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Internal structure parameters and synthesis conditions of polycrystalline diamond films

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The dependence of the internal structure parameters of polycrystalline diamond films on their thickness that is a function of the synthesis duration at the specified temperature has been studied. It has been established that the block size and the film micro-distortions are reduced at the temperature 1073 K and the gas mixture pressures of 10.6 and 21.3 kPa. The dislocation density remains almost unchanged when passing from "thin" films (4-6 μm) to "thick" ones (10-12 μm). At the temperature 1173 K and gas mixture pressures 10.6 and 21.3 kPa, the block size diminishes and micro-distortions increase when the film thickness rises. The dislocation density increases in this case. These two polycrystalline diamond films synthesis regimes are of good prospects for study of the polycrystalline diamond films electron properties formation, since the dislocations give rise to electrical active centers in diamond materials. The recrystallization of the polycrystalline diamond films crystallites starts at 1273 K and pressures of 10.6, 21.3, 31.9 kPa or at pressure 31.9 kPa and synthesis temperatures 1073 K, 1173 K, 1273 K. That effect hinders the control dislocation density control.

Изучена зависимость параметров внутренней структуры поликристаллических алмазных пленок от их толщины, которая является функцией продолжительности синтеза при заданной температуре. Установлено, что при температуре 1073 K и давлениях газовой смеси 10.6 и 21.3 kPa размеры блоков и микроискажения пленок уменьшаются, плотность дислокаций почти не изменяется при переходе от "тонких" (4–6 мкм) пленок к "толстым" (10–12 мкм). При температуре 1173 K и тех же давлениях газовой смеси увеличение толщины пленок приводит к уменьшению размера блоков, к увеличению микроискажений. Плотность дислокаций возрастает. Эти два режима синтеза поликристаллических алмазных пленок являются перспективными при изучении формирования их электронных свойств, так как дислокации являются источником электрически активных центров в алмазных материалах. При температуре 1273 K и давлениях 10.6, 21.3, 31.9 kPa, а также при давлении 31.9 kPa и температурах синтеза 1073 K, 1173 K, 1273 K начинается процесс рекристаллизации кристаллитов поликристаллических алмазных пленок, который затрудняет управление плотностью дислокаций.

The substantial advances in novel synthetic technologies of diamond films and coatings from gas media under low pressures [1] make it necessary to develop the processes for the electron property formation thereof needed in electronics, optics, and other fields. The researchers try to generate the electrically active centers in diamond by introducing the appropriate impurity atoms according to scheme developed for conventional semiconductors. However, two important factors remain out of account. First, it is known that in wide bang gap dielectrics, including diamond (the band gap width 5.5 eV), the impurities form an inverse system of energy levels with donor

impurities forming deep donor levels at the valence band top. In the Schottky notation, such impurities are referred to as "cis-donors". The acceptor impurities form deep acceptor levels near the conductivity band bottom. Such a system of energy levels is known when the matter concerns the arrangement of the levels resulting from surface centers in conventional semiconductors. Second, the semiconducting diamonds of IIb type discovered in 1952 have a mosaic internal structure that, according to Lang and co-workers [2] is formed due to plastic straining of insulating ("nitrogen-free") IIa type diamonds under natural conditions. The IIb type diamonds consist of weakly disoriented mosaic blocks with small-angle dislocation boundaries. The dislocation density in such diamonds attains 10^{11} to 10^{12} m^{-2} and more. But according to [3], the unsaturated bonds in the dislocation core of diamond-like structure crystals form acceptor levels and provide the hole type conductivity that is present in all the natural IIb diamonds.

When studying the plastically strained "nitrogen-containing" I type diamonds from Yakutian fields, we have found the same semiconducting properties therein as in the IIb ones [4, 5]. We have referred to such diamonds as Ic type ones. In those diamonds, all the singularities of electron properties are traced typical of the IIb ones with only quantitative differences. Basing on detailed studies of electron properties of the Ic diamonds and consideration of literature data on the IIb ones, we have developed a dislocation concept of the electron property formation in diamonds, including the semiconducting ones. This conception has been confirmed definitively in our further works [6, 7].

Since the problem of electron property formation in diamonds by impurity atoms remains unsolved in principle to date but is under study and discussion, we propose to extend the dislocation concept of the electron property formation onto undoped synthetic diamond films (DF). This work is devoted to dislocation structure formation in synthetic DF as a function of some important parameters of synthesis thereof from a gaseous phase. To that end, the main aims were to study the effect of the substrate temperature, the total pressure of gas mixture in working chamber, and the DF synthesis duration on the dispersity of mosaic blocks and microscale distortions, that define in the end the dislocation density therein.

In this work, the DF samples have been prepared, the DF internal structure has been determined (the mosaic block size and microscale distortions) by X-ray diffraction (XRD) technique, the density of dislocations forming the interblock boundaries has been estimated [8, 9].

