# Prospects for the synthesis of large single-crystal diamonds 

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#### Abstract

The unique properties of diamond have stimulated the study of and search for its applications in many fields, including optics, optoelectronics, electronics, biology, and electrochemistry. Whereas chemical vapor deposition allows the growth of polycrystalline diamond plates more than 200 mm in diameter, most current diamond application technologies require largesize ( 25 mm and more) single-crystal diamond substrates or films suitable for the photolithography process. This is quite a challenge, because the largest diamond crystals currently available are 10 mm or less in size. This review examines three promising approaches to fabricating large-size diamond single crystals: growing large-size single crystals, the deposition of heteroepitaxial diamond films on single-crystal substrates, and the preparation of composite diamond substrates.


Keywords: single-crystal diamond, chemical vapor deposition, epitaxy

## 1. Properties and prospects of applying diamond in optics and electronics

Practically every current scientific publication concerning diamonds begins with description of their unique, sometimes exceptional, properties (at room temperature), such as chemical inertness, hardness ( $80-100 \mathrm{GPa}$ ), thermal conductivity up to $20 \mathrm{~W} \mathrm{~cm}^{-1} \mathrm{~K}^{-1}$, Young's modulus of 1050 GPa ,

[^0]Debye temperature of around 2000 K , linear thermal expansion coefficient of $1.2 \times 10^{-6} \mathrm{~K}^{-1}$, refractive index of 2.41, optical transparency at wavelengths above 225 nm , coefficient of friction in the air of $0.05-0.1$, gap width of 5.4 eV , density of $3.515 \mathrm{~g} \mathrm{~cm}^{-3}$, breakdown electric field strength of $10^{7} \mathrm{~V} \mathrm{~cm}^{-1}$, dielectric constant of 5.7, charge carrier mobility of order $2000 \mathrm{~cm}^{2} \mathrm{~V}^{-1} \mathrm{~s}^{-1}$, velocity of charge carriers up to $10^{7} \mathrm{~cm}^{-1} \mathrm{~s}^{-1}$, and exciton binding energy of 80 meV [1]. Characteristically, certain phenomena manifested in diamonds at room temperature, e.g., exciton production, can be observed in other materials only under deep cooling conditions.

Thus far, the main fields of diamond applications have been the jewelry business and industry, including the production of abrasive instruments indispensable in many modern manufacturing segments. Synthetic diamonds are currently available in a variety of forms, such as single crystals and single-crystalline plates up to 15 mm in size, powders differing in the degree of coarseness and fineness, and polycrystalline plates with crystals of various shapes and sizes: from hundreds of micrometers to nanometers. Such diversity stimulated research and attempts to use diamonds in various fields, including electronics, optics and lasers, quantum computers and information processing, biology, high-pressure technologies, heat sink, tribology, electrochemistry and corrosion protection, thermal field emission, electroacoustics, microelectromechanical devices, radiation, and chemical sensors [2, 3].

The synthesis of boron-doped p-type diamonds gave rise to hopes that they can be utilized as an important material for semiconductor electronics and optoelectronics [4]. However, no diamond-based electronic device has yet been produced commercially, despite numerous presentations of different types of diodes and transistors. The difficulty arises due to the absence of small acceptors and donors. The activation energy of boron (acceptor) and phosphorus (donor) dopant atoms is 0.37 and 0.59 eV , respectively [2, 3]. Only a small fraction of
them undergoes ionization at room temperature, which accounts for a very high-ohmic resulting material. In modern electronics, diamonds may find application largely in powerful microwave instruments capable of operating under extreme conditions, and various types of ionizing radiation detectors [3, 5, 6]. The development of technologies for $\delta$-doping of diamonds to be used in semiconductor devices is currently underway [ 3,7$]$. The discovery of superconductivity in diamonds strongly doped with boron opened up interesting prospects for their new implementations [8].

Recent years have seen tremendous growth in diamond applications in optical systems for the detection, storage, transmission, and processing of information. The reader is referred to monograph [10] for a detailed analysis of these investigations. Ongoing studies aim to develop photolithography and other diamond treatment technologies to be used in designing optical circuits [11], resonators [12], optical waveguides, and optomechanical and micromechanical devices [13, 14]. Much attention is given to some optical centers in diamonds, first and foremost NV-centers (Fig. 1). Researchers learnt how to create individual optical centers and how to handle them. The NV-complex (nitrogen atom plus vacancy in the nearest neighbor positions) possesses unique properties. Specifically, a single-photon optical center operates at room temperature, has two charge states, and can be controlled by magnetic, electric, and microwave
impacts. These characteristics coupled to the possibility of selective addressing and narrow zero-phonon lines allow employing the coherence of light [15]. Such optical centers may find application in quantum nanotechnologies, including optical schemes for quantum data processing, the readout of individual spins, highly sensitive magnetometers, electrical and chemical sensors, and the optical coupling of adjacent centers (two-photon entanglement) [10]. The main methods for the creation of an NV-complex are electron irradiation or ion implantation followed by annealing.

Various applications of diamonds (including jewelry) require their treatment by cutting, polishing, and other methods. The properties of diamonds making them so valuable for application in technology and electronics account for the difficulty in processing them [16]. Diamond is the hardest-known material. It is almost free from plastic strain, has a high thermal conductivity, and exhibits strongly anisotropic wear properties; also, it is fragile due to a perfect cleavage plane running parallel to the octahedral faces and shows exceptional chemical stability. Diamonds intended for application in modern technologies must have a high-quality defectless surface layer, which is very difficult to achieve [17].

The adoption of diamond across modern electronics and optics requires the implementation of microelectronic technologies oriented to photolithographic procedures. The


Figure 1. (Color online.) Properties of the NV-center: (a) crystalline structure of the NV complex, (b) photoluminescence spectrum of $\mathrm{NV}^{-}$and $\mathrm{NV}^{0}$ optical centers at room temperature, (c) scanning confocal optical microscopy images of the regions irradiated by electrons at different doses (topbefore annealing, bottom - after annealing), (d) photoluminescence spectra of the regions shown in figure (c); luminescence intensity of NV-centers increases with the irradiation dose (taken from Ref. [9]).
main difficulty arises from the absence of single-crystal diamond plates suitable for the photolithography process. Commercially available single-crystalline plates of synthetic diamond are very expensive. For example, an $8 \times 8$-mm high-quality (electronic grade) plate costs 2,345 GBP (www.e6cvd.com). The crystalline structure and impurity content of synthetic diamonds make them as yet unsuitable for certain modern applications, despite continuous progress [18].

The present review focuses on prospects for the synthesis of large ( 25 mm and more) single-crystalline diamond. This problem becomes increasingly important in diamond technology, and it can be expected that the near future will bring its successful solution. Meanwhile, there is no relevant review, even in the English-language literature.

