JOURNAL OF MATERIALS SCIENCE 21 (1986) 763–767

The structure and mechanical properties of carbon layers formed by crystallization from pulse plasma

A. SOKOŁOWSKA, K. ZDUNEK, H. GRIGORIEW, Z. ROMANOWSKI
Warsaw Technical University, Institute of Materials Science and Engineering, ul. Narbutta 85, 02-524 Warsaw, Poland

The structure of amorphous carbon layers thicker than 10 μm, obtained from a pulse plasma has been studied. Their hardness, friction coefficient and response to the action of a uniaxial force were determined. The conclusions from X-ray diffraction data, especially from the atomic radial distribution, from annealing experiments and from investigation of the mechanical properties are complementary to one another.

1. Introduction

Papers concerning the crystallization of carbon films with electrical and optical properties similar to those of diamond have been published since 1971. The films were deposited mainly with the use of an ion beam and an electric discharge in a gas. More detailed information on the deposition of diamond layers may be found elsewhere [1–3]. Diamond-like layers vary widely in their hardness, ranging from HV = 10.000 [4] to HV > 600 [5]. These differences seem to be associated with differences in the structure and phase composition of individual layers.

Crystallization of thin solid carbon films from a pulse carbon plasma was described in our earlier papers [6–8]. Transmission electron microscope (TEM) measurements have shown that the layers thus obtained have the ultrafine-grained structure of diamond. The electric resistivity of the layers was $> 10^{10}\,\Omega$. The layers exhibit absorption in the ultraviolet.

This work was aimed at investigating the mechanical properties and strucure of relatively thick diamond-like layers some tens of micrometers in thickness.

2. Experimental details

The layers were deposited on steel substrates in apparatus similar to that described earlier [9]. The process parameters are given in Table I.

The pulse plasma was generated in a coaxial set of electrodes. A tantalum rod of diameter 15 mm was chosen as the central electrode so as to reduce as much as possible the process of electro-erosion. The external copper electrode was water-cooled. The gas used was a mixture of CH_4 and H_2 in the ratio 5 : 1. After 5000 "plasmashots", layers $\geqslant 10\,\mu$m thick were obtained and further investigated.

3. Layer structure

X-ray diffraction analysis of a powdered layer showed the presence of an amorphous phase in an amount much greater than that of the crystalline phase. The structure of the amorphous phase, i.e. the main component of the layer material, was found using the function of atomic radial distribution.

X-ray scattering was measured by a Siemens diffractometer, equipped with an Si(Li) counter. A generator containing a molybdenum anode was used as a radiation source. The Si(Li) counter allowed Compton scattering to be eliminated at angles > 40°; for smaller angles this effect was estimated on the basis of tabulated values. Corrections for polarization and absorption were made according to Millberg [10]. It was assumed as in Mitchell and Windle [11] that multiple scattering was subtracted together with the Compton component. Standardization was performed by the integral method. Corrections were introduced after Kaplow *et al.* [12].

The reduced interference function $F(K)$ plotted in reciprocal space (Fig. 1) shows characteristics indicative of the diamond-type ordering reported by Ergun [13], namely a maximum at $K \approx 2$ and an extended, slowly descending branch on the left side of the maximum at $K \approx 9$.

The reduced radial distribution function of atoms $G(r)$ was obtained by Fourier transformation of $F(k)$ without any preliminary assumptions concerning the structure. It is related to one carbon atom (Fig. 2). The positions of the maxima in this curve correspond to the interatomic distances in the material.

A comparison of the position of the maxima on the curve $G(r)$ with corresponding interatomic distances r in graphite and diamond crystals is presented in Table II.