It is known [1] that the temperature dependence of the single-crystalline and polycrystalline DF growth rate is described by a Gaussian function, no matter what is the synthesis technique. Its maximum is near 1173 K. The same dependence has been found in our experiments. The DF for electronics and optics are synthesized usually at 973 to 1173 K [1]. In those conditions, the grain (crystallite) size increases monotonously and the size of the coherent scattering regions that form the crystallites are diminished monotonously as the film thickness rises. As the synthesis process is complex and prolonged, we have used only three characteristic points in the temperature dependence of the DF synthesis rate, namely, 1073 K (in the ascending dependence branch), 1173 K (at its maximum) and 1273 K (in the descending branch). The experiment scheme is presented in Table 1.

DF sample preparation. The high-gradient transport chemical reaction technique [1] was used. The synthesis was carried out starting from methane /hydrogen (2/98 vol. %) mixture. The high-purity graphite heated up to about 2273 K was used as an activator. The diamond films were deposited onto single crystal silicon plates arranged at about 2 mm distance from the activator.

Two groups of DF were synthesized. The first consisted of "thin" (4 to 6 μm thick) films. The average synthesis duration of those samples was about 1 h. The second

Table 1. Polycrystalline DF synthesis conditions.

T_{synth}, K	P_{synth}, kPa	No. samples	
		"thin" (h = 4–6 μm)	"thick" (h = 8–11 μm)
1073	10.6	40	70
	21.3	1	31
	31.9	61	91
1173	10.6	50	80
	21.3	11	41
	31.9	71	2
1273	10.6	60	90
	21.3	21	51
	31.9	81	12

("thick") group samples were 8 to 11 μm thick (the synthesis duration about 3 h). Both groups were synthesized in identical conditions, except for the synthesis duration.

XRD studies were carried out using a standard DRON-2 instrument. A copper anode was used to provide the $K_{\alpha 1}$ emission that was discriminated out of CuK_{α} doublet using the Rachinger graphical method. The $\Theta/2\Theta$ scanning according to Bragg-Brentano scheme was used. The integral width of Bragg reflections were determined by calculating the intensity ratio thereof to the counting rate in the peak, the background values being subtracted. The diffraction peak positions was determined by the median method [10].

Since the synthesized diamond films are polycrystalline, the work is based on the common simplified model of polycrystals. In the model, the diffraction maxima are widened mainly due to micro-distortions caused by extended structure defects (predominantly by dislocations) and to finiteness of the X-ray coherent scattering regions (CSR). Such a simplification of polycrystalline (powdered) solids gives the same results that were obtained in [11] for chaotically oriented dislocations in single crystals. Basing on theoretical concepts [10, 11], we have determined the physical widening of the diffraction maxima β and then the CSR dispersity and micro-distortions. The experimental data were processed according to [4]. To that end, the line width B was measured in all the samples for two distant reflections θ_{111} and θ_{331} as well as the same widths for a reference sample (annealed nickel powder with particle size about 2000 Å). For the reference, $b_{111} = 2.0 \cdot 10^{-3}$ rad and $\theta_{331} = 4.15 \cdot 10^{-3}$ rad. When seeking for β, the diffraction maxima were approximated by Gaussian functions. For the convoluted Gaussian function, the following relationship is valid:

$$B^2 = b^2 + \beta^2. \tag{1}$$

From that expression, the physical diffraction peak widening β was calculated for the specified angles in all the samples.

When determining the contribution from CSR dispersity (m) and micro-distortions (n) into β, the approximating Gaussian functions were used, too. In this case, the relation

$$\beta^2 = m^2 + n^2 \tag{2}$$

is valid. Basing on that relationship and on the expressions for m and n depending on the diffraction angle in different fashions:

$$m = \frac{\lambda}{D\cos\theta}, \tag{3}$$

$$n = 4\varepsilon \cdot \mathrm{tg}\theta \tag{4}$$

the Hall plots were constructed for each of the samples and $1/D^2$ and ε^2 were found therefrom.

The average linear dimensions (D) of CSR along the normal to the reflecting planes and the average values of micro-distortion module $\varepsilon = \langle|\Delta d/d|\rangle$ are presented in Table 2. Since diamond is weakly anisotropic, the CSR dimensions can be assumed to be close to those of the mosaic blocks. In what follows, the symbol B will be considered approximately as the linear dimensions of mosaic blocks (MB).

Estimation of dislocation density. Using the data from Table 2 (D and ε values), the dislocation density in each sample has been estimated basing on the results taken from [4] and employing the following relationships.

If the reflection widening is due mainly to the block dimension D and the relation $\sec\theta_{331}/\sec\theta_{111} \approx \beta_{331}/\beta_{111}$ is valid, then the dislocation density can be estimated as

Table 2. Parameters of internal structure.