## 2. High-pressure synthesis of single-crystal diamonds

The discovery of thermodynamic phenomena underlying the existence of graphite and diamond phases [19] made it possible to implement in the 1950s diamond crystal growth technology at high pressures and high temperatures (HPHT) [20, 21]. The HPHT method is employed to grow diamond grits and powders for large-scale applications mainly in the toolmaking industry. In 1971, General Electric Research Center (USA) proposed a modified HPHT technique by adding the temperature gradient across the reaction chamber [22]. This method was further employed to grow yellow (nitrogen-containing) single-crystal diamonds of good quality weighing 1-2 carats and measuring 5-6 mm in size. Ten years later, the temperature gradient method came to growing $7-8$-carat clear crystals ( 10 mm in size) [23]. These crystals are superior to the best natural ones. They are transparent to electromagnetic radiation with a wavelength above 225 nm and contain small amounts of impurity (less than 0.1 ppm of nitrogen). The best specimens of such diamonds have few crystalline defects and are free from internal stresses.

Diamonds synthesized by the temperature gradient method are grown in high-pressure chambers at around 6 GPa and $1600-1700 \mathrm{~K}$. A variant of such chambers is schematically depicted in Fig. 2. The carbon source is positioned in the top (hottest) part of the chamber over the solvent-catalyst metal (usually $\mathrm{Fe}, \mathrm{Ni}$, or Co ). A small seed crystallite (or crystallites) is placed in the bottom (coldest) part of the chamber. The driving force of crystallization is created by the difference between carbon solubilities in the metal across the temperature gradient. The growth rate of a high-quality crystal is $6-9 \mathrm{mg} \mathrm{h}^{-1}$ [24], and its maximum size reaches $15 \mathrm{~mm} . \mathrm{Ti}$ and Al , known to form stable complexes with nitrogen, are added to serve as its getters. Another variant of diamond growth chambers is a press-free 'split-sphere' apparatus, proposed by Pal'yanov et al. [25].

Crystals grown by the temperature gradient method have a sectoral structure (Fig. 3) and frequently contain inclusions of a metal solvent or carbides. Sectors differ in crystalline perfection and impurity content. The (001) growth sector has the most perfect crystalline structure and the lowest impurity level [24]. Sectors are bounded by a material with a high amount of dislocations [26, 27]. Despite considerable progress in HPHT technology, it remains of small value for fabricating large single-crystal diamond plates. The growth of large single-crystal diamonds by this method requires large reaction vessels and huge high-pressure apparatuses, the cost and technical complexity of which sharply increase with chamber linear dimension [27]. At the same time, HPHT-grown singlecrystals are the best substrates for epitaxial chemical vapor deposition (CVD) growth. Because an epitaxial material inherits as a minimum extended structural defects from the substrate [26], the most perfect crystalline substrates need to be utilized for epitaxial diamond growth. Today, it is possible to synthesize a diamond with the most perfect crystalline structure from (001) growth sectors of HPHT-grown crystals [28] (see the central square region in Fig. 3 borrowed from Ref. [26]).


Figure 2. Schematic of a belt type high-pressure chamber and high-pressure cells for growing single-crystal diamonds by the temperature gradient method (taken from Ref. [24]).


Figure 3. (Color online.) HPHT-grown single-crystal (001) plate (taken from Ref. [26]): (a) growth sectors are revealed by etching in an oxygen-hydrogen plasma, (b) photoluminescence topographic image, (c) scanning electron microscopic (SEM) image, and (d) schematic of growth sector identification: (100) faces are shown in white or grey (1), (110) in pink (2), (113) in blue (3), and (111) in green (4).

The CVD method for diamond synthesis is free from spatial limitations on single-crystal growth. It is applied to produce polycrystalline diamond films $10 \times 50 \mathrm{~cm}$ in size (http://condias.de/en/products/diachem/index.html).

## 3. Method of chemical vapor deposition for diamond synthesis

Diamond synthesis by the chemical vapor deposition technique is usually realized in a special reactor. The main stages of diamond growth by the CVD method are shown schematically in Fig. 4. They include feeding gas into the reactor, thermal or plasma activation of the reactants, transport of active radicals and molecules toward the growing surface, chemical and diffusion processes on the surface, and the production of the diamond and other carbon crystal forms. A hydrocarbon (usually methane) highly diluted with hydrogen is used as a carbon source. Sometimes, oxygen or nitrogen compounds are added to the gas mixture. Plasma excitation in a microwave discharge provides the most efficacious and widely used tool for gas mixture activation.

The growth of diamonds under low pressures was first proposed in Ref. [30] and has come under intense study in the 1980s, when the improvement in the CVD method [31, 32] opened up numerous possibilities for the application of synthetic diamonds. The 'standard model' describing phenomena in the gaseous phase and on the growing diamond surface was elaborated by the late 1990s [33]. This model is based on in situ diagnostics of chemical components in the reactor and the ex situ measurements of the chemical reaction products on the diamond surface and of the structure taking into consideration the results of organic chemistry research. The standard model fairly well describes the main features of CVD diamond synthesis, shows ways to accelerate crystal growth, and improve the crystal quality [34]. The key role in CVD technology [36] is played by hydrogen involved in chemical processes in the gaseous phase [35] and on the diamond surface:
(1) atomic hydrogen reacts with neutral molecules, such as $\mathrm{CH}_{4}$, and turns them into active radicals, e.g., methyl radical $\mathrm{CH}_{3}$ which serves as a source of diamond growth:

$$
\begin{equation*}
\mathrm{CH}_{4}+\mathrm{H} \leftrightarrow \mathrm{CH}_{3}+\mathrm{H}_{2} ; \tag{1}
\end{equation*}
$$

(2) atomic hydrogen saturates 'dangling' bonds (open positions) on the diamond surface and thereby prevents its graphitization;


Figure 4. Main stages of CVD diamond synthesis (taken from Ref. [29]).
(3) atomic hydrogen activates the diamond surface and thus secures a fraction of surface carbon atoms with a dangling bond on which the hydrocarbon radical may adsorb; hydrogen adsorbed on the diamond surface promotes the important process of surface migration for hydrocarbon groups [37];
(4) atomic hydrogen releases $\mathrm{sp}^{2}$-carbon (graphite) much faster than $\mathrm{sp}^{3}$-carbon (diamond); in this way, atomic hydrogen turns any graphite-like cluster from the growing surface back into the gaseous phase;
(5) atomic hydrogen rapidly breaks up long-chain hydrocarbon molecules into small radicals; in this way, it prevents the formation of polymers or ring structures in the gaseous phase that can deposit onto the growing surface and thereby interfere with diamond growth.