The position of the first maximum at 0.155 nm coincides with the interatomic distance in carbon with sp^3 hybridization, as for example in diamond. The position of the second maximum at 0.258 nm also conforms better to diamond (0.252 nm) or even better to lonsdaleite (0.252 and 0.258 nm) than to graphite (0.245 nm). The distance 0.258 nm is equal to the length of the "boat-shaped" ring measured between the extreme atoms. The positions of the sample maxima correspond best to the interatomic distances in

0022–2461/86 $03.00 + .12

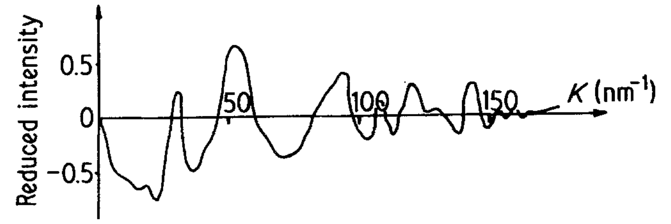


Figure 1 The reduced interference function $F(K)$.

TABLE I Process parameters

Duration of the pulse /half period/ (μsec)	Mean plasmoid velocity (m sec^{-1})	Energy dissipated in the pulse (J)	Discharge repetition frequency (Hz)	Pressure (Pa)	Substrate temperature (K)
50	10^4	1250	0.01	20	300

TABLE II Interatomic distances (nm)

Sample	0.155	0.258	0.312	0.367	0.415 to 0.44	0.498	0.541	0.588	0.632	0.663	0.711
Diamond (cubic hexagonal)	0.154	0.252 (0.258)	0.296	0.356 to 0.389	0.437 0.412	0.463 to 0.483 0.504	0.527 to 0.564	0.585 0.600	0.618 0.620 0.637	0.685	0.713
Graphite	0.142	0.245	0.284	0.356 to 0.360 0.389	0.427	0.496 to 0.51	0.568 (very weak)		0.620	0.650	0.710

lonsdaleite (hexagonal diamond). It is especially true for the 0.258 and 0.252 nm values and for 0.412 and 0.60 nm. The remaining values correspond to cubic and hexagonal diamond. The positions of the initial maxima on the $G(r)$ function differ most from those in graphite; what is more, in the structure of the latter the distances 0.541 and 0.588 nm are lacking (Table II).

The positive variations in some of the distances (e.g. 0.312 nm) and the fusing of neighbouring peaks into bands indicates that the crystal structure has been imperfectly reproduced in fragments of the amorphous structure, i.e. that dispersion and extension of interatomic distances have occured. As compared with bituminous coal, the atomic order is very poor because the first peak of the $G(r)$ curve for coal is several times higher than the corresponding peak in the present sample.

On the $G(r)$ curve the amplitudes at $r = 0.5$ nm are twice as low as at $r = 0.3$ nm. $r = 0.7$ nm is a limit value beyond which the amplitude practically vanish. Hence it can be assumed that the extension of the structure fragments that coherently scatter X-rays does not exceed 0.7 nm.

In order to find the coordination number the radial atom distribution curve $4\pi r^2 \varrho(r)$ was determined. This required that the density of the material be specified, which was done by a pycnometric method using acetone and dioxane under a reduced pressure. The density value thus obtained was $d = 1.35 \pm 0.2$ g cm^{-3}. The area enclosed below the first maximum of the $4\pi r^2 \varrho(r)$ curve, (Fig. 2b) corresponds to the average coordination number which is about 1.5.

In view of the surprisingly low density and thus the small coordination number calculated from it, the small-angle scattering of X-rays was studied in order to determine the void size distribution. The measurements were made in a Kratky-type camera (manufactured by Paar) associated with a Siemens

