

Two extreme crystal size scales of diamonds, large single crystal and nanocrystal diamonds: Synthesis, properties and their mutual transformation

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Abstract: Diamonds with two extreme sizes, large single crystal and nanocrystalline, have completely different properties, and have aroused the continuous attention of researchers. Each has its own merits and can be converted into the other. The synthesis of large single crystal diamond can be described as the aggregation, assembly and combination of nanocrystalline nuclei, i.e., diamond transforming from the nano-scale to the inch scale. A large single crystal diamond can be transformed into nanocrystals by surface nanocrystallization. The preparation methods, properties and applications of single crystal diamonds of different sizes are introduced and the transformations between them are described. Research interest in controlling the crystal size is discussed.

Key words: Large-scale single crystal diamond; Nanocrystalline diamond; Morphology transformation; Grain size controlling

1 Introduction

Diamond is a kind of atomic crystals composed of carbon atoms with strong C—C sp^3 bond^[1], resulting in some extreme properties, such as the highest hardness (1.04×10^4 kg mm⁻²), high Young Modulus (1 220 GPa) and thermal conductivity ($2\ 200$ W m⁻¹·K⁻¹) in nature. Meanwhile, other properties including wide band gap (5.5 eV), high electron/hole mobility ($2200/1600$ cm V⁻¹·s⁻¹), negative electron affinity, chemical inertia and particle bombardment resistance^[2, 3] also guarantee a wide application prospect. Typical applications are wear-resistant coatings, tools, heat sinks, optical windows, sensors, and electronic or optoelectronic devices, such as transistors.

Since the first synthetic diamond appeared in the 1950s, the manufacturing technologies of diamond and diamond-like carbon (DLC) have been developing prosperously. By means of direct solid phase transformation of graphite under static pressure and chemical vapor deposition (CVD)^[4], materials with the similar properties as natural diamond can be prepared. Processing technology plays an active role in

improving the properties of diamond. Doping has a positive effect on electrical properties^[5], and boron-doped diamond (BDD) is one of the most promising electrode materials^[6]. The formation of metal carbides makes it possible to stabilize metal catalysts^[7]. Defects also add better performance to diamond. The luminescence defects (color centers) can generate non-classical state of light and emit single photon at room temperature, which is the key in the quantum optical communication system^[8]. In particular, a device containing NV color centers can be used as a memory for long-distance quantum communication^[9].

As the two limits of diamond grain size, large-scale single crystal has no grain boundary, less defects, and high purity^[10], while the nanocrystal contains a large number of grain boundaries and interface atoms^[11]. In the traditional and newly-emerging areas, these two kinds of crystals with the tremendous difference in the grain size have shown their irreplaceability to attract continuous attention of researchers.

In this paper, the main preparation methods of bulk single crystal and nanocrystalline diamond are introduced. Their structure, properties, and applications are discussed. In addition, the concepts of states

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transformation for as-grown crystal and surface nanocrystallization are emphasized, and the theoretical and experimental research directions are prospected.

2 Large-scale single crystal diamond

In order to produce diamond devices which can achieve the performance predicted by material properties, it is necessary to obtain bulk raw material with high structural integrity and chemical purity^[12]. Therefore, the preparation of inch size single crystal wafer has become a focus for decades^[13].

2.1 Preparation of bulk single crystal diamond

2.1.1 High pressure high temperature (HPHT) method

The high pressure high temperature (HPHT) method simulates the formation conditions of diamond growth in nature^[14], which is widely used in industry to synthesize single crystal diamond wafer. Graphite is used as raw material, and transition metals or alloys are added as catalysts. After they are mixed, a constant high pressure of 5–7 GPa and temperature of 1 300–1 700 °C are applied^[15]. Thus, the thermodynamic condition for the formation of diamond as a stable phase in the carbon phase diagram is met, and the graphite will be transformed into diamond.

Due to the harsh growth conditions, even after decades of development, the size of diamond products is still limited to about 1 cm³. Impurities are also easy to be introduced, such as N from the atmosphere, Fe and Co from metal catalysts^[16]. As a result, the quality of products is difficult to control to meet the requirements of advanced scientific research and application fields.

2.1.2 Chemical vapor deposition (CVD) method

Chemical vapor deposition (CVD) is a technique for diamond growth at low pressure. Owing to the deviation from thermodynamic equilibrium conditions, the temperature can be reduced, which makes it possible to grow thin films on large area substrates^[17]. Among them, microwave plasma-assisted CVD (MP-CVD) is one of the most widely studied ones^[18], whose principle is as follow. Microwave band electromagnetic wave is employed to accelerate electrons to

cause collision with H₂ and CH₄ molecules and discharge to generate H* and CH₃* radicals under intense discharge heat^[19] as shown in Fig. 1.

CVD diamond must be deposited on a substrate, process of which can be classified into two types: homoepitaxial growth where a single crystal diamond prepared by HPHT or CVD method is employed as a substrate^[20], and heteroepitaxial growth where a non-diamond substrate is used^[21]. The common methods of homogeneous epitaxy include the three-dimensional technology of repeated growth in different directions on {100} crystal planes^[22], and mosaic technology, in which several seeds are spliced into a larger substrate^[23]. By setting a substrate consisting of a few CVD single crystal wafers which are grown and then stripped by "lift-off" method on the same HPHT seed, a large-scale monocrystal film of 40 mm × 60 mm can be prepared^[24].

