

Distribution of the dimensions of micropores in thin layers using the SAXS method

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Investigations of the distribution of the dimensions of micropores (D_n/R) were carried out for three thin films, obtained by the pulse plasma method. The films consisted of carbon, borazone and titanium nitride respectively. The investigations were carried out using the SAXS method, i.e. averaging results for different depths and surfaces of the films. The obtained (D_n/R) functions show a fuzzy maximum in the region of 3–190 nm. These films, different in the character of chemical bond, the condensation mechanism and the structure show the same micropore size distribution. Therefore such a micropore size distribution seems to be a general property of thin layers condensed from a gaseous phase.

1. Introduction

Microporosity of thin layers is an important technological parameter which influences their utilitarian properties. In the case of layers strengthening, microporosity affects essential properties, e.g. shear resistance and adhesion. What is essential is not only the total volume of micropores, but also their dimensions. Meanwhile, the studies on microporosity are mainly concentrated on the determination of their relative volume. Apart from the classic method of the determination of microporosity by saturating the solid with gases, after investigations have been applied, e.g. luminescent radiation interference [1], changes in some electric or electrochemical parameters [2, 3] or measurements of X-ray spectra [4]. It is also interesting to note observations of the morphology of layers by TEM methods which would, however, have to be carried out at different depths in the layer and for small surface areas, creating problems of averaging the results.

I know of no studies determining the distribution of the dimensions of micropores in thin layers. Such a distribution can be determined directly by applying the SAXS (small angle X-ray scattering) method. This was carried out in this study for thin layers created by different mechanisms of their deposition. What was also interesting was the determination of the micropore distribution and the relation between this distri-

bution and the mechanism of layer condensation from the gaseous phase.

2. Experimental details

2.1. Condensation of thin layers and their structures

Layers were formed from three materials: (a) of carbon with covalent bonds (b) borazone with covalent-ionic bonds and (c) titanium nitride with metallic-covalent bond. The melting temperatures of these materials are respectively 3800 K for C, 3873 K for BN and 3222 K for TiN.

The condensation process took place in pulse-plasma in the conditions presented in Table I and Fig. 1.

The mechanism of the condensation process was investigated by the observation of the TEM method for the surfaces of layers deposited from a gaseous phase. In the case of carbon and borazone, a fully smooth surface was obtained, indicating atomic dispersion of these materials in the condensation process. On the other hand, in the case of titanium nitride this surface is grained (Fig. 2a) indicating that condensation from dispersive clusters took place. The function of size distribution of particles on this surface is shown in Fig. 2b.

Structural studies on these layers demonstrated that carbon and borazone layers have an amorphous structure, and the titanium nitride has a polycrystalline one

TABLE I Properties of the pulse plasma used in the experiments

Pressure (Pa)	Duration of pulse ($\times 10^{-6}$ sec)	Excitation temperature (K)	Mean plasmoid velocity (m sec^{-1})	Energy dissipated in the pulse (J)	Thermodynamic and electrical state of the plasma
80	175	10^4	4000	2000	non-equilibrium non-isothermal

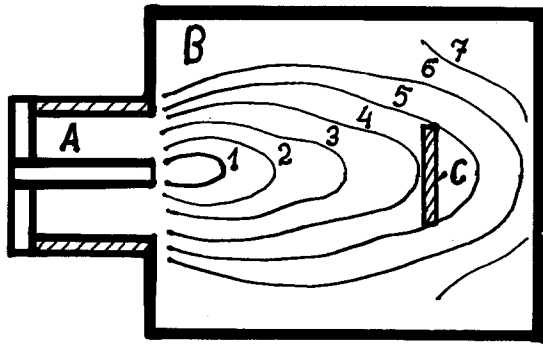


Figure 1 Scheme of the condensation experiments (A) coaxial plasma accelerator, (B) vacuum deposition chamber, (C) substrate. Isotherms of the temperature in the pulse plasma: (1) 1830 K, (2) 1810 K, (3) 1750 K, (4) 1670 K, (5) 1580 K, (6) 1430 K, (7) 1270 K.

(Fig. 3). From the fuzziness of lines on the TiN diffractogram, the size of crystallites was estimated by using the Scherer formula. They are about some tens of nanometres.

Previously, diffraction studies carried out by the RDF (radial distribution function) method on the structure of amorphous layers demonstrated that in carbon layer areas with crystal-like ordering do not exceed 0.6–0.7 nm [5, 6], and that their structure is diamond-like. On the other hand, in a BN layer they are even smaller, reaching up to the second neighbour-atom, i.e. about 0.3 nm [7].

