

## EFFECT OF CRYSTALLITE SIZE ON OPTICAL SPECTRA OF DIAMOND POWDERS AND POLYCRYSTALLINE FILMS

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The present work submits the results of an investigation of diamond polycrystalline films, synthetic diamond powders and single crystals. Using photoacoustic spectroscopy, it was found that in the optical absorption spectra of all the three types of diamond materials studied there is a band corresponding to interband absorption for quanta with energy exceeding 5.5 eV. For single-crystal samples an absorption band due to nitrogen impurities was detected and for polycrystalline films and powders there was observed a broad band due to structural defects. The specific feature of the spectra of films and powders is a strong light scattering in the ultraviolet region (250–300 nm), the efficiency of which increased with decrease of crystallite size from  $\sim 100$  to  $\sim 1$   $\mu\text{m}$ . Further decrease of the size of diamond particles (down to 0.25  $\mu\text{m}$  and less) diminished the share of scattered light because of the change of particles faceting and their coalescence.

The development of new technologies of growing diamond films by chemical vapor deposition (CVD) opened up new possibilities of wide practical utilization of the unique properties of diamond in science and engineering [1–3]. As a rule, diamond CVD films have a polycrystalline structure. Some of the specific properties of polycrystalline films may be expected to be analogous to the properties of diamond powders and their comparative study would be useful for establishing general relationships and differences in their properties.

In the present work, we were concerned with the study of standard (synthesized at high temperatures and pressures) powders of the ASM type with crystallites of the following sizes: 125–100, 60–40, 28–20, 20–14, 7–5, 5–3, 2–1, 1–0  $\mu\text{m}$  (produced by the research and production association "BARS", Aleksandrov, Russia) and powders of the IRM type with grain size smaller than 0.25  $\mu\text{m}$ . (Asahi Diamond Corp., Japan). Diamond films were grown by the CVD method in the plasma of a d.c. discharge on substrates of polished silicon. The substrate temperature was about 900°C, the pressure of a gaseous mixture of methane and hydrogen, about 8 kPa, and the methane concentration, about 2%. The film thickness was dependent on the duration of the growth process: 10 and 50  $\mu\text{m}$  for 1 hr and 6 hrs, respectively. Apart from powders and polycrystalline films we also studied single crystals of synthetic diamond measuring  $4 \times 4 \times 0.3$  mm. The crystals had specular polished surfaces with a (100) orientation and a characteristic golden tint due to a nitrogen impurity.

The spectral dependence of optical absorption was determined by photoacoustic (PA) spectroscopy, which is noted for high efficiency when used to study powder-like materials and films with a rough surface, in which case the application of standard techniques is a problem because of the diffuse light scattering

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[4, 5]. The PA spectra were measured on a modified spectrometer (Model 6001, Princeton Applied Research Corporation). Used as a light source was 1-kW xenon lamp with a grating monochromator. The slit spectral width of the monochromator is 4 nm in the ultraviolet (UV) and visible regions and 32 nm in the infrared (IR) region. The double normalization of spectral relationships of the amplitude of the PA signal to the spectrum of the carbon black standard and to the signal from a pyroelectric detector, which measured the intensity of radiation impinging on the specimen, made it possible to take into account both the spectral characteristics of the lamp and possible variations of the light intensity during measurements. Some of the measurements were made using the focused emission of a 150-W deuterium lamp. In both cases the intensity of the light beam impinging on the specimen was modulated by a mechanical chopper with a frequency ranging from 20 to 3000 Hz. The sealed PA cell was filled with air at normal pressure; measurements were carried out at room temperature.

The methods of optical and scanning electron microscopy have shown that the polycrystalline films were composed of randomly arranged crystallites with a characteristic diamond facet [1, 2] and about 5 and 10  $\mu\text{m}$  in size for films 10 and 50  $\mu\text{m}$  thick, respectively. When examining "in transmitted light", we noticed that diamond crystallites of up to 1  $\mu\text{m}$  in size readily transmit visible light without changing essentially its color. Upon illumination from above (from the side of the objective) it was found that geometrically irregular crystallites have plane faces which specularly reflect the incident light (Fig. 1a). The electron microscopy of powders of the IRM type showed that the more characteristic surface for diamond crystallites smaller than 0.25  $\mu\text{m}$  in size is the one which cannot be represented in the form of several sufficiently extended plane and specular smooth areas. The resolving power of the optical microscope was insufficient in order to determine the shape of such small crystallites. Examining both in reflected and in transmitted light, they appeared as particles diffusely scattering light.