No. samples	Linear dimensions (D), nm	Micro-distortion module $\varepsilon \cdot 10^{-3}$
40	57	1,6
50	53	1.3
60	34	1.8
70	45	0.45
80	30	1.5
90	60	1.5
1	49	2.4
11	46	1.2
21	30	2.4
31	33	1.9
41	43	1.9
51	45	1.7
61	22	1.7
71	53	1.9
81	19	0.9
91	36	0.48
2	53	1.7
12	35	0.1

$$\rho_p = \frac{3n}{D^2}, \quad (5)$$

where n is the number of dislocations on the block plane; D, the block average linear dimension. In our estimations, $n = 1$.

If the reflection widening is due mainly to the micro-distortions ε and the relation $tg\theta_{331}/tg\theta_{111} \approx \beta_{331}/\beta_{111}$ is valid, then the dislocation density can be estimated as

$$\rho_s = \frac{k}{F} \cdot \frac{\varepsilon^2}{b^2}, \quad (6)$$

where for diamond, $k = 19.2$, $\mathbf{b}$ is the Buergers vector along [110] axis. The factor F takes into account the dislocation interaction. For non-interacting or weakly interacting dislocations, F can be supposed to be 1. In this case,

$$\rho_s = \frac{19.2 \cdot \varepsilon^2}{b^2}. \quad (7)$$

Since the parameter ε is sensitive to internal stresses $\sigma_{total} = \sigma_{thermal} + \sigma_{intrinsic}$, we have carried out the strain-gauge studies of all the considered PDF samples. The $\sin^2\Psi$ method [12] was used to that end. The PDF grown on silicon substrates were found to be not affected appreciably by σ_{total} within the measurement accuracy of the unit cell parameter of $2 \cdot 10^{-4}$ nm. Thus, the internal stresses $\sigma_{intrinsic}$ caused by structure imperfection are low enough as well as those due to thermal factors ($\sigma_{thermal}$).

If the diffraction maxima are widened due to the block dimensions D and micro-distortion values ε, then, the dislocation density can be estimated as the geometric mean of ρ_p and ρ_s, that is,

$$\rho = \sqrt{\rho_p \rho_s}. \quad (8)$$

The estimation results of the dislocation density in "thin" and "thick" DF are presented in Fig. 1a, b. The Figures illustrate the local density values Γ for dislocations concentrated within a thin interlayer between the adjacent MB. Those are similar to the dislocation densities at the interface of two crystals with unit cell parameters close to one another [4].

Since according to our suppositions, the electron properties formation in diamond is due mainly to dislocations that are related directly to the DF growth rate, Fig. 1 shows the estimated dislocation density in combination with dependences of "thin" and "thick" DF growth rate on the substrate temperature. For the "thin" films (Fig. 1a), it is seen that as the total gas pressure in the reaction chamber is increased from 10.6 kPa to 31.9 kPa, the dislocation density in the ascending Gaussian branch (1073 K) increases from $1.1 \cdot 10^{16}$ m^{-2} to $3.4 \cdot 10^{16}$ m^{-2} while in the descending branch (1273 K), $1.3 \cdot 10^{16}$ m^{-2} to $4.2 \cdot 10^{16}$ m^{-2}. However, at the DF synthesis temperature near 1173 K, the dislocation density in the films synthesized under various pressures from 10.6 kPa to 31.9 kPa takes minimum values near $1.1 \cdot 10^{16}$ m^{-2} (from $9.1 \cdot 10^{15}$ m^{-2} to $1.7 \cdot 10^{16}$ m^{-2}). This result corresponds to the dislocation density minimum determined by us basing on the Hook law and the MB surface tension energy in those samples [4].

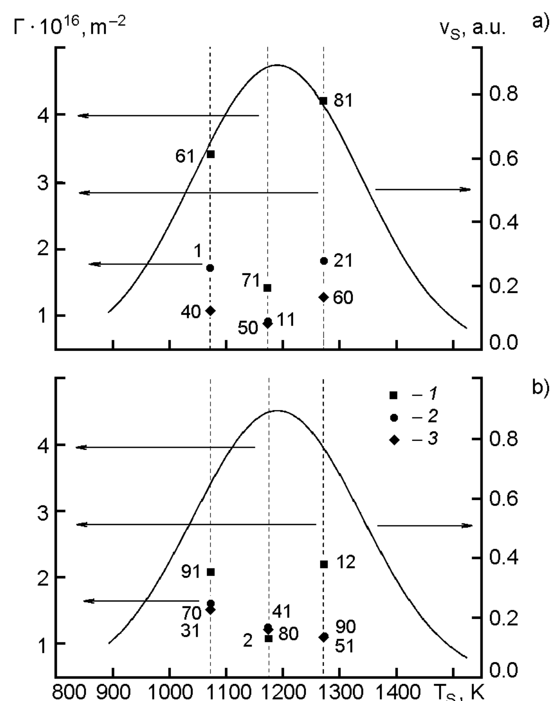

Fig. 1. Dependence of dislocation density in DF on the substrate temperature T_s and the total gas mixture pressure in the growth chamber p_s against the background of the growth rate for 5–6 μm (a) and 9–11 μm (b) thick samples.