2.2. Principles of SAXS method

This method considers the radiation diffraction on whole particles having interphase boundaries and the mean electron density (ρ) different from that of the medium (ρ_0). Such particles can be pores or ones with a different structure, or chemical composition from those of the medium. The intensity of radiation (I) scattered by the particles is proportional [8] to:

$$I(K) \approx (\rho - \rho_0)^2 (\Sigma K)^2$$

where K is a wave vector, $K = 4\pi \sin \theta / \lambda$ and λ is the radiation wavelength. The total radiation intensity, scattered in the small-angle region, can be expressed

by the formula [9]:

$$I(K) = \int_0^\infty D_n(R) m^2(R) \Phi(KR) dR$$

where $D_n(R)$ is the function of the size distribution of particles depending on their linear parameter R . In the case of spherical particles, R is the radius of a sphere. $m^2(R)$ is an integral over excess density in the medium surrounding the particle, $\Phi(KR)$ is the factor of the particle shape. Considering the correction for the collimation effect and the wavelength effect, this equation can be written:

$$I_{\text{exp}}(K) = 2 \int_0^\infty dR \int_0^\infty d\lambda \int_0^\infty dt \int_0^\infty dx \times Q(x) P(t) W(\lambda') D_n(R) m^2(R) \Phi(\beta) \quad (1)$$

where $\lambda' = \lambda / \lambda_0$ and $W(\lambda')$ is the wavelength distribution; $Q(x)$ is a weight function for the aperture width effect; $P(t)$ is a weight function for the aperture length effect;

$$\beta = R[h^2 - x^2 + f^2]^{1/2} / \lambda$$

From Equation 1 it is possible to calculate the function $D_2(R)$ by the inverse Fourier transform method.

2.3. Thin layers studies by SAXS method

Research samples were made from layers about $5 \mu\text{m}$ thick, removed from the substrate and powdered. The sample thickness were optimum for the radiation $\text{CuK}\alpha$ applied. The measurements of the intensity of scatter X-rays were performed in a compact small angle camera vacuum chamber, coupled with a Siemens diffractometer.

The measurement range corresponded to particle sizes from 1 to 30 nm. Also, appropriate measurements were carried out in order to include wave effect and the collimation effects in Equation 1. The function $D_n(R)$ was calculated by the method proposed by Glatter [9] by applying his computer programme MTP-79. A spherical particle shape was assumed.

As a result of the studies, function of particle size

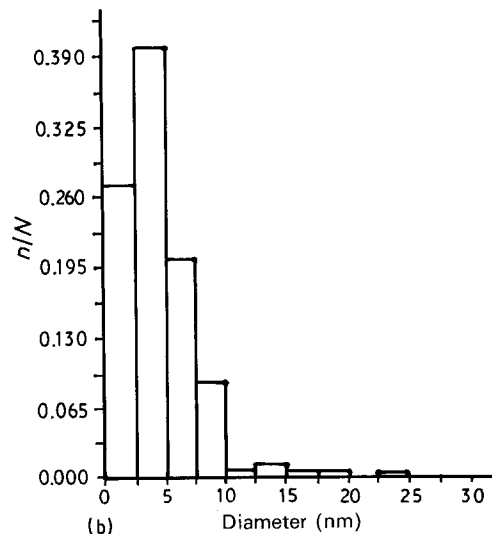
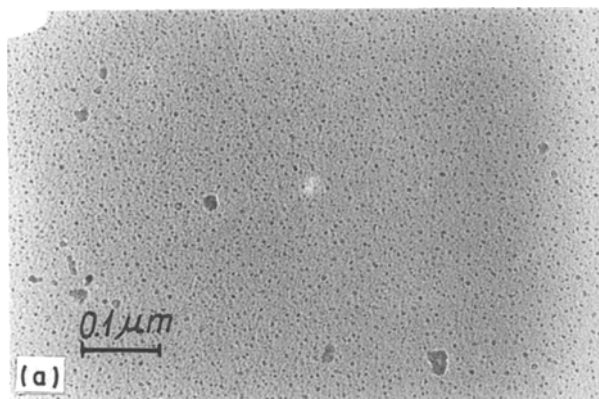


Figure 2 TiN deposited on a carbon after 10 discharge pulses: (a) electron micrograph, (b) particles diameter distribution function.