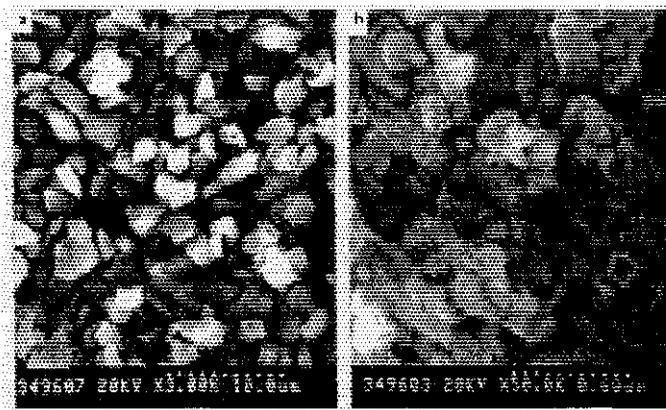


Fig. 1

Photomicrographs of diamond powders of type ASM 2/1 (a) and IRM 0.25/0 (b) obtained with the aid of a scanning electron microscope.

The photomicrograph in Fig. 1a demonstrates another characteristic feature of diamond powders with a crystallite size larger than 1  $\mu\text{m}$ : the presence of voids which are large in volume because of the incomplete contact between the particles. In the case of fine-grained powders (IRM) a spontaneous coalescence of particles was observed (Fig. 1b).

We will begin the consideration of the data of PA spectroscopy with diamond single crystals. The major contribution to the amplitude of an acoustic wave set up in the gas being in contact with the specimen is made by the heat evolved due to the absorption of light in the layer within the thermodiffusion length  $\mu = [2k/(\rho C\omega)]^{1/2}$  (where  $k$  is the thermal conductivity of the material studied,  $\rho$  is its density and  $C$  is its specific heat;  $\omega$  is the light modulation frequency) [4]. With account being taken of a high thermal conductivity of diamond ( $\sim 20 \text{ W}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$  [2, 3]), the quantity  $\mu$  must be much greater than the thickness of the single crystals used over the entire frequency range (20–3000 Hz) available. Under these conditions the amplitude of the PA signal will be determined by the material of which the measuring cell is made (stainless steel). However, if several crystals are placed one on another in the cell, the thermal conductivity

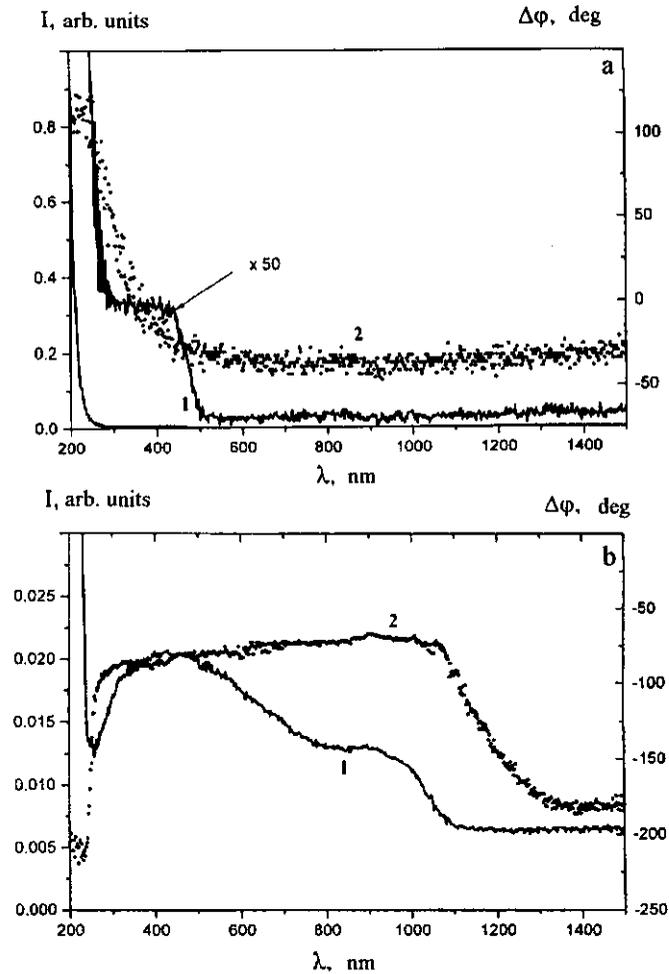


Fig. 2

Dependence of the amplitude  $I$  (solid curves 1 on an ordinary scale and with  $\times 50$  magnification) and of the phase  $\Delta\phi$  (dots, curves 2) of the photoacoustic signal on the light wavelength  $\lambda$  for a single crystal of synthetic diamond (a) and a polycrystalline diamond film on a silicon substrate (b).