The main reactions on the diamond surface [34] can be written in the most general form as

$$
\begin{align*}
& \mathrm{C}_{\mathrm{D}} \mathrm{H}+\mathrm{H} \leftrightarrow \mathrm{C}_{\mathrm{D}}^{*}+\mathrm{H}_{2},  \tag{2}\\
& \mathrm{C}_{\mathrm{D}}^{*}+\mathrm{H} \leftrightarrow \mathrm{C}_{\mathrm{D}} \mathrm{H},  \tag{3}\\
& \mathrm{C}_{\mathrm{D}}^{*}+\mathrm{C}_{x} \mathrm{H}_{y} \leftrightarrow \mathrm{C}_{\mathrm{D}}-\mathrm{C}_{x} \mathrm{H}_{y} \rightarrow \mathrm{C}_{\mathrm{D}} \mathrm{H} . \tag{4}
\end{align*}
$$

Here, $C_{D}$ is the carbon atom at the diamond surface, $C_{D}^{*}$ is the diamond surface atom with a dangling bond, and $\mathrm{C}_{\mathrm{D}} \mathrm{H}$ is the diamond-surface carbon atom with a hydrogen-saturated bond. Reaction (2) describes the formation of an open position with a dangling bond on the diamond surface, reaction (3) describes the saturation of this bond with atomic hydrogen, and reaction (4) describes the saturation of this bond with a hydrocarbon radical resulting in diamond phase growth. The temperature dependences of reaction (2)-(4) rate constants are described in Ref. [38]. In the approximation of a small hydrocarbon fraction in the growth medium, the fraction of carbon atoms with a dangling bond ( $\mathrm{C}_{\mathrm{D}}^{*}$ ) on the diamond surface is determined by the ratio of reaction (2) to (3) rate constants and depends on temperature alone. It has been shown that in CVD technology the $\mathrm{CH}_{3}$ radical is a gasphase precursor of diamond growth [36, 39]. Chemical phenomena on the growing $\{100\}$ diamond surface are illustrated in Fig. 5.

The main parameters governing the process of CVD diamond synthesis are the gas mixture pressure $P$, gas excitation power $P_{\mathrm{m}}$ (determining the gas temperature $T_{\mathrm{g}}$ ), the hydrocarbon fraction in the gas mixture, and substrate temperature $T_{\mathrm{s}}$. Usually, the pressure varies in the range from tens to hundreds of Torr, $P_{\mathrm{m}}=600-6000 \mathrm{~W}$ (with $T_{\mathrm{g}}=$ $2000-3000 \mathrm{~K}$; it may exceed $10,000 \mathrm{~K}$ only in arc plasmatrons), while hydrocarbon content in the gas mixture varies from several fractions of a percent to a few percent, and $T_{\mathrm{s}}$ from 700 to $1100^{\circ} \mathrm{C}$.

By way of example, Fig. 6 shows the general layout of an ASTeX type microwave reactor (Seki Diamond Systems, USA) for growing diamonds by the CVD method (http://


Figure 5. (Color online.) Schematic of chemical phenomena on hydrogenated and reconstructed $2 \times 1\{100\}$ diamond surfaces. Carbon and hydrogen are represented as grey (1) and red (2) spheres, respectively (taken from Ref. [40]).


Figure 6. (Color online.) Growing diamonds by the CVD method: (a) the layout of an ASTeX type reactor (taken from Ref. [41]), and (b) the central part of the image demonstrates the substrate holder with individual singlecrystalline substrates; the upper left-hand corner exhibits microwave plasma photoluminescence above the Mo stage; samples of single- and polycrystalline diamonds are shown in the lower right-hand corner (taken from site http://www.seocal.com).
sekidiamond.com/). In such facilities, the reactor vessel serves as a resonator and microwave power is fed from above through a waveguide. Here, the region of a uniform diamond growth is up to 50 mm . The largest reactor of this company is operated at a frequency of 2.45 GHz and a power of 8 kW to ensure a diamond growth rate of $7 \mu \mathrm{~m} \mathrm{~h}^{-1}$. The growth rate of $15 \mu \mathrm{~m} \mathrm{~h}^{-1}$ is achieved at a frequency of 915 MHz and a power of 75 kW . In the latter case, the substrate diameter may be as large as 8 inches ( $\sim 200 \mathrm{~mm}$ ). Figure 6b illustrates the work of the reactor.

In order to enhance the effectiveness of the diamond growth process by the CVD method, the authors of Refs [42, 43] undertook modeling the electromagnetic field in microwave reactors and proposed some modifications of their construction and design. The modifications include the use of several tuning elements [44] and a pyramidal-shaped substrate holder [45], reduction of the holder size and adjustment of the holder position [46], design of the reactor for operation in the combined $\mathrm{TM}_{0} / \mathrm{TEM}_{001}$ microwave mode [26], the employment of a large resonator operating in a high microwave mode (see www.cyrannus.com), and 'pressing' the microwave plasma region to the substrate in a hat-shaped chamber operating in the combined $\mathrm{TM}_{01} / \mathrm{TM}_{02}$ mode [47] with the help of a copper cylinder [48].


Figure 7. (Color online.) (a) Morphological structure of a $500-\mu \mathrm{m}$ thick homoepitaxial film deposited on a synthetic HPHT substrate (faces are colored as described in Fig. 3d), (b) SEM image of the crystal, and (c, d) plots of face growth rates versus methane concentration and substrate temperature (taken from Ref. [54]).

There are good prerequisites for the industrial production of large single-crystal diamond plates and films by the CVD technique, provided a substrate suitable for growing singlecrystalline diamonds is available. The present review describes the main approaches toward this goal. Comprehensive reviews on technologies and applications of synthetic diamonds grown by the CVD method with reference to certain aspects of producing large single-crystalline diamonds are presented in Refs [2, 6, 10, 49-53].

## 4. Growth of single-crystal diamond by chemical vapor deposition

A direct method for growing large single-crystal diamonds is the epitaxial growth of seed crystal faces, resulting in the enlargement of all crystal dimensions. As a crystal grows homoepitaxially, all its faces, including the lateral ones, become extended. For example, all surfaces of a parallele-piped-shaped substrate with polished upper and lateral faces grow in size [26]. Figure 7 illustrates the process of epitaxial growth of a seed crystal having all $\{100\}$ faces polished [54]. The habit of a crystal changes during its growth; specifically, the area of the (001) face decreases, while $\{111\},\{110\},\{311\}$ faces appear. The growth of $\{111\}$ and $\{110\}$ faces is accompanied by the formation of structural defects, twins, and non-epitaxial regions and a rise in the high impurity uptake rate [55-57]. As the crystal growth continues, a polycrystalline 'coat' forms on the substrate periphery that hinders further growth of the crystal (Fig. 8). Figure 7b presents the formation of twins and nonepitaxial defects on $\{111\}$ faces that can grow into a polycrystalline 'coat'. The growth of the 'coat' is accompanied by increased mechanical


Figure 8. 2.4 and 0.25 carat brilliants fabricated from CVD-grown singlecrystal diamonds (taken from Ref. [59]).
stress [58] threading the growing epitaxial material, which eventually causes the crystal to crack. The polycrystalline coat has to be removed (Fig. 8).