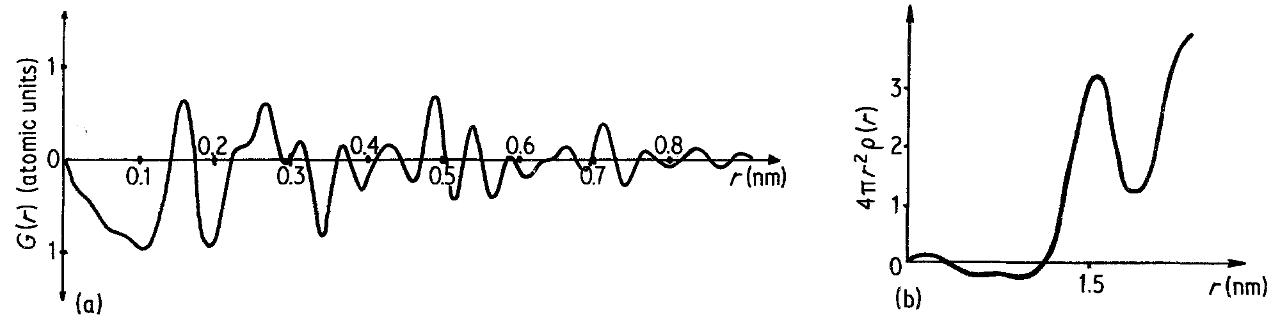


Figure 2 The radial distributon function $4\pi r^2 \varrho(r) = 4\pi r^2 \varrho_0 + (2r/\pi)G(r)$. (a) $G(r)$; (b) first peak.

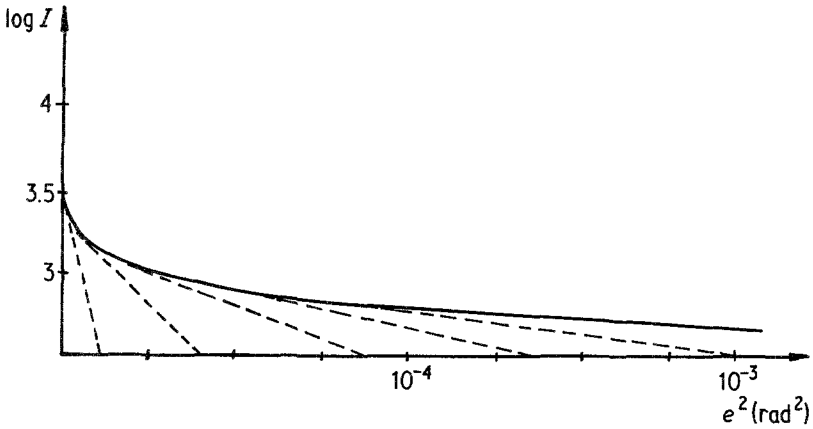


Figure 3 Small-angle X-ray scattering $\log I = f(e^2)$, where I = intensity and e = angle in radians.

diffractometer, using Cu$K\alpha$ radiation. Small angle X-ray scattering (SAXS) was observed and the results plotted as $\log I = f(e^2)$ are shown in Fig. 3. The parabolic shape of the plot indicates that the distribution of void dimensions is continuous. The void dimensions calculated from the curve by the method of tangent lines according to Guinier and Fournet [14] fall within the range 1 to 10 nm. The interference phenomena which would indicate the existence of particles at repeating distances were not observed.

It is probable that the existing minor pores lower the value of the density measured by immersing in a liquid.

4. Annealing of layers

Layers from 100 nm to a few micrometers thick were annealed in argon for 1 h at temperatures of 760, 1040 and 1180 K.

At a temperature of 1000 K, crystallization of well-developed crystals of what is called cubic carbon (ASTM 18–311) from the amorphous phase could be observed (Figs. 4a and 4b). Cubic carbon is known as a phase formed by transformation from a single graphite crystal at 150 kbar (15 GPa) and 180 K. The growth of the cubic carbon crystals disturbed the layer compactness. In the regions where the layer remained thin it kept a structure of amorphous diamond.

The electric conductivity σ of the material remained unchanged, except that its temperature coefficient $\mathrm{d}\sigma/\mathrm{d}T$ varied during the annealing process.

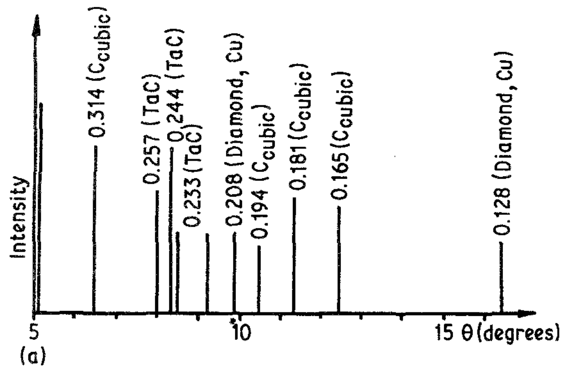
These observations seem to confirm additionaly the σsp^3 electron configuration of carbon atoms in the layer.