Despite the significant progress that homogeneous epitaxy has made, the requirement of diamond seeds as substrates brings about limitations in both cost and size. Moreover, many defects occur in the joints between the seeds. Therefore, researchers have been looking for a foreign substrate suitable for the preparation of single crystal diamond of large size and low number of defects under a relatively low cost^[25]. The early studied materials were Si, c-BN, Pt, Ni, SiC, etc., but the epitaxial products were mostly polycrystalline diamond films with nearly uniform orientation^[26]. At present, Ir (100) is the only available substrate in compliance with the goal, on which a high-quality free-standing single-crystal diamond wafer with a diameter of 91 mm has been successfully obtained^[27]. However, the stability and repeatability of the process need to be further confirmed to realize extensive manufacturing.

2.2 Properties and applications of bulk single crystal diamond

Compared with polycrystalline diamond, single crystal diamond has excellent optical properties, especially optical transmittance^[35], due to the absence of grain boundary, which reduces the absorption from

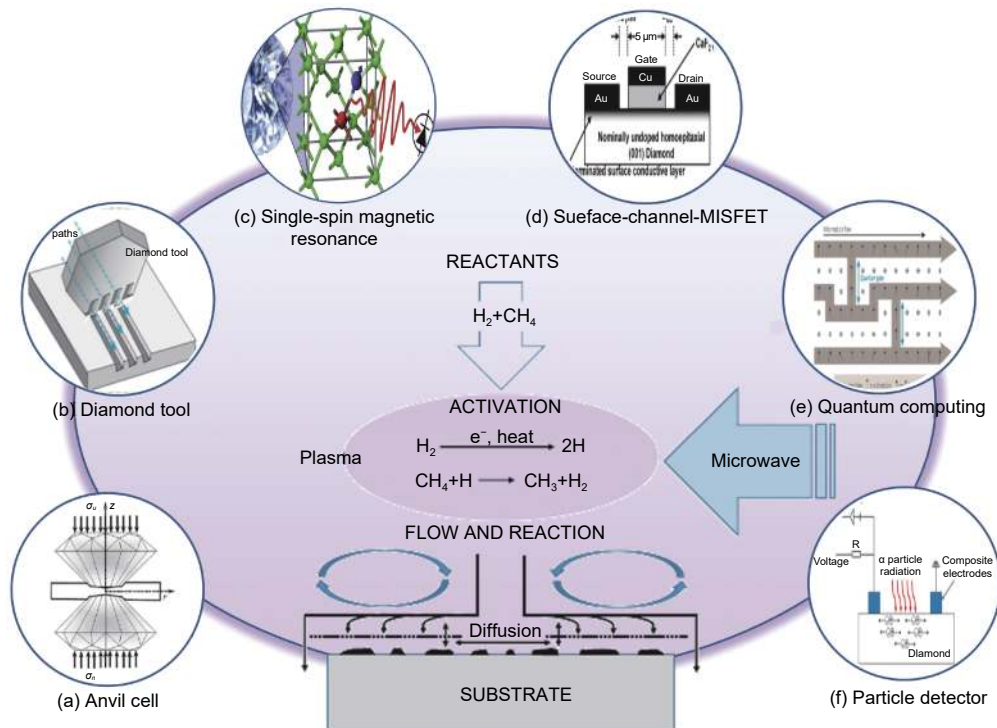


Fig. 1 Principle of single crystal diamond growth by CVD^[28-34], the background diagram showing the reactions during the generation of radicals in the chamber, (a)-(f) display six of the most common devices which call for high-quality, large-scale diamond wafer. Reprinted with permission.

amorphous carbon and impurities, and the scattering of infrared light by irregular large-size grains^[36]. A comparison of the HPHT single crystal diamond purchased from Zhengzhou Sino-Crystal Diamond Co., Ltd., the CVD single crystal diamond from Irish Element Six, and the CVD polycrystalline diamond from American II-VI Incorporation of their infrared transmissivity is shown in Fig. 2, which was obtained by a Fourier Optics infrared spectrometer by PerkinElmer with a measurement accuracy for absorption of 0.07% and a measuring range of 4 000–400 cm^{-1} .

The transmissivity of two single crystal diamonds, either synthesized by HPHT or CVD methods, is much higher than that of polycrystal diamond. Except for the intrinsic optical absorption (2.6–7.8 μm), there is a peak at 1 430–1 000 cm^{-1} of the HPHT diamond, associated with the N impurity in the lattice while the CVD single crystal diamond is highly transparent at low wavenumber bands, whose transmissivity can reach 70%, close to the theoretical value of 71.4%^[37].