Thus, it is necessary to avoid the extension of structurally imperfect $\{111\}$ and $\{110\}$ faces in the course of epitaxial crystal growth. An approach to this problem was developed by researchers at the Laboratory of Materials Science, Université Paris Sud 13 (France) [60]. The evolution of the morphological structure of the crystals during their growth depends on the growth rate $V$ of the main low-index faces, such as $\{100\}$ and $\{111\}$, as well as $\{110\}$ and $\{311\}$. According to the laws of crystal growth, the equilibrium shape of a crystal is determined by the slowest growing faces. For convenience, dimensionless parameters characterizing the ratios of the growth rates of low-index faces to that of one of them, $\{100\}$, are introduced in the analysis:

$$
\begin{equation*}
\alpha=3^{1 / 2} \frac{V_{100}}{V_{111}}, \quad \beta=2^{1 / 2} \frac{V_{100}}{V_{110}}, \quad \gamma=11^{1 / 2} \frac{V_{100}}{V_{311}} . \tag{5}
\end{equation*}
$$



Figure 9. (Color online.) Qualitative diagram of the equilibrium shapes of crystals that can be grown from the starting cubic $\{100\}$ substrate in the space of $\alpha, \beta$, and $\gamma$ parameters (taken from Ref. [60]; faces are colored as described in Fig. 3d).

Usually, coefficients characterizing $\langle 111\rangle,\langle 110\rangle$, and $\langle 311\rangle$ vector moduli are introduced into parameters $\alpha, \beta, \gamma$, respectively. When one of the parameters is much higher than the other two, the equilibrium shape of the crystal is represented by a Platonic polyhedron, such as an octahedron with $\{111\}$ type faces, a rhombic dodecahedron with $\{110\}$ type faces, and a trapezohedron with $\{311\}$ type faces. Moreover, polyhedrons with different types of faces can form. Figure 9 displays schematically conceivable crystal shapes depending on parameters $\alpha, \beta, \gamma$.

Results of an analysis of this scheme and experimental data suggest the impossibility of growing cubic crystals having only $\{100\}$ faces. It is a disappointing inference, because crystals with $\{100\}$ faces are the best materials in terms of both structural perfection and impurity composition. The diagram in Fig. 9 demonstrates the possibility of growing crystals shaped like a trapezohedron with $\{311\}$ faces and avoiding the formation of undesirable $\{111\}$ and $\{110\}$ faces [61], given the growth parameters are $1<\alpha<1.8$, $\beta<1$, and $\gamma>11 \alpha / 5$. This corresponds to a $T_{\mathrm{s}}$ value in the range from 850 to $950^{\circ} \mathrm{C}$ and methane content of at least $4 \%$, provided $P$ and $P_{\mathrm{m}}$ are high enough. In a narrower range of conditions ( $1<\alpha<5 / 4, \beta<1,11 \alpha / 5<\gamma<11 \alpha / 4$ ), with epitaxy beginning from a (001) substrate, the area of the upper (001) face will increase during the crystal growth, despite the appearance of growth $\{311\}$ type faces (Fig. 10). True, the growth conditions for lateral faces deteriorate in such a configuration.

According to the crystal growth concept based on the periodic bond chain theory [62], three types of crystal faces are distinguished, depending on the set of periodic bond chains, viz. smooth (F), stepped (S), and curved (K) faces. It should be noted, without going into details of this theory, that F type faces grow smooth through the atomic step growth mechanism with a minimum rate. In diamonds only $\{111\}$ faces pertain to a type $F,\{110\}$ and $\{311\}$ faces to a type $S$, and $\{100\}$ faces to a type K. However, it was shown in Ref. [63] that hydrogenated and reconstructed (in the course of CVD synthesis) $2 \times 1\{100\}$ diamond surface (see Fig. 5) is an F-type face, i.e., a slow-growing one. That is why numerous experiments on the growth of poly- and singlecrystalline diamonds yield mostly crystals with $\{111\}$ and $\{100\}$ faces. Observation of the slow stable growth of $\{311\}$


Figure 10. (Color online.) $600-\mu \mathrm{m}$ thick epitaxial film on a substrate with polished $\{100\}$ faces, grown with the addition of nitrogen under conditions of the predominant growth of $\{100\}$ and $\{311\}$ faces (taken from Ref. [61]).
diamond faces suggests that they are of a type F as well. Reference [64] demonstrated theoretically that reconstruction of the $\{311\}$ face in a diamond must strikingly lower its surface energy; thus far, however, there has been no experimental evidence of such a reconstruction. The influence of impurities on morphological features of the growing F type surface provides indirect evidence of $\{311\}$ face growth by the stepped growth mechanism characteristic of F type faces. These faces grow smoothly at a low content of impurities. The faces become uneven with a large number of steps as the concentration of impurities poisoning the steps, e.g., nitrogen, increases. Such a correlation is typical of the growth of $\{100\}$ (see Fig. 10) and $\{311\}$ diamond faces.

The material on growing $\{311\}$ faces is of a good quality [61]. Nitrogen concentration in growth $\{311\}$ sectors of HPHT crystals is even lower than in $\{100\}$ sectors [65]. Therefore, it may be possible to epitaxially build up a flat substrate with the polished (113) plane. The results of experiments with a cylindrical plate and the polished top (113) face from Ref. [61] are presented in Fig. 11. In the course of epitaxial growth, a crystal must acquire only $\{311\}$ faces, in accordance with the crystal growth parameters. However, modeling showed that other faces, e.g., $\{111\}$ and $\{100\}$, may develop temporally at the intermediate growth stages depending on the shape of the starting substrate. Figure 11 illustrates the formation of $\{100\}$ and $\{111\}$ faces with their characteristic twins and other structural defects. The material growing


Figure 11. (Color online.) (a) $300-\mu \mathrm{m}$ thick epitaxial film grown on a $\{113\}$ cylindrical substrate 2 mm in diameter, and (b) crystal shape following epitaxial growth predicted by a model with growth parameters $\alpha=2.0$, $\beta<2 \alpha / 3, \gamma=3.0$; faces are colored as described in Fig. 3 (taken from Ref. [61]).


Figure 12. Substrate cutting schemes for epitaxial CVD diamond: (a) conventional cutting into a parallelepiped, (b) cutting into a pyramidal shape with a $20^{\circ}$ deflection in the $\langle 100\rangle$ directions, and (c) cutting into a pyramidal shape with a $20^{\circ}$ deflection in the $\langle 100\rangle$ directions (taken from Ref. [56]).


Figure 13. Epitaxially grown crystal on a pyramidal substrate with a $20^{\circ}$ deflection in the $\langle 100\rangle$ directions (Fig. 12b) of $90 \mu \mathrm{~m}$ (a), $270 \mu \mathrm{~m}$ (b), and $500 \mu \mathrm{~m}$ (c) films (taken from Ref. [56]).
at these sites inherits such defects, which may have fatal consequences for crystal quality and even initiate coat growth.