of such a stack of diamond plates will be rather low, which will allow the PA spectrum to be recorded. In our case, it was sufficient to place two crystals in the cell. The spectral dependences for the amplitude and phase of the PA signal are shown in Fig. 2a (curves 1 and 2, respectively). The shape of the amplitude signal is analogous to the absorption spectra for diamonds of the Ib type: the increase of the amplitude of the PA signal on the UV-portion of the spectrum corresponds to the edge of the fundamental absorption near 250 nm, and the band with a long-wave edge near 500 nm is evidently due to the absorption at nitrogen centers [2, 6].

Figure 2b shows the PA spectra of a thin (10  $\mu\text{m}$ ) diamond film on a silicon substrate. An increase in the amplitude of the PA signal and the variation of its phase for quanta with an energy greater than the diamond forbidden band width equal to 5.5 eV ( $\sim 250$  nm) is noted. Appreciable absorption is also recorded in the visible light region, where the spectral dependence of the PA signal amplitude is similar to the absorption spectra of diamond monocrystals with various structural defects formed upon electron or neutron irradiation [2, 6]. Moreover, the amplitude dependence in Fig. 2b exhibits peculiarities not characteristic of single-crystalline specimens, in particular, a "dip" in the range from 250 to 350 nm. An analogous behavior was displayed by the photoconductivity spectra of polycrystalline diamond CVD films [7, 8].

The phase spectrum (curve 2 in Fig. 2b) in the visible region exhibits the character of a monotonic

dependence. Such a difference between the amplitude and the phase of the PA signal is probably associated with the fact that the amplitude is determined by the absolute value of energy of the light beam absorbed in the specimen and the phase reflects the spatial distribution of the evolved heat and depends on the relationship between the thermodiffusion length ( $\mu$ ), the depth of light absorption and the specimen thickness [4]. Thus, the experimental data point to a decrease in the share of light energy absorbed in the film within a relatively narrow range of the UV region without an appreciable change of the light absorption depth (the specimen thickness and the thermodiffusion length remain unchanged). This may occur if diffuse scattering or specular reflection of light in this spectral region increases [9].

The efficiency of diffuse scattering on a rough surface increases with a decrease of the light wavelength ( $\lambda$ ) by the law of  $\lambda^{-4}$  [10]. The specular reflection coefficient for diamond increases with decreasing  $\lambda$  in the same spectral region [6, 11]. Thus, the action of these two factors (scattering and reflection) may lead to a decrease of the share of light absorbed in the specimen in the UV region.

Another characteristic feature of polycrystalline films is a sharp decrease of the PA signal in the IR region, beginning with the light wavelength of  $\sim 1000$  nm corresponding to quantum energy close to the forbidden bandwidth of silicon ( $\sim 1.1$  eV). It is natural to presume that the indicated spectral peculiarity is due to the silicon substrate rather than to the diamond film. Indeed, as pointed out above, because of a high thermal conductivity, the thermodiffusion length in diamond (including polycrystalline films), just like the light absorption depth in the IR region, must exceed the film thickness and, accordingly, the PA signal will depend on the properties of both the film and the substrate. As the light modulation frequency increases, the effect of the substrate on the form of the PA spectra must diminish because of the decrease of the thermodiffusion length ( $\mu$ ). However, in accordance with the theory of the PA effect, the signal amplitude will also decrease simultaneously [4, 5]. The PA signal in the visible and IR regions for single crystals and polycrystalline films exceeded the amplitude of the noise signal for the modulation frequency of up to 200 Hz (up to 700 Hz in the UV region). All the spectra considered above (Fig. 2) were recorded at an optimal frequency of 90 Hz.

In contrast to single crystals and polycrystalline films, specimens of diamond powders may have a thickness exceeding the thermodiffusion length even at relatively low modulation frequencies. The signal-to-noise ratio increases also in a high-frequency range. Typical spectra recorded at light modulation frequencies of 90 and 1350 Hz are shown in Fig. 3. At a light modulation frequency of 90 Hz, the form of the spectral dependence of the PA signal amplitude for coarse-grained powders of the ASM type (up to  $1 \mu\text{m}$ ) is similar to the spectra of polycrystalline films. As the crystallite size decreases, the depth of the dip in the UV region increases and an enhancement of the PA signal in the visible region is also observed, this being an indication of the absorption increase due to structural defects of diamond [2, 6]. At a modulation frequency of 1350 Hz (Fig. 3b) the UV dip was observed only in the spectra of powders with crystallite size smaller than  $5 \mu\text{m}$ , which may be accounted for by a decrease of the thermodiffusion length. Accordingly, the number of faces through which the light propagates decreases and, hence, the share of the light specularly reflected from and diffusely scattered on these faces also decreases. The dependence of the PA spectra on the modulation frequency for coarse-grained powders is most pronounced.