CVD single crystal diamond with high purity and quality has been applied in various high-tech fields

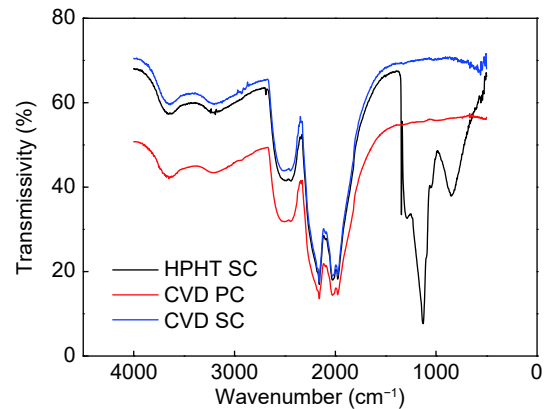


Fig. 2 Infrared transmissivity of single crystal (SC) and polycrystal (PC) diamond samples, the SC samples were produced by HPHT and CVD methods.

such as the diamond-based particle detectors with extreme-sensitivity^[38], the tools that can be used to mill surface into mirror-polished one^[39, 40], the optical windows with excellent optical transmittance^[41] and the anvils used as ultra-high pressure vessels^[42]. Undoped single crystal diamond has a band gap of 5.45 eV, which is an ideal material for semiconductors^[43], such as diodes, field-effect transistors, radio frequency electronic devices, and other electrical devices^[44]. At the same time, due to its high thermal conductivity, it has great advantages in harsh environments such as

high temperature, strong radiation and large current owing to its high thermal conductivity, which can be manufactured into high-temperature, high-power, and high-frequency semiconductor devices^[45].

3 Nanocrystalline diamond

Since the 1990s, a series of breakthroughs have taken place in the area of nanodiamond, making it a research hotspot. The main progress includes the preparation of stable colloidal suspensions^[46], the realization of chemical modification of particle surface^[47], and the success in purification technology^[48].

3.1 Preparation of nanocrystalline diamond

Despite a variety of approaches are used to prepare nanocrystalline diamond, including phase transformation of graphite under high pressure^[49], confined pulse laser deposition (CPLD)^[50], high energy ball milling (HEBM)^[51], glow plasma chemical vapor deposition (GPCVD)^[52], and pulsed-laser^[53] or ultrasound cavitation induced^[54] transformation, detonation is the earliest and most mature one^[55], in which the products come from explosive molecules, and the mechanism is as shown in Fig. 3(a).

Nanodiamond particles are created under the energy provided by explosion, accounting for more than 75 wt% in the products along with a mixture of other carbon allotropes and impurities^[57]. The diameters of these particles are 4–5 nm. Although the temperature and pressure are not enough to form bulk liquid carbon, they are sufficient for the formation of small droplets of nano-scale. Thus, the formation mechanism of nanodiamonds can be described as a multistage sequential process of condensation, homogeneous nucleation and crystallization in liquid carbon from supersaturated carbon vapor^[58] (Fig. 3b).

3.2 Properties and applications of nano-crystalline diamond

Nanomaterials are known as "the most promising materials in the 21st century". As a kind of them, nanodiamond retains most of the physical and chemical properties of bulk material, including outstanding mechanical, thermal^[59], optical^[60], electrical perform-

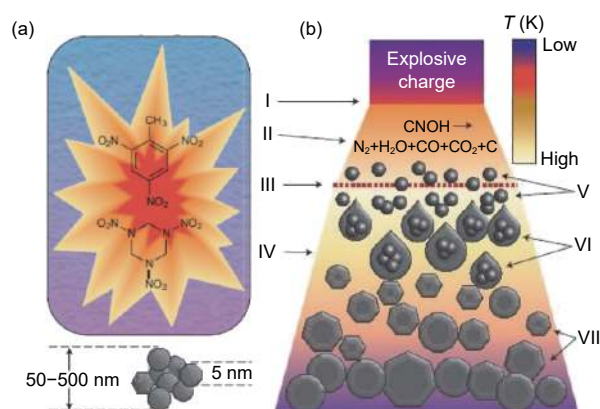


Fig. 3 Detonation synthesis of nanodiamonds: (a) explosive reactants are detonated in a closed metallic chamber to form diamond-containing soot and (b) schematic of the detonation wave propagation, in which molecules form carbon nanoclusters, coagulate into liquid nanodroplets, and finally turn into nanodiamonds by crystallization, growth and agglomeration^[56].

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ance^[61]. It also possesses various characteristics of nanomaterials, such as a large specific surface area, a high chemical activity and a large number of structural defects and oxygen-containing functional groups on the surface.

Due to its small particle size, the number of atoms on the surface of nanomaterials increases rapidly. The lack of adjacent atoms around the surface atoms results in many dangling bonds that are unsaturated and easy to combine with other atoms. In addition, nanodiamond with good dispersion^[47] has high surface energy, leading to high catalytic activity in different reactions^[62].

The nitrogen-vacancy (NV) color centers can be generated in nanodiamond irradiated by high energy particles and annealed in vacuum at 600–800 °C^[63], which contribute to fluorescence characteristics. The spin polarization of the NV color centers is controllable^[64]. The application of fluorescent NV color centers in allotope-pure diamond (diamond crystals containing only one carbon allotrope) in quantum computing is expected^[65].

Because of its unique properties, nanodiamond is important for theoretical research and applications. Nanodiamond can be added into lubricant to effectively reduce the wear of friction pairs and prolong the service life of engines^[66]. On the one hand, the ultra-high hardness of nanodiamond can be used to polish the surface and to enhance surface hardness. On the

other hand, due to its small particle size, it can be filled into the surface micro concave to reduce roughness. In addition, diamond nanoparticles are spherical or quasi-spherical, the "ball bearing" effect will play a positive role on the friction surface. Its excellent mechanical and thermal properties in combination with surface chemical activity also guarantee nanodiamond to be a well-welcomed reinforcing phase of nanocomposites^[51, 67].