5. Mechanical properties

The microhardness of the layers was measured over the sample surface by the Vickers method with the use of a Hanemann hardness tester under loads from 10 to 100 g. The behaviour of the layers under tensile stress was observed *in situ* using a special holder in the TEM (Philips EM300).

The friction coefficient of the layers was measured using an A–135 Amsler tester under a load 2 kg and a rotation speed of 200 min^{-1}.

In hardness measurements we did not succeed in obtaining indentation of a diamond penetrator up to the load 10 g on layers thicker than 10 μm. On a layer 5 μm thick the characteristic indentations appeared under loads of 10, 20, 50 and 100 g. They can be seen



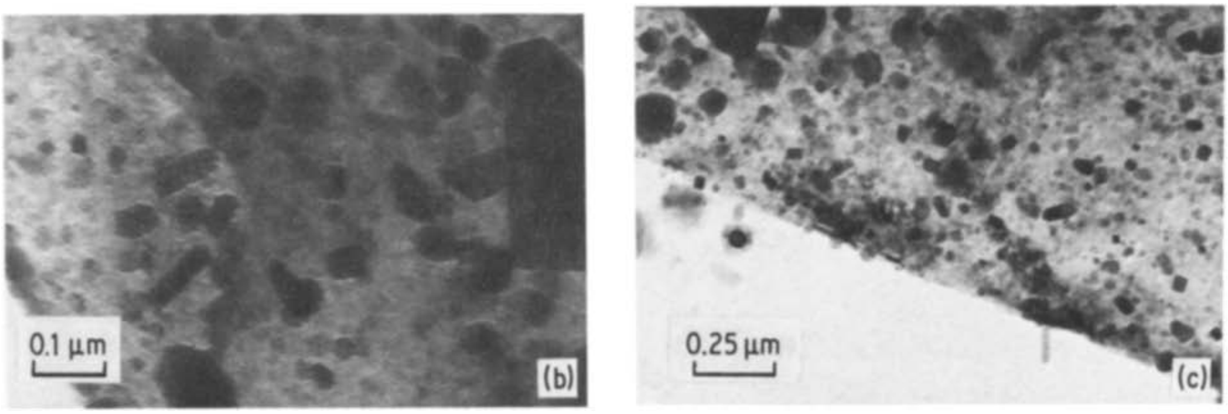


Figure 4 (a)X-ray diffraction data for layers annealed at $I > 1000$ K (labels give Bragg spacings in nm). (b, c) Electron micrographs of a layer annealed at $I > 1000$ K.

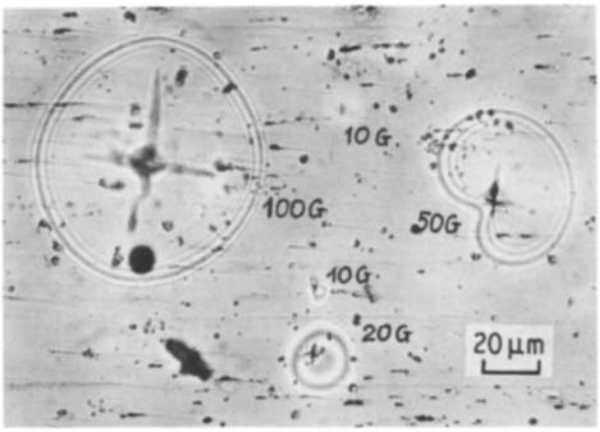


Figure 5 Vicker traces obtained under loads of 10, 20, 50 and 100 g.

in Fig. 5. One can observe typical cracks and irregularities symptomatic of a brittle material, but there are no typical Vickers traces.

In our opinion a precise quantitiative determination of hardness seems to be infeasible under these conditions. If in microhardness estimation the length of the cracks could be assumed to be as seen, then the microhardness values obtained would not be higher than $HV_{20} = 700$.