The spectra of powders of the IRM type (particle size  $0.25 \mu\text{m}$ ) (curves 3 in Fig. 3a and b) do not practically exhibit a broad absorption band in the visible region of the spectrum, which is evidently associated with the specificity of the technology of synthesis and purification of this material. Another marked difference was the absence of a UV dip in the course of the spectral dependence. Such small particles presumably form, as a result of coalescence, a dense structure with an insignificant surface roughness, which together with the absence of specularly reflecting faces, leads to a decrease of the corresponding loss of light. This is confirmed by the fact that the shape of the spectral curves for this type of powder varies slightly with frequency (see Fig. 3).

From the experimental results considered above it follows that the frequency dependence of the PA signal may serve as an additional source of information about the properties of diamond materials. However, the sensitivity of the system that records the acoustic signal in the photoacoustic spectrometer was insufficient for such measurements at high frequencies. Therefore, the frequency dependences were determined using a 150-W deuterium lamp as a light source. The radiation of the lamp, the major portion of which is in the UV region (200–300 nm), was focused directly onto the specimen. Thus it was possible to increase the PA signal amplitude and to conduct measurements for frequencies of up to 3 kHz.

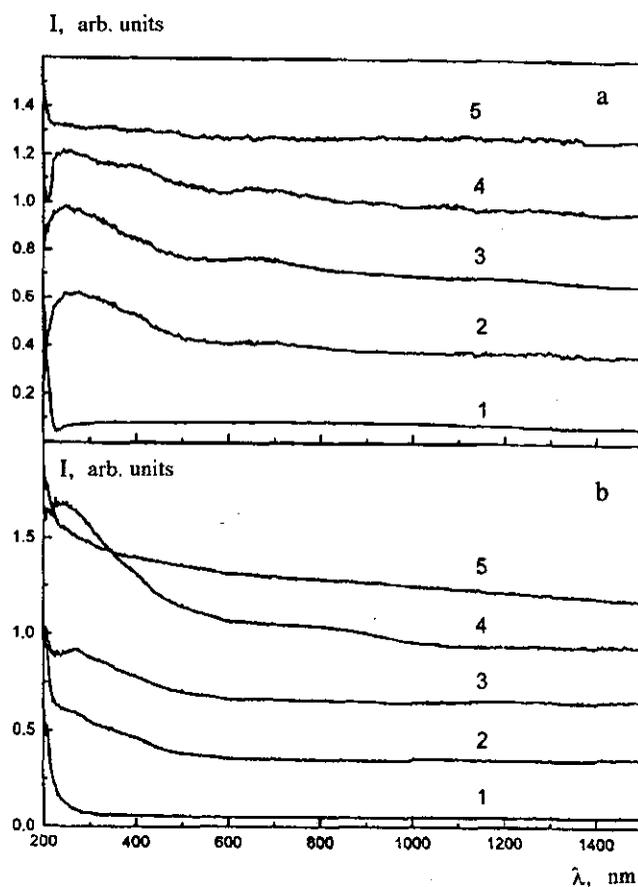


Fig. 3

Spectral dependence of the amplitude of the photoacoustic signal  $I$  for various diamond powders (ASM 125/100 (1), ASM 7/5 (2), ASM 5/3 (3), ASM 1/0 (4), IRM 0.25/0 (5) measured at light modulation frequency of 90 Hz (a) and 1350 Hz (b).

According to the theory and experimental data for materials with a high light absorption coefficient and a rather low thermal conductivity (in particular, for amorphous carbon black), the PA-signal amplitude is inversely proportional to the light modulation frequency [4, 5]. Based on this reliably established fact, we preliminarily determined the frequency dependence of the sensitivity of the recording system, which was then used to correct the frequency dependence of the PA-signal amplitude for the study of specimens of diamond materials.