Fig. 1a illustrates the possibility to control the dislocation density by varying the gas mixture pressure at constant temperature. As the synthesis temperature approaches that of the maximum growth rate (1173 K), the range of dislocation density variation is converged. The dislocation density can be controlled also by another man-

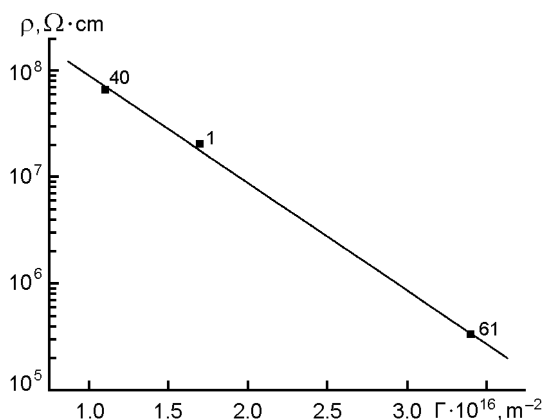

Fig. 2. Relationship between the conductivity and growth rate in DF synthesized at T_s = 1073 K and the gas mixture pressures (kPa) 10.6; 21.3, and 31.9.

ner, by varying the substrate temperature at constant gas mixture pressure. In this case, the dislocation density variation range is enlarged as the pressure rises and is essentially unchanged at 10.6 kPa.

In Fig. 1b, presented is the relation between the dislocation density in "thick" DF and the synthesis temperature and total the gas mixture pressure in the reaction chamber. The relation is similar to that for "thin" DF. However, the film thickness increase and the respective synthesis time increase influences the dislocation structure. The range of dislocation density variation as a function of the gas mixture pressure is about thrice narrower. However, the dislocation density in "thick" DF at the maximum growth rate is the same at any pressure and takes the minimum values close to that in the "thin" films, i.e., about $1.1 \cdot 10^{16}$ m^{-2}.

To illustrate the applicability of the dislocation conception to DF, the conductivity thereof was measured. The results for "thin" films synthesized at 1073 K (the ascending branch of the growth rate dependence on the synthesis temperature) is presented in Fig. 2 that illustrates the relationship between the conductivity and dislocation density. As the dislocation density increases (due to increasing gas pressure), the conductivity drops. This effect is more pronounced as low substrate temperature. In the descending branch of the above dependence (at 1273 K), the DF conductivity decreases also as the dislocation density increases, but in another manner that in the ascending branch. At 1173 K, the conductivity varies within a narrow range ($1 \cdot 10^5$ Ω·cm to $6.5 \cdot 10^5$ Ω·cm) for all the samples, in accordance with the narrow range of the dislocation density therein.

The results obtained evidence the possible ways to control the internal dislocation structure and conductivity of DF by varying the synthesis parameters. The control is most effective when the synthesis temperature corresponds to the ascending branch of the growth rate dependence on the substrate temperature (973 to 1173 K). The conductivity dependence on the dislocation density for DF is similar to that for bulk diamond crystals.

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Параметри внутрішньої структури полікристалічних алмазних плівок і умови їх синтезу

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Дослідженно залежность параметрів полікристалічних алмазних плівок відносно їх товщини, яка є функцією тривалості синтезу при заданій температурі підкладок (температурі синтезу). Встановлено, що при температурі 1073 K і тиску газової суміші 10.6 та 21.3 кПа розміри блоків та мікровикривлення плівок зменшуються, густина дислокацій майже не змінюється при переході від синтезу "тонких" (4–6 мкм) плівок до "товстих" (10–12 мкм). При температурі 1173 K і тих же умовах тиску газової суміші збільшення товщини плівок приводить до зменшення розміру блоків і до збільшення мікровикривлень. Густина дислокацій збільшується. Ці два режими синтезу полікристалічних алмазних плівок є перспективними для дослідження процесів формування електронних властивостей полікристалічних алмазних плівок, так як дислокації являються джерелом створення електрично активних центрів в алмазних матеріалах. При температурі синтезу 1273 K і тиску 10.6, 21.3, 31.9 кПа, а також при тиску 31.9 кПа і температурах синтезу 1073 K, 1173 K, 1273 K починається процес рекристалізації кристалітів полікристалічних алмазних плівок, що утруднює управління густиною дислокацій.