The application of nanodiamond in medical sci-

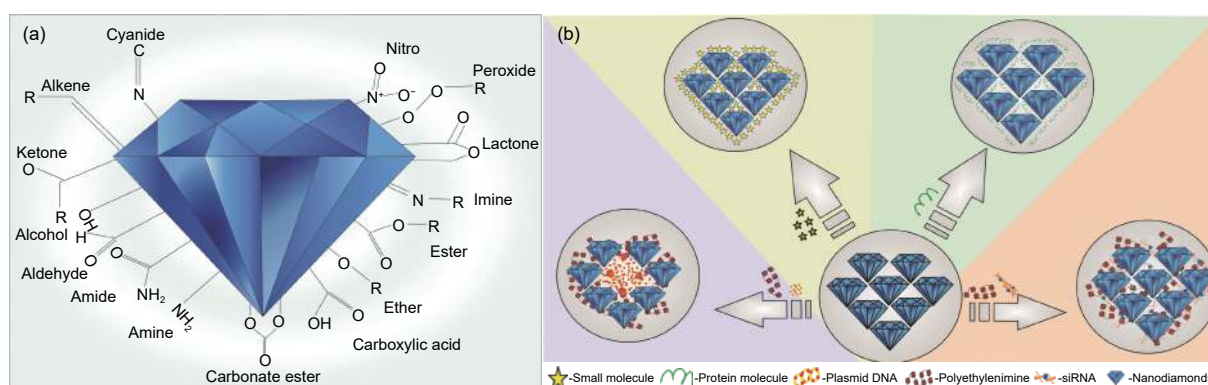


Fig. 4 Surface modification of nanodiamond for potential medical applications: (a) the ability of bonding with various functional groups on the surface and (b) nanodiamonds as a drug delivery platform^[74]. Reprinted with permission.

Furthermore, nanodiamond can be used as an additive for electroplating and electroless plating^[75], as a catalyst for chemical industry to oxidize CO into CO₂^[76], and as a polishing fluid for fine polishing of various optoelectronic crystals, optical components, and semi-conductor integrated circuits. Nanodiamond can be used as a seed layer to enhance the nucleation density of CVD diamond film for crystal growth, and sintered into bulk polycrystals. Boron-doped nanodiamond is conductive for electrical analysis, electrochemical double-layer capacitor, and battery, while undoped non-conductive particles exhibit redox activity in electrochemical system^[77].

Nanodiamond can be used to form new allotropes by phase transformation, such as the formation of a structure called "new diamond" (a metastable phase of carbon with a face centered cubic structure)^[78]. Carbon nano-onion, obtained by graphitization of nanodiamond, shows potential applications in energy storage, composite materials and catalysis^[79].

ence is mostly based on its self-assembly ability^[68], non-toxic^[69] and surface modifiability^[70] by different functional groups (Fig. 4a). With a high dispersion capacity in water, nanodiamond is highly anticipated in targeted therapy and drug delivery^[71] (Fig. 4b). Taking worms as experimental objects, fluorescent nanodiamond does not induce stress reaction^[72]. Its high optical stability and emission ability of high brightness and multi-frequency fluorescence are favorable for its application in biological imaging^[73].

4 Mutual transformation between nanocrystalline diamonds (NCDs) and bulk single crystal diamond (SCD)

4.1 From NCDs to SCD: The growth of large-size single crystals

During the growth of large-size single crystal diamond, the interconnection between nanocrystals can be observed and considered to be the mechanism, similar to that of the growth of other crystals^[80]. The formation of an amorphous carbon layer in which primitive nuclei are wrapped occurs first^[81] when diamond deposits on a heterogeneous substrate. A bias negative voltage can be applied to increase the nucleation density, which is called bias enhanced nucleation (BEN) method^[82]. After the termination of bias voltage, active atomic hydrogen [H] in the plasma will quickly etch the amorphous carbon layer, leaving the nanometer size diamond nucleus^[27].

The carbon atoms on the substrate surface dissolve into the crystal lattice to form a supersaturated

solid solution^[83] and the precipitation following decreases the carbon concentration in the solid solution. The dissolution-precipitation process continues and maintains a dynamic equilibrium^[84], triggering a rapid change of surface morphology. The surface morphology change is conducive to the translation, rotation, aggregation, and self-assembly of nanoscale nuclei. Grain boundaries are eliminated through the oriented attachment (OA) growth^[85], which is an approach to obtain single crystal diamond^[86] through the combination of primitive nuclei into secondary ones until a bulk single crystal is formed^[87, 88]. The process is shown in Fig. 5.

Although nucleation mechanism is rarely referred in the growth of large-size single crystal diamond on a homogeneous substrate, it can still be included^[90] by considering that the diamond seed (that is, the substrate) is a pre-setted crystal nucleus. In addition, the pits formed by removing surface defects during the etching and the edge regions not connected to other crystal nuclei can also be regarded as discontinuous growth islands^[91]. New grains attach on the steps of the pits and edge regions, rapidly aggregate and cement^[92] according to the Frank-Vander Merwe

mode.