This phenomenon emphasizes the importance of the correct choice of the initial substrate shape excluding the formation of $\{111\}$ and $\{110\}$ faces at any stage of epitaxy. Both numerical simulation and experiment indicate that (113) cylindrical (see Fig. 11) and (100) parallelepiped-shaped (Figs 7, 10) substrates do not meet this requirement. It stimulates attempts to use nonplanar substrates for diamond epitaxy by the CVD method. In particular, pyramidal substrates were employed to study diamond growth [56]. The idea is to hamper the development of undesirable $\{111\}$ and $\{110\}$ faces at substrate edges and prevent the formation of the polycrystalline coat in order to obtain the equilibrium shape of the crystal. Figure 12b, c shows two types of such substrates with deflections of pyramidal faces in the $\langle 100\rangle$ and $\langle 110\rangle$ directions. Pyramidal substrates with $20^{\circ}, 30^{\circ}$, and $40^{\circ}$ deflections from the ( 001 ) plane were prepared and used to grow epitaxial layers by the CVD method with the growth parameters $\alpha=1.8, \beta=1.1$, and $\gamma=4.0$.

The results of epitaxial growth of diamond on a pyramidal substrate confirm the excellent prospects for the application of such an approach. Figure 13 illustrates the evolution of the crystal shape parallel to the thickening of the epitaxial film. Clearly, neither $\{111\}$ nor $\{110\}$ growth faces develop, and no polycrystalline coat forms, even after long-term growing. The area of the (001) face increases, while that of the inclined faces gradually decreases. Relevant research has demonstrated the structural perfection of the crystals and the absence of internal stresses. Growth dislocations, if any, deflect toward the crystal's edges as they develop and thereby ensure the especially high perfection of the central part. Due to this, epitaxially grown crystals can be extended in thickness up to the millimeter scale. There is hope that further development of this approach will enable researchers to grow large bulk crystals of diamond.

## 5. Textured and heteroepitaxial diamond films

The absence of single-crystal diamonds in the form of plates suitable for modern photolithographic technologies stimulated attempts at their heteroepitaxial growth. By heteroepitaxy is meant growing one single-crystalline material on another. This method provides a good alternative for the synthesis of certain materials, e.g., GaN [66], unavailable in the form of single-crystal plates. Results of early research suggested the possibility of heteroepitaxy only when there was excellent coordination of the lattice parameters of substrate crystals and epitaxial material [67]. Later studies demonstrated heteroepitaxial pairs with markedly different lattice parameters. Nevertheless, the thorough coordination of lattice parameters of the substrate and the epitaxial material allows reducing the number of mismatch dislocations at the interface and improving the crystalline perfection of the epitaxial material. The following factors are of importance as far as diamond heteroepitaxy is concerned: (a) substrate stability during CVD diamond growth, (b) interaction of the substrate material with carbon, carbide synthesis, and carbon dissolution in the substrate, (c) crystalline structure of the substrate and coordination of its lattice parameter with a diamond, (d) availability of high-quality large-size substrates, and (e) a thermal expansion coefficient close to that of diamonds.

Of special significance for diamond heteroepitaxy is the initial film growth stage, i.e., nucleation. In the case of heteroepitaxy, neither abrasive nor ultrasonic treatment is usually practiced because of the random orientation of small diamond fragments digging into the substrate surface layer and functioning as nucleation centers. Bias enhanced nucleation (BEN) appears to be the most suitable procedure for diamond heteroepitaxy, which needs to be optimized taking into consideration a concrete substrate material. Thorough theoretical and experimental investigations into the BEN mechanisms demonstrated the key role of ion bombardment and surface diffusion for diamond nucleation [68], which occurs in three stages: (a) the formation of sites with a high surface energy on the substrate and hydrogen removal under the action of ion bombardment, (b) the formation of carbon clusters during ion bombardment-induced diffusion, and (c) the formation of stable diamond nuclei once carbon clusters reach a certain size.

The following crystal growth stages are distinguished based on the size and mutual orientation of diamond crystallites: heteroepitaxy proper, a mosaic structure, texture, and (at worst) uniaxial texture. The oriented and heteroepitaxial diamond growth is exemplified by such different materials as sapphire [69], Co [70], Pt [71], TiC [72], graphite [73], BeO [74], $\mathrm{Ni}_{3} \mathrm{Ge}$ [75], and Re [76], which are not discussed below. Detailed reviews of the synthesis of heteroepitaxial and textured diamond films can be found in monographs [2, 6, 49]. Sections 5.1-5.5 of the present communication deal with the most promising forms of oriented and heteroepitaxial diamond growth on certain substrates.

## $5.1 \mathrm{c}-\mathrm{BN}$

Cubic boron nitride, $\mathrm{c}-\mathrm{BN}$, is the closest analog of diamond. It has a crystal lattice similar to that of diamond with a lattice parameter of 0.3615 nm (only $1.3 \%$ greater than the 0.3567 nm in diamond) and low thermal expansion coefficient. The high surface energy of c-BN accounts for a high diamond nucleation density $\left(10^{10} \mathrm{~cm}^{-2}\right)$ without any preliminary treatment of the surface.


Figure 14. SEM images of diamond films grown on c-BN faces: (a) (001) and (b) (111) (taken from Ref. [78]).

Diamond epitaxy on c-BN was first undertaken in the early 1990s [77]. Its main features are summarized in Ref. [78] as: (a) growth of a high-quality diamond film on $\{100\}$ faces of c-BN crystals (Fig. 14a), (b) epitaxial diamond growth on $\{111\}_{\mathrm{B}}$ faces of c-BN crystals (Fig. 14b) in the absence of growth on $\{111\}_{\mathrm{N}}$ faces due to the difference in binding energies $E_{\mathrm{C}-\mathrm{N}}<E_{\mathrm{C}-\mathrm{C}}<E_{\mathrm{C}-\mathrm{H}}$ and $E_{\mathrm{B}-\mathrm{H}}<E_{\mathrm{B}-\mathrm{C}}$ [79], and (c) the diamond heteroepitaxy by CVD method on $\{100\}$ faces of c-BN crystals at a high methane concentration and lowered $T_{\mathrm{s}}$; in contrast, heteroepitaxy on $\{111\}$ faces of $\mathrm{c}-\mathrm{BN}$ crystals occurs at a low methane concentration and high $T_{\mathrm{s}}$.

The main problem facing diamond heteroepitaxy on c-BN crystals is that their size for the moment turns out to be even smaller than that of diamonds. At present, it is diamonds that provide good substrates for c-BN heteroepitaxy rather than the other way around, which allows interesting heterostructures to be created [80].

## $5.2 \beta-\mathrm{SiC}$ and $\alpha-\mathrm{SiC}$

Another suitable material for heteroepitaxial diamond substrates is cubic silicon carbide, $\beta-\mathrm{SiC}$. In Ref. [81], a heteroepitaxial $\beta-\mathrm{SiC}$ layer was deposited onto Si , allowing highly oriented diamond crystallites to be grown by the BEN method, applying a negative substrate bias despite a substantial ( $22 \%$ ) lattice parameter mismatch. Later on, the authors of Ref. [82] considerably improved the nucleation and oriented growth processes, which helped to create highly oriented smooth diamond films of excellent quality, suitable for many optical and electronic applications. X-ray diffraction revealed a perfect coordination between diamond and $\beta-\mathrm{SiC}$ lattices, as well as a small width of X-ray reflection $\left(0.6^{\circ}\right)$ in heteroepitaxial diamonds (Fig. 15).