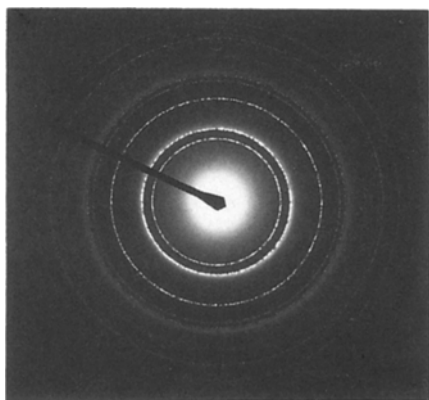


Figure 3 Electron diffraction pattern TiN deposited on a carbon after 100 discharge pulses.

distributions $D_n(R)$, shown in Figs 4 to 6 were obtained. Because of the fact that the function $D_n(R)$ represents the relative values of the number of particles, in these figures the heights of main peaks were equated for better comparison of them. Slight drops below zero on these curves apart the main maximum are characteristic of this method.

3. Discussion

It can be seen for Figs 4 to 6 that for all the investigated layers the functions of particle size distribution $D_n(R)$ are very similar for the range of radii of spheres (R) up to 20 nm.

What is observed in this range is a strong, asymmetric fuzzy maximum extending from 3 to 19 nm, with a peak at about 7 nm.

The structural studies on layers described in Section 2.1. and [5-7] show that for no material can this maximum have any relation with particles with crystalline ordering, since those dimensions are about 0.3 nm for borazone, 0.6 to 0.7 nm for carbon and a few tens of nanometres for TiN. Therefore, this maximum must correspond to the size distribution of micropores treated as particles in the SAXS method.

It turned out that the thin layers, different in the character of chemical bond, the condensation mechanism and the degree of structural ordering, have the same micropore size distribution. This is a continuous size distribution over the range of radii varying between 3 and 19 nm. Therefore, such a micropore size distribution seems to be a characteristic property of thin layers condensed from a gaseous phase.

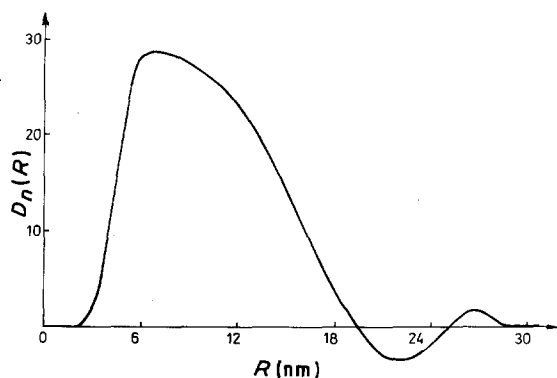


Figure 4 $D_n(R)$ function of carbon.

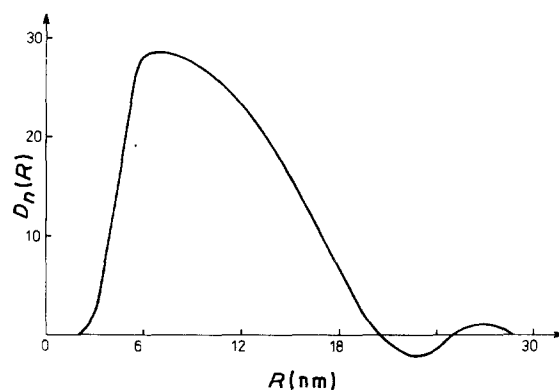


Figure 5 $D_n(R)$ function of BN.

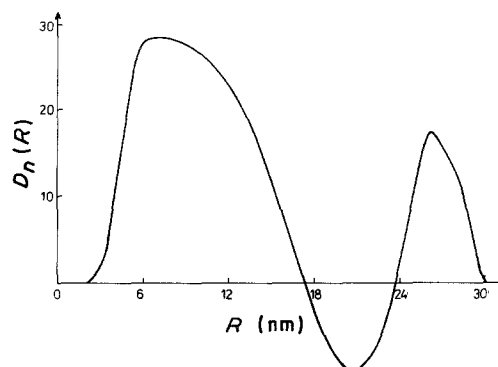


Figure 6 $D_n(R)$ function of TiN.

In Fig. 6 it is possible to observe still another maximum, for $R = 26$ nm, which is symmetrical and relatively narrow. Because of the fact that it is absent from $D_n(R)$ of layers with an amorphous structure and its position agrees with the size of crystallites in this material, as approximately estimated (Section 2.1.), it should be presumed that the particles in $D_n(R)$ corresponding to this maximum are crystallites. These crystallites have a very small size scatter (Fig. 6) indicating the homogeneity of the crystallization process.

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