Homo- and hetero-epitaxy can be considered as two different approaches from nanodiamonds to large-size single crystal diamonds^[93]. The nucleation, lateral growth by heteroepitaxy, and morphology transformation from bottom to top by homoepitaxy are described as follows:

(1) Interaction between carbon atoms and the substrate. The bias voltage at the initial stage of heteroepitaxy allows carbon ions or groups to shallowly implant into the subsurface of the Ir substrate to form a supersaturated solid solution, which ensures the continuous dissolution-precipitation circulation (Fig. 5a), and the formation of carbon sp^3 covalent bonds between C and Ir atoms. That is the reason why the Ir(100) substrate has the optimal potential and uniqueness for the growth of the large-size single crystal diamond. Although without much description of the interaction between each two atoms during homoepitaxy, the deposited carbon atoms may migrate on the surface and bond with the substrate atoms by the formation of sp^3 bonds.

(2) Formation of a primitive nucleus. The left "islands" by pretreatment and defect removal in homo-

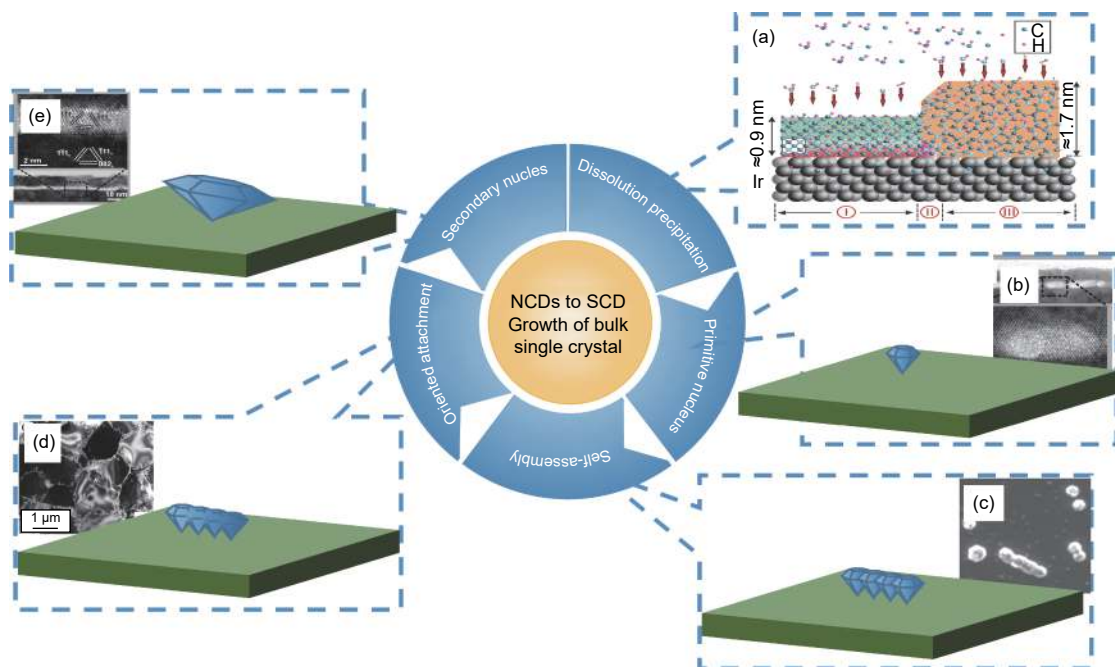


Fig. 5 Growth of large-size single crystal diamond from connection of nanocrystals, the main steps of growth process are shown by the ring in the middle: (a) dissolution-precipitation process of C atoms^[27], (b) formation of a primitive nucleus^[27], (c) self-assembly of primitive nuclei, (d) oriented attachment and disappearance of boundaries^[89] and (e) formation of a secondary nucleus^[27]. Reprinted with permission.

geneous epitaxy are equivalent to the preparation of a diamond primitive nucleus besides the diamond wafer itself. For the heteroepitaxial growth, the C sp^3 covalent bonds may be retained during atomic hydrogen etching^[27], leading to the formation of a more stable, diamond-like structure by connecting the surrounding nearly- sp^3 bonds until a primitive nucleus with the size of about 10 nm is formed (Fig. 5b).

(3) Aggregation and self-assembly of primitive nuclei. Generally, it is easier to observe the movement and self-assembly of grains in liquid^[94]. Although the diamond grains grown on solid substrates cannot move as freely as they do in liquid, the newly formed nuclei tend to concentrate near the original ones to form "crystal domains", that is, a large quantity of crystal nuclei with a similar orientation. In our experiment, the aggregation and self-assembly of these high density diamond nuclei on Pt(111) substrate are also much apparent (Fig. 5c). A decrease in sp^3 carbon content of the vicinity of nuclei happens after the formation of a primitive nucleus on the substrate surface, resulting in a carbon concentration gradient with the faraway regions, which provides a driving force for the further carbon-containing groups to supply the nucleation site. The rising surface energy also promotes the self-assembly. During homogeneous epitaxy, the formation of new nuclei can also be regarded as a result of the aggregation of the pre-set "nuclei" (mainly refer to the diamond substrate itself).