The $\alpha$-SiC substrates are utilized to grow oriented diamond crystallites with ratios of $(0001)_{\alpha-\text { SiC }} / /(111)_{\text {diamond }}$; $[1120]_{\alpha-\mathrm{SiC}} / /[110]_{\text {diamond }}$ characteristic of the coordination between the cubic and hexagonal lattices [83]. It may be


Figure 15. Highly oriented diamond film $20 \mu \mathrm{~m}$ in width on a $\beta-\operatorname{SiC}(001)$ substrate: (a) $\{111\}$ X-ray reflections, (b) SEM image of the film surface (taken from Ref. [82]).
supposed that imperfect lattice coordination accounts for the formation of only isolated poorly oriented diamond crystallites.

### 5.3 Si

Silicon, the most popular material in modern electronics, is widely used as a substrate for diamond heteroepitaxy, with the main difficulty arising from discoordination of diamond and Si lattice parameters ( $52 \%$ ) and the low surface energy of Si ( $1.5 \mathrm{~J} \mathrm{~m}^{-2}$ for a $\{111\}$ face).

The authors of Ref. [84] applied a three-step procedure to grow a highly oriented diamond film on Si that included: (1) Si surface carbidization, (2) BEN, and (3) diamond oriented growth. At stage 1 , the $\mathrm{Si}(001)$ near-surface layer is actually transformed into $\beta-\operatorname{SiC}(001)$; thereafter, diamond oriented growth on $\beta-\mathrm{SiC}$ occurs (see Section 5.2). Thus far, this method has allowed obtaining a textured film in which individual crystallites are disoriented a few degrees with respect to one another.

X Jiang and co-workers [85-87] realized a two-step process (without the initial carbidization stage) to grow an oriented ( 001 ) diamond film on $\mathrm{Si}(001)$. Transmission electron microscopy (TEM) revealed that (001) diamond grows directly on $\operatorname{Si}(001)$ (Fig. 16) without the formation of an intermediate layer [85].

Later on, the authors significantly improved the quality of diamond oriented growth on Si and reached a high homogeneity of structure and properties in a surface area up to


Figure 16. High-resolution TEM image of the diamond/Si interface in the diffraction zone of [110] diamond and Si (taken from Ref. [86]).


Figure 17. SEM image of a highly oriented diamond film grown on Si (taken from Ref. [87]).


Figure 18. SEM images of diamond films of different thicknesses on Ni surfaces: (a) (100), (b) (111), (c) (100), and (d) (111) (figures a, c, d are taken from Ref. [90], and figure $b$ is taken from Ref. [89]).

30 mm . Disorientation angles between crystallites in the film decreased as it grew thicker. Figure 17 illustrates a morphological pattern of such a film; it almost completely depends on (001) faces of highly oriented diamond crystallites.

### 5.4 Ni and Cu

Nickel and copper have face-centered cubic lattices with the parameters 0.3517 and 0.3608 nm , respectively, that are by $1.2 \%$ smaller and $1.1 \%$ greater, respectively, than in diamonds. However, their properties with respect to carbon
differ. Nickel is employed as a solvent-catalyst in the HPHT growth of diamonds and, therefore, may be a suitable material for diamond heteroepitaxy. The problem is that the strong catalytic action results in hydrocarbon decomposition yielding graphite instead of diamond. Nevertheless, the authors of Ref. [88] managed to grow diamond individual oriented crystallites on Ni single-crystalline (111) and (100) faces. Making use of a three-step process with carbon saturation of the Ni surface layer as the key stage enabled them to grow heteroepitaxial diamond films (Fig. 18) [89],


Figure 19. Size and density changes in diamond crystallites on $\operatorname{Ir} / \mathrm{MgO}(001)$ depending on current density (BEN method): (a) $70 \mathrm{~mA}^{-2}$, (b) $105 \mathrm{~mA} \mathrm{~cm}^{-2}$, (c) $140 \mathrm{~mA} \mathrm{~cm}^{-2}$, (d) $175 \mathrm{~mA} \mathrm{~cm}^{-2}$; (e) smooth heteroepitaxial diamond film about $1 \mu \mathrm{~m}$ thick on $\mathrm{Ir} / \mathrm{MgO}(001)$ (taken from Ref. [6], p. 141).
including continuous ones [90]. Electron diffraction studies revealed a surprising (for CVD conditions) formation of an $\mathrm{Ni}_{4} \mathrm{C}$ layer at the interface that in all likelihood serves as a source of diamond nucleation.

Unlike nickel, copper does not form carbides, nor can it dissolve carbon. Graphene and graphite are readily formed on the Cu surface in a hydrocarbon medium, which gives rise to a textured $\{111\}$ diamond growth even on a polycrystalline Cu foil [91]. The adhesion of a diamond film to a Cu substrate is so weak that it gets detached upon cooling, just because the diamond and Cu thermal expansion coefficients are different.

### 5.5 Ir

For almost 20 years, iridium has been regarded as the most promising material for heteroepitaxial growth of large diamond plates. The first research teams headed by A Sawabe [ 92,93 ] and B Stritzker [94] reported heteroepitaxial diamond growth on Ir substrates. Singe-crystal iridium being unavailable, the authors used heteroepitaxial Ir films deposited on the (001) faces of MgO [93, 93] and $\mathrm{SiTiO}_{3}$ [94]. The lattice parameter of the face-centered cubic Ir is 0.385 nm or $7.6 \%$ greater than in diamond. But on the other hand, iridium does not form carbides under CVD conditions and does not catalyze graphite formation. Applying the BEN method permits producing highly oriented crystalline diamond nuclei (Fig. 19a-d).

Realizing the advantages of heteroepitaxial diamond films on Ir requires understanding and controling the nucleation process, texture growth, and development of technologies for fabricating large-size diamond plates. These issues are considered in dozens of publications, including comprehensive reviews $[2,6,50]$. The central task is to elucidate the unique diamond nucleation mechanism on the Ir substrate. The BEN procedure causes the following three major changes to the Ir surface: increased roughness [95], the appearance of a $1-\mathrm{nm}$ thick carbon layer [96], and the appearance of spots producing bright contrast SEM images that can either increase or decrease, depending on BEN conditions [95, 97]. Surprisingly, these spots are only 1 nm high and in no other way distinguishable from the surrounding material [98]. Nevertheless, they give afterwards rise to diamond growth (Fig. 20). One of the experimentally substantiated models of diamond nucleation on Ir is proposed in Ref. [97]. It envisages the formation of a strongly nonequilibrium carbon phase on the Ir surface in the course of ion bombardment. Termination of electrical bias at the end of the BEN procedure results in ultrafast condensation of the carbon phase into ordered structures serving as diamond nucleation sources. Nevertheless, the other BEN models have also been described [99].

