in a solid favours the establishment of the π configuration.

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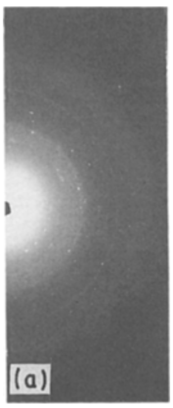
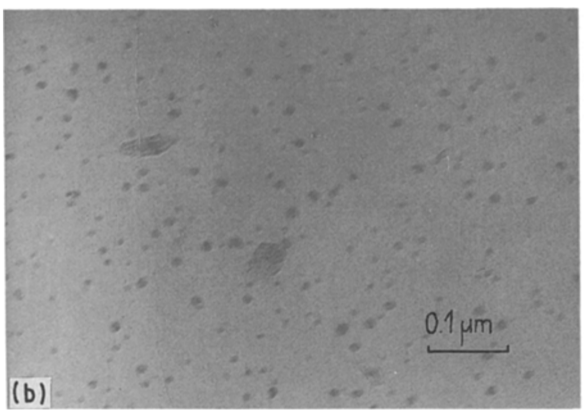
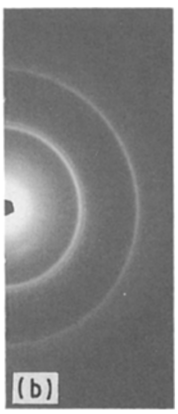


Exp. d (nm)	Carbon cub. d (nm)
0.117	–
0.138	0.148
0.201	0.196
0.248	0.247
0.330	0.321

Figure 4 Transmission electronmicrographs of carbon film after heating at 673 K: (a) unirradiated; (b) irradiated.





Exp. d (nm)	Graphite rhomb. d (nm)
0.105	–
0.120	0.120
0.168	0.168
0.196	0.197
0.208	0.211
0.339	0.338

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