(4) Disappearance of grain boundaries and the formation of a secondary nucleus. The perfect struc-

ture of the original nucleus and the substrate causes the orientation and ordered alignment of subsequent grown nanocrystals. When the distance between nuclei is close to the atomic layer spacing, the adjacent grains can undergo OA growth, which transforms grain boundaries into line defects (dislocations or disclinations, Fig. 5d)^[95], thus forming a secondary nucleus. Fig. 6a shows the synthesis of bulk single crystal diamond from nanoscale particles by OA or nearly-OA routes. Because of the limited movement of grains on the solid substrate, only when the orientation difference between two grains is small enough (some studies point out that the value needs to be within 1° ^[96]), can planar defects be replaced by line defects. In addition, OA growth requires the existence of unsaturated dangling bonds on the grain surface^[97], which can be easily met in chemical vapor deposition.

(5) The aggregation of secondary nuclei into single crystal diamond. When a material deposited on a homogeneous substrate, it will grow directly according to the Frank-Vander Merwe mode. When a material is deposited on a foreign substrate the Stranski-Krastanov mode is obeyed. During heteroepitaxy, the "domains" generated by aggregation of secondary crystal nuclei after the self-assembly and OA growth in the above steps (3) and (4), gradually form an epitaxial layer with the increase of the film thickness. Then the layer becomes seed crystals, and in the subsequent growth stage, which is similar to that of homoepitaxy, even typical homoepitaxial growth steps may be observed on the surface.

The above process will inevitably leave evid-

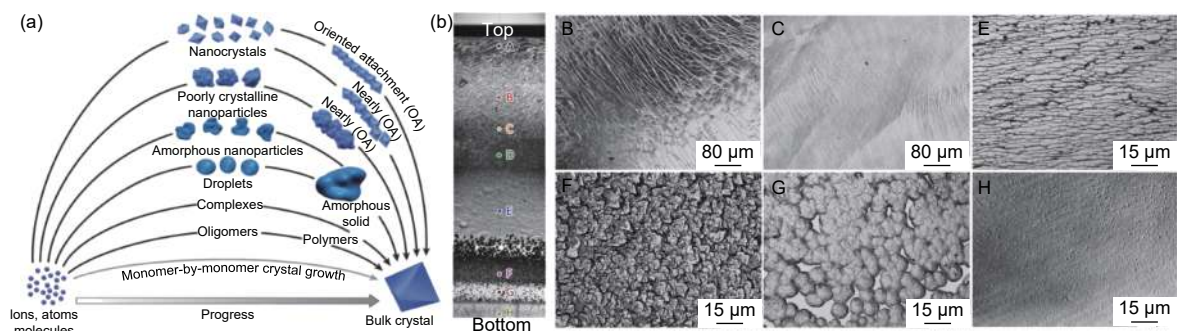


Fig. 6 Process of single crystal diamond growth: (a) several routes toward bulk single crystal diamond, including OA and nearly-OA growth^[98], (b) laser scanning microscopic cross section morphology of homogeneous epitaxial diamond, in which different crystal forms from nanocrystal to single crystal can be seen from the bottom to the top^[99]. Reprinted with permission.

ence of the gradual transformation from nanodiamond to bulk single crystal on the cross section, as shown in Fig. 6b, which can be observed in both homo- and hetero-epitaxy. Thus, it can be considered that the morphology transformation from nano-crystal to large-size single crystal diamond is the mechanism behind the epitaxial growth.

Furthermore, the control of the grain size is expected to be realized by adjustment of the thickness of sediment^[100]. Then different crystalline states from nanocrystals to monocrystals can be formed on the same type of substrate (even different regions of the same Ir(100) substrate wafer) when different manufacturing conditions are employed. In our experiments, we have realized nanodiamond on the Ir(100) substrate when bias voltage is applied all the time, and a continuous heteroepitaxial film is formed when a bias voltage is applied for only a few seconds during nucleation.

The transformation from NCDs to SCD can be regarded to be spontaneous, although it only occurs on some specific substrates (mainly diamond^[101] and iridium^[102]). There will be more optional substrates to

be found, or even an arbitrary substrate might be applied^[103]. The realization of accurate grain size controlling on the same substrate is still under investigation, which is expected to be achieved by adjusting the growth parameters, especially the bias voltage. Once the method is developed, it will be more convenient to regulate the grain size in the growth process.

4.2 Transformation from SCD to NCDs: surface nanocrystallization of SCD

Reactive ion etching (RIE) is one of the most popular techniques for preparing single crystal diamond nanowires^[104] from bulk material, which is a top-down method for preparing micro- or nano materials^[105].