The width of an X-ray reflection in $8-\mu$ m thick $\operatorname{Ir}(001)$ continuous diamond films is $0.34^{\circ}$ and the azimuthal angular distribution covers $0.65^{\circ}$; the same parameters in $34-\mu \mathrm{m}$ thick films are 0.17 and $0.38^{\circ}$, respectively [100]. This observation reflects a characteristic manifestation of the improvement in the texture of highly oriented films with increasing their thickness and is apparent in the case of heteroepitaxy on Si (see Fig. 17), $\beta-\mathrm{SiC}$, and other materials. The merging of diamond crystallites into a continuous film on Ir substrates with high nuclei density occurs in films less than 100 nm in thickness. The film grows further in accordance with the van der Drift model of competitive grain growth [101], which leads to the formation of faces with the least growth rate described by the growth parameters $\alpha, \beta$, and $\gamma$. As a result,


Figure 20. SEM images of Ir substrate morphological features following the BEN procedure for the time indicated under each photograph and the buildup of diamond layers (taken from Ref. [95]).
poorly oriented crystallites become overgrown by neighboring ones optimally oriented and shaped for the given growth conditions, which improves the texture quality. Moreover, neighbor crystallites merge through the disclination mechanism [102].


Figure 21. (Color online.) Schematic representation of multilayer structures: (a) $\mathrm{Dia} / \mathrm{Ir} / \mathrm{SrTiO} 3 / \mathrm{Si}(001)$, and (b) $\mathrm{Dia} / \mathrm{Ir} / \mathrm{YSZ} / \mathrm{Si}(001)$; SEM images of the surface (c) and cross section (d) of a $\mathrm{Dia} / \mathrm{Ir} / \mathrm{YSZ} / \mathrm{Si}(001)$ sample (taken from Ref. [104]).

Up to now, buffer Ir layers have been deposited using only oxides, such as MgO [92, 93], $\mathrm{SrTiO}_{3}$ [94], and $\mathrm{Al}_{2} \mathrm{O}_{3}$ [103]. Future technologies for diamond plate production need substrates of a proper size. Today, MgO and $\mathrm{SrTiO}_{3}$ substrates $\sim 50 \mathrm{~mm}$ in diameter and $\mathrm{Al}_{2} \mathrm{O}_{3}$ substrates $\sim 100 \mathrm{~mm}$ in diameter are accessible. The thermal expansion coefficient of the substrate material is also of a primary importance. The diamond CVD synthesis and the cooling of diamond films on $\mathrm{Al}_{2} \mathrm{O}_{3}, \mathrm{SrTiO}_{3}$, and MgO substrates being completed, they experience compression stresses of 4,6 , and 8 GPa , respectively [104]. Once the films are more than a few micrometers thick, these stresses cause them to detach from the substrate. On an Si substrate, compression stress does not exceed 0.7 GPa , but this material cannot be directly used for the purpose, since Ir tends to form silicides. The difficulty can be obviated by depositing a buffer heteroepitaxial oxide layer of, e.g., $\mathrm{SrTiO}_{3}$ or YSZ (yttrium-stabilized zircon) on the Si substrate. Figure 21 displays the multilayer structures described in Ref. [104]. For the $\mathrm{Dia} / \mathrm{Ir} / \mathrm{YSZ} / \mathrm{Si}(001)$ structure, the polar and azimuthal angular distributions of crystallites in a $10-\mathrm{cm}^{2}$ diamond film are only $0.16^{\circ}$ and $0.34^{\circ}$, respectively. This approach allowed growing a high-quality heteroepitaxial diamond film $\sim 100 \mathrm{~mm}$ in diameter [105].

### 5.6 Properties and applications of heteroepitaxial diamond films

The advantages of heteroepitaxial diamond films account for their numerous applications. Heteroepitaxial diamonds on Si substrates are exploited to manufacture various electromechanical and electrochemical devices $[106,107]$ in which heteroepitaxial diamond films have the advantage of smallscale roughness compared with polycrystalline films. Also, heteroepitaxial diamond films are superior to smooth nanocrystalline ones in terms of heat conductivity and defectiveness. The lower density and defectiveness at intercrystallite boundaries are responsible for the high sensitivity of UV detectors based on homoepitaxial diamond films on Si [108]. The poorly developed mosaic pattern of diamond films on $\beta$-SiC allowed fabricating field transistors with characteristics comparable with those of heteroepitaxial materials [109].

Electron emission studies demonstrated that heteroepitaxial diamond films on Ir ensure a more uniform current and lower turn-on voltage than polycrystalline ones [110].The p-type heteroepitaxial diamond films on Ir and Si showed Hall mobility at room temperature ( 345 and $165 \mathrm{~cm}^{2} \mathrm{~V}^{-1} \mathrm{~s}^{-1}$, respectively) [111, 112]. 'Diamond-on-Ir' structures were used as detectors for heavy-ion tracking [113]. These structures did not provide a record energy resolution, but their time resolution was estimated at 10 ps .

## 6. Composite diamond substrate

The absence of large-area single-crystalline diamond substrates stimulated the development of methods for fabricating composite substrates as a palliative from smaller separate single-crystal plates.

### 6.1 Mosaic diamond substrate

The first successful studies $[114,115]$ included attempts to make mosaic structures from several plates. Specifically, two or three single-crystal (001) diamond plates were butt-joined to serve as a substrate for epitaxy in a CVD reactor. In the course of epitaxial growth, they merged together into a single diamond plate. A bolster-shaped diamond material formed at the junction, which suggested an enhanced growth rate. True, this material proved to be saturated with screw dislocations and stacking faults. In similar research [116, 117], the substrate consisted of up to seven single-crystal (001) diamond plates. All the plates for the mosaic substrate were specially fabricated to have a $2.5^{\circ}$ deflection from the (100) plane in order to ensure stepwise growth [118]. The formation of twins and hillocks during CVD diamond growth was suppressed by adding nitrogen to the gas mixture [119].

An analysis of the intergrowing of plates into a single substrate showed that diamond growth at the joints strongly depends on the initial crystallographic orientations of the constituting components, the difference between the thicknesses of adjacent plates, the discoordination of crystallographic directions in the plane of the plates, and conditions of the CVD process. There are three structural forms of material for (001) diamond plates at their junctions. One is


Figure 22. (a) Diamond microcrystals regularly arranged over a specially shaped Si substrate, and (b) the same substrate overgrown with a $240-\mu \mathrm{m}$ thick diamond layer (taken from Ref. [120]).