During TEM examination of the layer elongation no plastic deformation was observed. The sample immediately began to crack in a way typical of a brittle fracture. The direction in which the cracks propagated as compared with the direction of action of the tensile force seems to indicate that the formation of cracks may be primarily attributed to the local properties of the samples investigated. The cracks boundaries are sharply defined. Typical images of a sample under tension are shown in Fig. 6.

The layers with rather smooth surfaces (as shown in Fig. 7, which is an image from a scanning microscope) have friction coefficients as presented in Table III. Adhesion of the layers to the substrate is weak. A characteristic bubbling away of the layer was observed, and this was reflected for example in the traces of the styles during adhesion measurements by the scratch method (Figs. 8a and b). This suggests that internal stresses occur in the layer.

Examination of the mechanical properties of the carbon layers deposited from a pulse plasma indicates that they are hard and brittle. They decidedly differ from polymers, even from crystalline ones. The layers are considerably harder than graphite (whose hardness is unity on the Mohs scale) but are less hard than diamond.

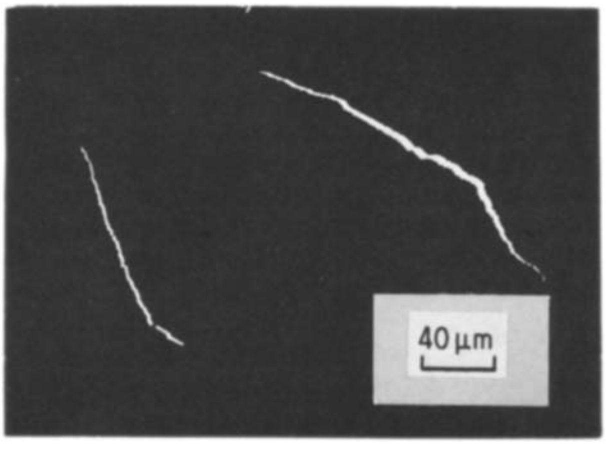


Figure 6 Tensile failures of a diamond layer (TEM).

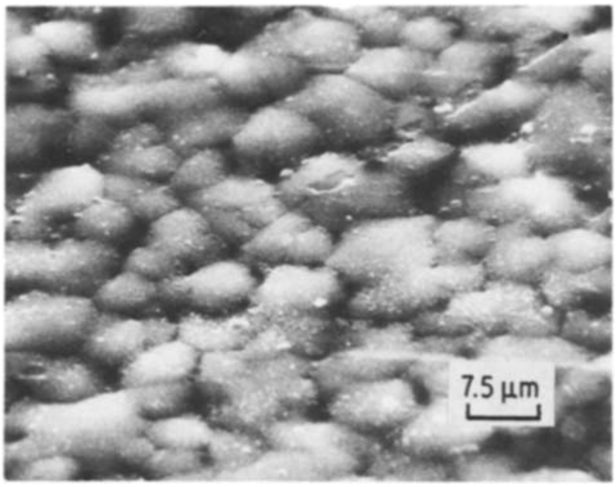


Figure 7 Surface of a diamond layer (scanning electron micrograph).

6. Conclusions

An investigation by X-ray diffraction of the relatively thick carbon layers obtained from a pulse plasma justifies the conclusion that the structure of this material is loose and poorly ordered. The width of the regions where the material is compact and coherently scatter X-radiation is not greater than 0.7 nm. In these regions there occur carbon atoms with the σsp^3 electron configuration, which most probably form those fragments of the layer lattice that are similar to the diamond lattice. The lattice consists of "boat"- and "chair"-type rings. Nevertheless such a structure should have a coordination number of at least 1.7. Since the calculated value is 1.5 one might infer that short linear carbon chains are present. However, because of the significant porosity of the material the calculated coordination number is certainly too low.

The mechanical properties of the material, first of all the presence of slight plasticity, indicate that fragments of the diamond lattice linked to one another by atomic (covalent) bonds are arranged in a disordered manner. Thus the cross-linked structure may contain numerous micropores of various sizes, and the relatively low hardness measured in the layers can easily be accounted for by the microporosity of the materials.

Acknowledgement

This work was supported by the Ministry of Science, Higher Education and Technology under contract MR.I.21.