Diamond nanowires (Fig. 7a) can be obtained by etching planar diamond films with the help of masks, including metals (Al, Mo, Ni, Fe, Au, etc.), oxides (SiO₂, Al₂O₃, etc.), and diamond nanoparticles^[106]. Direct etching of HPHT or CVD single crystal diamond can achieve ordered single crystal nanowire arrays^[107] which are suitable for quantum information processing^[108] and DNA sensing^[109] or platforms for biofunctionalization. The diamond nanowires can also

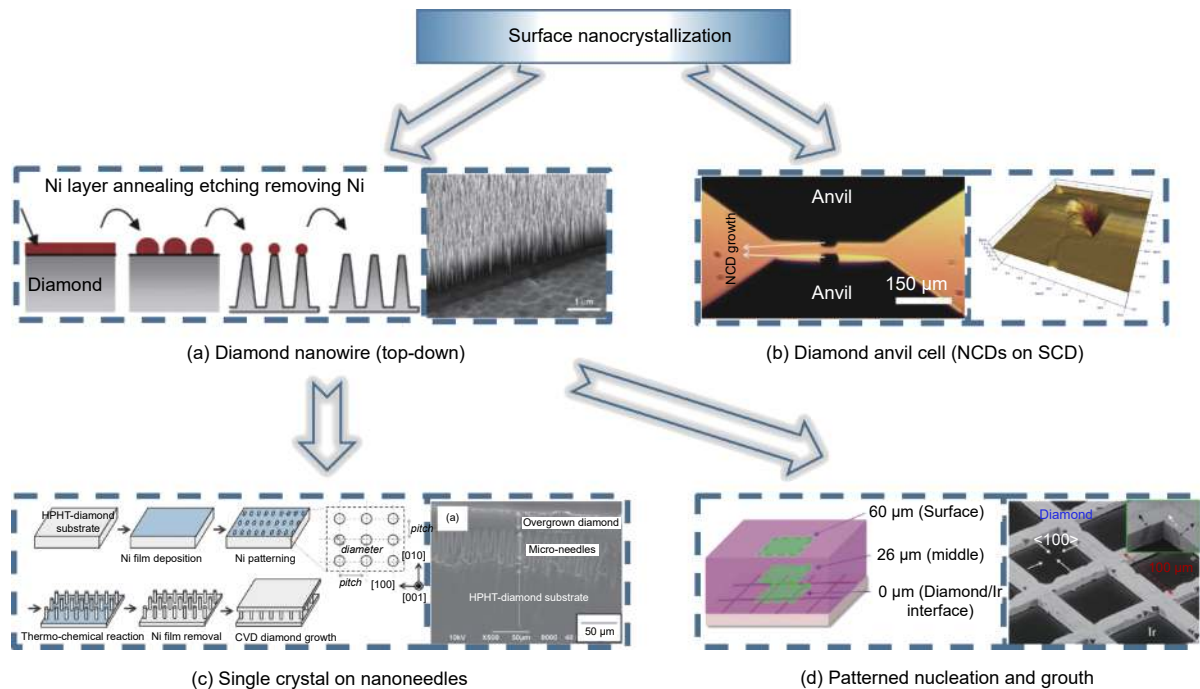


Fig. 7 The ways of diamond surface nanocrystallization: (a) top-down preparation of diamond nanowires, Ni was used as a mask during the etching of HPHT bulk crystal to obtain nearly vertical arrayed single crystal nanowires^[125], (b) a secondary anvil is formed by adding nanodiamonds to the single crystal diamond anvil cell (NCDs on SCD)^[126], (c) post growth of single crystal diamond on micro- or nano-needles, which can effectively improve the epitaxial quality^[117] and (d) patterned nucleation and growth on a foreign substrate, which is equivalent to the regular preset of crystal nuclei^[123]. Reprinted with permission.

be doped^[110] or further modified by other particles^[111], or be broken up and restructured^[112], resulting in a variety of morphologies and properties^[113].

The above technology is not only a method of controllable surface nanocrystallization of microcrystalline structure^[114] or bulk single crystal, but also a way to the high quality large-size single crystal diamond. It can be described as post-growth on the basis of diamond micro- or nanowires, which might be applied at the growth stage^[115] or later. After the deposition of a diamond film on a homogeneous HPHT wafer or heterogeneous Ir(100) substrate, it is etched into microwires or nanowires, followed by the continued growth on the structure obtained^[116], as shown in Fig. 7c. This treatment can effectively improve the quality of diamond films and reduce the full width at half maximum (FWHM) of rocking curve of the (004) diffraction peak from 0.22° to 0.07°^[117].

This is essentially an implemented case of patterned nucleation and growth (PNG), which is commonly used in the epitaxial growth for semiconductors^[118] to reduce the generation of threading dislocations at the interface between the substrate and diamond film^[119]. After diamond nucleation, the surface is etched into a designed pattern of different shapes, such as trenches and vias^[120], dot-arrays^[121] and stripes^[122], which is also equivalent to presetting regular crystal arrays. For example, grid network with Ir as the growth template and diamond crystals as the border^[123] can be obtained. Among the options of candidate mask materials, Ir might be the most suitable one^[124], due to the auxiliary function it can play on diamond nucleation.

Except for surface etching, nanocrystal bonding on single crystal diamond (nanocrystals on monocrystal, or NCDs on SCD) can also be used to realize surface nanocrystallization. The addition of a nanodiamond secondary anvil (Fig. 7b) to the bottom-tip structure of the traditional single crystal diamond anvil can eliminate brittleness of the single crystal diamond while maintaining the structural integrity of the primary anvil. In particular, nanodiamond particles prepared by the HPHT method can be positioned on

the bottom-tip surface^[127]. Nanocrystals can also be grown directly on the single crystal by the CVD method, which is of high stability and repeatability due to selective growth and chemical bonding^[125].