The corrected frequency dependences (Fig. 4) are well linearized on a log-log scale. The slope of the corresponding straight lines decreases monotonically with decreasing size of diamond crystallites (from 300  $\mu\text{m}$ , which is the thickness of the single crystal, to 1  $\mu\text{m}$ ). For the single crystal the PA-signal amplitude is proportional to  $\sim \omega^{-3/2}$ , which corresponds to the case where the effective depth of light absorption exceeds the specimen thickness and the thermodiffusion length [4]. This is consistent with the known value of the light absorption coefficient for diamond [2, 6]. For the ASM 1/0 powder the slope of the straight line corresponds to the inverse proportional dependence of the PA-signal amplitude on the frequency ( $\sim \omega^{-1}$ ), just as in the case of the amorphous carbon black. It is necessary to note that the PA-signal amplitude for the ASM 1/0 powder is close in absolute value to that for carbon black; for a powder of the IRM type the amplitude is somewhat lower, which is evidently accounted for by a certain increase of the light absorption depth due to a decrease of light scattering and reflection and also by a possible increase of the thermodiffusion length because of a close contact of diamond particles.

The frequency dependence (curve 7 in Fig. 4) obtained for a polycrystalline film 50  $\mu\text{m}$  thick has the same slope as in the case of a diamond single crystal. Though the exact determination of the slope

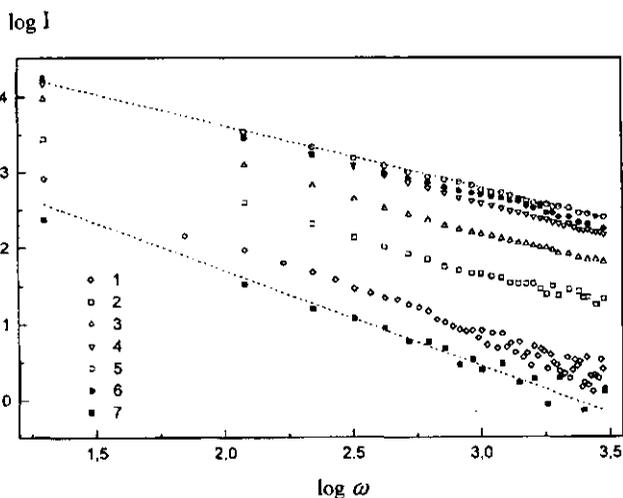


Fig. 4

Dependence of the amplitude of the photoacoustic signal on the light modulation frequency for a diamond single crystal (1), diamond powders: ASM 125/100 (2), ASM 20/14 (3), ASM 7/5 (4), ASM 1/0 (5), IRM 0.25/0 (6), and for a diamond polycrystalline film (7).

this dependence in a high-frequency range is hampered because of the impaired signal-to-noise ratio, the experimental data allow us to arrive at the conclusion that the thermodiffusion length for such films is not smaller than their thickness and, hence, the thermal conductivity is not lower than  $10 \text{ W}\cdot\text{cm}^{-1}\cdot\text{K}^{-1}$ .

Thus, the optical properties of polycrystalline CVD films and powders exhibit, along with the peculiarities of diamond single crystals (the presence of the fundamental absorption edge near 5.5 eV and absorption bands due to the crystal structure defects), differences determined by the scattering and reflection of light on the crystallites faces. The efficiency of such scattering increases with a decrease of the size of diamond particles to fractions of a micrometer. Upon further decrease of the crystallite size (below  $0.25 \mu\text{m}$ ), the efficiency of diffuse scattering decreases because of the coalescence of particles and that of specular reflection decreases because of the absence of plane faces.

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## REFERENCES

1. B.V. Spitsyn, in: *Handbook of Crystal Growth*, vol. 3 (ed. by D.T.J. Hurtle), Elsevier Science B.V., Amsterdam, 1994.
2. K.E. Spear and J.P. Dismukes, eds., *Synthetic Diamond: Emerging CVD Science and Technology*, Wiley & Sons, Inc., New York, 1994.
3. V.B. Kvaskov, ed., *Diamond in Electronic Engineering* (in Russian), Moscow, 1990.
4. A. Rosencwaig, *Photoacoustics and Photoacoustic Spectroscopy*, J. Wiley & Sons, New York, 1980.
5. A. Rosencwaig, *Rev. Sci. Instr.*, vol. 48, no. 9, p. 1133, 1977.
6. J.E. Field, ed., *The Properties of Diamond*, Academic Press, London, 1990.
7. M.D. Whitfield, R.D. McKeag, L.Y.S. Pang et al., *Diamond and Related Materials*, vol. 5, p. 829, 1996.
8. S. Salvatori, R. Vincenzoni, M.C. Rossi et al., *Ibid.*, p. 775.
9. R. Tilgner, *Appl. Opt.*, vol. 20, p. 3780, 1981.
10. G.S. Landsberg, *Optics* (in Russian), Moscow, 1976.
11. H.R. Phillip and E.A. Taft, *Phys. Rev.*, vol. 127, p. 159, 1962.