Figure 23. 1-mm thick diamond film grown by the CVD method on a mosaic substrate from 16 single-crystal plates $4 \times 4 \mathrm{~mm}$ each. Initial substrates are removed (taken from Ref. [122]).
characterized by the perfect intergrowing of neighboring plates with a roughly twofold rise in the growth rate of the bolster-shaped diamond material at the junctions. The bolster material is epitaxial carbon which has, however, structural defects. The second type of material exhibits a nonepitaxial
structure. In the third type of material, the epitaxial layer of one plate spreads over an adjacent one, thus giving rise to a macrostep. It became clear that crystallographic and spatial discoordination of the plates should not exceed $2^{\circ}$, and they must be equal in height if a quality diamond material is to be grown over the entire mosaic substrate.

Interesting attempts to grow a single-crystal diamond from smaller crystallites were made in Refs [120, 121]. In Ref. [120], for example, small diamond crystallites of a cubooctahedral habitus of about $100 \mu \mathrm{~m}$ in size were regularly arranged within pyramidal-shaped depressions of a Si substrate (see Fig. 22a), so that their upper (001) faces lay in the horizontal plane. The overgrowth of such a substrate by CVD method resulted in the formation of a continuous mosaic structure (Fig. 22b).

A marked impetus to the mosaic technology was given in Refs [122, 123]. The authors used 16 identical single-crystal (001) diamond plates $4 \times 4 \mathrm{~mm}$ each that were butt-joined into a single mosaic substrate on which a $1-\mathrm{mm}$ thick epitaxial diamond film was grown by the CVD method. Close compliance with the conditions for matching initial plates and optimization of the growth process made it possible to obtain a complete diamond wafer $16 \times 16 \mathrm{~mm}$ in size with high-quality material at the junctions and the absence of bolster-shaped structures. Then, the initial substrates were removed to have a plate made from CVD material alone. The result is given in Fig. 23. The finished wafer appears not to be strictly single-crystalline due to minor disorientations between the initial plates, but the quality of the material, including the nitrogen content, is on the whole fairly good. Importantly, manufacturing electronic devices by photolithography on such plates is much more convenient than on 34 mm long plates. A photomask can be designed so that active regions of the device do not coincide with those sites on the plate that inherit material at the junctions of the initial plates.

In striving to improve the quality of material at the junctions of initial plates, researchers arrived at applying pyramidal substrates to prepare a composite substrate (see Section 4 and Figs 12, 13) and simultaneously reduce the defectiveness of the growing material by hindering formation of undesirable $\{111\}$ and $\{110\}$ faces at the substrate edges.


Figure 24. (Color online.) Fabrication of cloned plates and 'tiled' composite substrate (taken from Ref. [126]): 1 -ion implantation, 2 - epitaxial growth of diamond, 3 - separation of the diamond plate by etching of graphite, 4 - repetition of procedures $1-3$ on identical substrates, 5 - connection of identical plates into a composite substrate and their epitaxial intergrowth, and 6 - repetition of cloning procedure on a substrate of greater area.


Figure 25. Composite single-crystalline diamond plates produced by the mosaic method (taken from Ref. [126]).


Figure 26. Schematic representation of a composite substrate with square or circular regions of single-crystalline (1) and polycrystalline (2) diamond (taken from Ref. [130]).

### 6.2 Fabrication of composite substrates by the cloning method

Most problems pertaining to the quality of material at the junctions of initial substrates can be resolved by using identical ('cloned') plates 'cut' from the same crystal. It is certainly possible to first shape a diamond crystal as a cube or parallelepiped, say with $\{100\}$ faces, and thereafter cut it into similar plates. But only $3-4$ plates can be obtained in this way, and they will be somewhat different due to the mechanical inaccuracies of cutting and the facet pattern.

Another method for preparing clones was proposed in Ref. [124]. The method consists in implantation of light ions, e.g., $\mathrm{He}^{+}$, with a high energy (several megaelectron-volts) and dose (above the critical dose of graphitization). The subsequent high-temperature annealing causes transformation of the strongly implantation-damaged diamond layer at a depth of a few micrometers into a graphitized material and restoration of the overlying diamond. The graphitized material can be etched electrochemically [125]. True, only very thin (some $1 \mu \mathrm{~m}$ ) and practically unworkable diamond plates can be obtained by this method. The way out is to build up an epitaxial layer over the ion-implanted crystal. A large number of identical substrates can be fabricated in this way to assemble them like tiles into a large composite substrate [126].

Figure 24 demonstrates the sequence of technological operations for the fabrication of a composite substrate by the cloning method. Stage 5 of this process concerns overgrowth of the substrate by the CVD method and the formation of a single substrate. The cloning procedure can be applied to it again at stage 6 .

This technology has already allowed fabricating of singlecrystal plates over 25 mm in size (Fig. 25) [126]. The resulting material is of a fairly good quality [127], but the method has two drawbacks. First, it is a multistep technique involving a


Figure 27. Combined substrate 76 mm in diameter obtained by intergrowing poly- and single-crystalline diamonds at the Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod (reprinted with permission of A L Vikharev).
complicated cloning procedure (although a single large singlecrystalline plate once obtained can be cloned multiple times). Second, the epitaxial material inherits radiation defects induced by ion implantation. The latter disadvantage can be obviated by the improvement of technology as proposed in Ref. [128] that allows simultaneously decreasing the influence of polishing defects on the diamond surface [129].

### 6.3 Combined single- and polycrystalline diamond substrates

The simplest and most cost-effective approach to fabricating large single-crystal diamond plates is described in Ref. [130]. A number of single-crystalline substrates of usual size (34 mm ) are placed on a polycrystalline diamond plate to be overgrown by the CVD method in a regime that provides for simultaneous epitaxial growth of single-crystalline diamond and polycrystalline diamond growth (Fig. 26). The edges of single-crystal plates and the polycrystalline material tend to intergrow into a single composite substrate.

This method can be applied to growing perfect epitaxial thin films at single-crystalline sites to manufacture diamondbased electronic devices. As mentioned in Section 6.1, it is possible to design photomasks so that active regions of the device coincide with the sites occupied by high-quality singlecrystalline material. In any case, the plate has to be cut into separate chips at the final stage of the technological process. Moreover, surface planarization of the composite plate is mandatory for the photolithographic technology to be implemented. To meet this requirement, it is proposed to fill up depressions on the plate surface with various materials, such as polyimide [131], amorphous silicon dioxide [132], glass, or metallic paste, suitable for microelectronic technologies. A composite substrate 76 mm in diameter is exemplified in Fig. 27.

## 7. Conclusion

Recent progress in diamond technology based around the CVD method made it possible to grow high-quality polycrystalline diamonds on large substrates ( $>50 \mathrm{~cm}^{2}$ ). The present review focuses on the prospects for the synthesis of large ( 25 mm or more) single-crystal diamond plates and films suitable for photolitographic technology. This problem is becoming increasingly important in diamond technology, and it can be expected that the near future will bring its successful solution. The CVD technique is appropriate for
fabricating large single-crystal diamond plates and films. The most promising approaches to the achievement of this goal are the growth of large bulk diamond single-crystals, heteroepitaxial growing of diamonds on single-crystal substrates, and fabrication of composite diamond substrates.

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