The process described above belongs to the concept of a bottom-up approach^[128], which is an alternate method for the preparation of diamond nanoclusters^[129] or nanowires^[130]. It relies on the self-assembly of molecules caused by physical or chemical interactions^[131]. Precise position control and the enhancement of the binding force with the primary structure are extremely necessary for the use in high-tech fields, which could be paid more attention to.

5 Conclusion and outlook

The research on the two extreme crystal size diamonds (large-size single crystal and nanocrystal diamonds) has been going on for several decades, and the topic is still attracting the attention of investigators. The two particle sizes represent different growth dimensions of the same kind of crystal materials, which leads to the innovation of a crystal growth theory.

As a three-dimensional material, bulk single crystal diamond has grown from epitaxial film from an area of 100 μm to a self-standing wafer with a thickness of more than one millimeter and a diameter of several inches. In terms of quality, the CVD crystal has almost no closed grain boundaries and threading dislocations with high purity, low defect density and structural integrity, which is comparable to that of natural diamond.

Nanodiamond is a kind of materials with a low dimension. Different preparation methods of zero dimensional nano-particles have been developed, which greatly improves the homogeneity and integrity of the particles when the particle size is decreased. The applications of one-dimensional diamond nanowires in the field of quantum computing and biological detection also allow a new development direction for nanodiamonds.

In this paper, the two kinds of materials are introduced, and the main preparation methods, properties, and applications are described. The concepts and ap-

proaches of crystalline state transformation and controlling are emphasized. The growth mechanism of large-size single crystal diamond is the aggregation and connection of nanocrystals, during which different morphologies and scales can be designed by adjusting growth parameters or layer thickness. The preparation of diamond nanowires and the selective deposition of diamond nanocrystals on single crystals are two ways of surface nanocrystallization, which can modify and change the morphology of crystal surfaces. They are effective ways to expand the theoretical research and application fields of diamonds.

There is still a lack of systematism and integrity in the research of diamond granularity transformation both in theory and experiment. The in-situ observation technology for the synthesis of large-size single crystal diamonds is not mature enough, and the description of the growth process is yet to be completed by more evidences as well. The development of the use of in-situ transmission electron microscopy may become an anticipated means to obtain detailed information, but the preparation temperature of large-size single crystal diamonds usually exceeds the working conditions, which needs to be further solved.

In addition to expect an improvement of observation methods, the routine of particle size transformation from nanocrystals to monocrystal itself still calls for expanding, and the realization process needs to be simplified. The future development direction can be based on the treatment under different temperatures and pressures for small-size nanodiamonds obtained by detonation. In this way, diamond crystals with an arbitrary particle size can be prepared by regulating the conditions and can be monitored by in-situ and real time observation, which can expand the particle size range of the products and make the process more controllable, leading to an extensive application scope.

Surface nanocrystallization of a single crystal, diamond, especially in the preparation of nanowires, has been verified by many experiments, but the theoretical investigation are still insufficient, so more researches are expected to be carried out to reveal the basic mechanism. Besides, large-size and high-quality

CVD single crystal diamond products have been prepared by an etching-assisted growth technology, which is realized by the introduction of micro- or nano- wires after the deposition of diamond wafer. They are promising candidate materials for a variety of devices with high performance. However, there is still a long way from laboratory to industrialization, which may be brought about by prematuration of device design.

The selective growth of nanodiamonds on the surface of a large-size single crystal diamond, whether as a functional material or a new structure material, is short of further attempts to find other applications. For example, it can be used as a method of precision adjustment to the structure, such as the preparation of gear microteeth, compensation of single crystal defects, and a secondary structure for hydrophobic material and so on.

In conclusion, many concepts of grain size controlling in growth and surface nanocrystallization after growth are still in the stage of theoretical imagination and need to be confirmed by experiments. It is also recommended that further work be undertaken to build universal principal theories.

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两种极限粒度的金刚石:从大尺寸单晶到纳米晶

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摘 要: 作为具有各种极端特性的金刚石材料的两种晶态, 宏观大尺寸块体单晶金刚石和微观纳米单晶金刚石均因其优异的性能, 引发了研究者的持续关注。近些年来, 两类金刚石的制备方法不断得到改进, 其性能改善的技术层出不穷, 更多的应用领域已被开发或处于探索之中。两种尺度的单晶金刚石在性能上各有千秋, 同时二者之间具有千丝万缕的联系, 两种晶态对应的晶粒尺度之间可以发生可控的互相转化。可以将块体单晶金刚石的合成过程描述为纳米晶的聚集、自组装和定向附着生长, 从而从纳米晶转化为英寸级大单晶形态。反之, 亦可以通过表面纳米化的方法将大尺寸单晶转化为纳米晶。本文介绍了两种不同尺度单晶金刚石的制备方法、性能和应用, 对块体单晶和纳米晶之间的相互转化方式进行了重点阐述, 并对这两种尺度的金刚石晶体的粒度调控等研究方向进行了说明和展望。通过晶态转化和粒度调控, 可以实现生长过程中对产物形貌和粒度的设计, 从而制备出新的结构或功能材料, 同时促进晶体生长理论的完善。

关键词: 大尺寸单晶金刚石; 纳米金刚石; 晶态转化; 晶体粒度调控

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