TABLE III Friction coefficients of diamond layer and substrate

Counter-sample	Diamond layer	Steel substrate
Steel	0.153	0.107
Copper	0.093	0.170

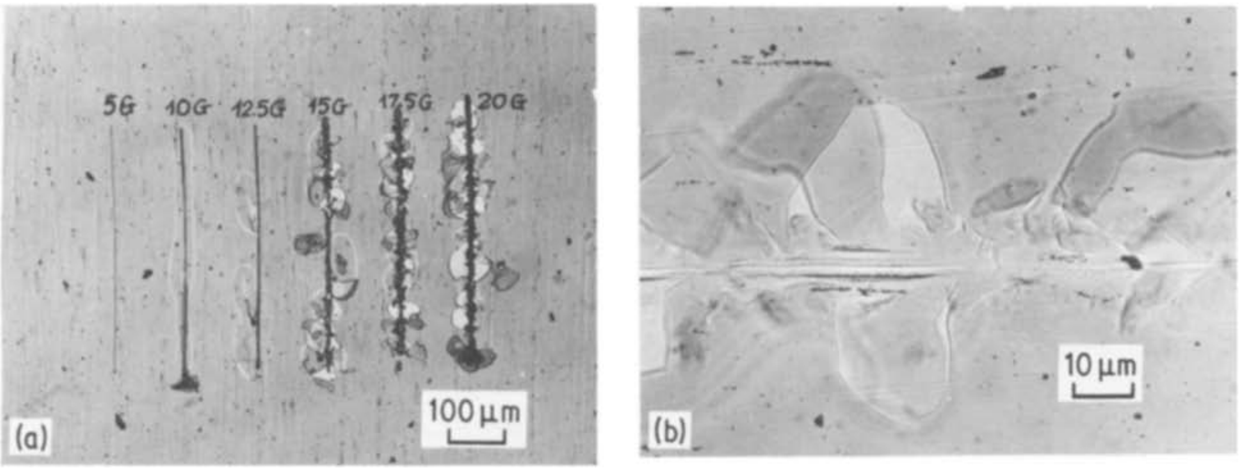


Figure 8 (a) Scratches obtained under loads of 5, 10, 12.5, 15, 17.5 and 20 g. (b) Scratch obtained under a load of 15 g.

References

1. D. W. FIEDOSIEJEW, W. P. VARNIN, A. SOKOŁOWSKA and A. MICHALSKI, *Archiwum Nauki o Materialach* **5** (1984) 171.
2. C. WEISSMANTEL, *Thin Solid Films* in press.
3. L. A. ANDERSSON, *ibid.* **86** (1981) 193.
4. W. E. STRELNICKI, W. G. PADALKA and S. J. VAKULA, *J. Techn. Phys.* **48** (1978) 377.
5. C. WEISSMANTEL and C. SCHÜRER, *Thin Solid Films* **61** (1978) L5.
6. M. SOKOŁOWSKI, *J. Crystal Growth* **46** (1979) 136.
7. M. SOKOŁOWSKI, A. SOKOŁOWSKA, B. GOKIELI, A. MICHALSKI, A. RUSEK and R. ROMANOWSKI, *ibid.* **47** (1979) 421.
8. M. SOKOŁOWSKI, *ibid.* **54** (1981) 519.
9. M. SOKOŁOWSKI, A. SOKOŁOWSKA, A. MICHALSKI, R. ROMANOWSKI, A. RUSEK-MAZUREK and M. WRONIKOWSKI, *Thin Solid Films* **80** (1981) 249.
10. M. E. MILLBERG, *J. Appl. Phys.* **29** (1958) 1.
11. G. R. MITCHELL and A. H. WINDLE, *ibid.* **13** (1980) 135.
12. R. KAPLOW, S. L. STRONG and B. L. AVERBACH, *Phys. Rev.* **138** (1965) A1336.
13. S. ERGUN, "Chemistry and Physics of Carbon", edited by P. Walker (London, 1966) p. 2825.
14. A. GUINIER and G. FOURNET, "Small Angle Scattering of X-rays" (J. Wiley, New York, 1955) p. 187.

Received 22 October 1984
and accepted 29 March 1985