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Diamond Nanowire Synthesis, Properties and Applications

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Abstract

Due to the superior hardness and Young's modulus, biocompatibility, optical and fluorescence nanodiamond seems to be outstanding among carbon nanomaterials. In this footpath, the development of diamond nanowires (DNWs) is known to be a significantly innovative field due to their diverse applications such as sensors, semiconductors, and electrochemical utilities. Compared to carbon nanotubes, DNWs theoretically have energetic and mechanically viable structures. However, DNW synthesis in a reproducible way is still a challenging task. In fact, most of the DNWs can be successfully synthesized by chemical vapor deposition (CVD) and reactive-ion etching (RIE) techniques. By contrast, solution-based DNW synthesis has also emerged recently. A detailed study on DNW structures may help the emerging researchers to direct toward diverse applications. In this chapter, we comprehensively presented the up-to-date applications of DNWs along with their synthesis, structures and properties.

Keywords: diamond nanowires, nanowire synthesis, reactive-ion etching, chemical vapor deposition, semiconductors, electrochemical studies, sensors

1. Introduction

The development of nanowires for the effective applications still seems to be interesting and a challenging task [1–3]. So far, many kinds of nanowires have been constructed from various sources such as metals, polymers, inorganic-organic hybrid systems and semiconductor materials [4–7]. Those nanowires have the diverse mechanical, electrical, thermal and multi-functional properties [8, 9]. Further, nanowires can be effectively utilized in electrical transport studies, electrochemical studies and solar energy conversions [10, 11]. In this footpath,

diamond nanowires (DNWs) are also known as a material of extremes, in which, its properties are exceptional in terms of band gap, electron affinity, chemical inertness, resistance to particle bombardment, hardness and thermal conductivity [12]. Moreover, upon tuning the n- or p-doping on DNWs, the diverse field emission, semiconductor and sensory applications can be attained. The diverse applications may be attributed to the lattice structures of those DNWs as well as the carbon-carbon bond or existence of sp^2/sp^3 ratio [13, 14]. However, the presence of defects such as nitrogen vacancy center (NV^-) and impurity channels also enhances the benefits of DNW-based extensive research [15]. As a consequence of those defects or impurity channels, DNWs have the color centers, which enable their photonic applications such as single-photon emission [16]. Moreover, the toughness and wear resistance of DNWs may be enhanced due to the hindering of dislocation movement by the impurities.

Attributed to the utilities of DNWs, numerous reports on their synthesis have been available so far. However, the synthesis of DNWs was claimed to be a low probability event in terms of reproducibility, which makes it as a thought-provoking task. Therefore, researchers tend to develop the suitable methods to grow the DNWs due to its potential benefits in ultraviolet (UV) light detectors and emitters [17, 18] radiation particle detectors [19], high-speed and high-power field effect transistors [20], field emission sources [21, 22], position-sensitive biochemical substrates [23] and room temperature-stabilized high-efficiency single-photon emitters [24]. So far, DNWs were grown from (1) Plasma-assisted reactive-ion etching process (RIE) with mask and maskless techniques; (2) chemical vapor deposition (CVD) techniques with diverse templates assistance, plasma enhancement, catalyst assistance, and so on; (3) sp^2 -hybridized carbon and sp^3 -hybridized diamondoids (post-treatment of multiwalled carbon nanotubes (MWCNTs) with hydrogen plasma and from fullerenes). Similar to the above reported techniques on DNW growth, the development of hybrid graphene-DNWs (G-DNWs) also attracted the modern scientific research because of their diverse conductivity or semiconductor applications [12]. However, such nanowire (DNWs and G-DNWs) growth is still a challenging task; hence, an overview on its synthesis, structures and applications is required.

In this chapter, we tend to present a brief report of the diamond nanowires, with discussions on DNW synthesis along with their structures, properties and applications. Wherein, the important synthetic pathways to grow the DNWs are pinpointed. Then, the comprehensive discussions on the structures and properties of the DNWs are derived from the available theoretical and experimental reports. Subsequently, the applications of those DNWs in diverse fields are summarized.

2. Synthetic strategies for DNW growth

2.1. Plasma-assisted reactive-ion etching

Reactive-ion etching (RIE) is an etching technology applied in micro- or nanofabrication, which may apply the dry etching than that of wet routes [25]. Wherein, plasma has been used to remove material deposited on substrates. A schematic diagram presented in **Figure 1** represents a typical RIE setup.

In general, the plasma is generated by an electromagnetic field under vacuum. Then, plasma produces the high-energy ions, which react with the surface of the sample to provide the desired nanostructures. However, its output also depends on the parameters such as power density, frequency, pressure, dc bias, gas composition, flow rate and so on. In 1997, Shiomi et al. informed the DNW growth by means of plasma-assisted RIE technique [26]. Thereafter, RIE technique has been widely applied for the growth of DNWs. However, later on, DNWs were grown up either with the support of mask or maskless processes.

2.1.1. RIE with masks for DNW growth

The planar diamond films can be etched to obtain the DNWs. This also was attained with the support of several masks such as (1) metal nanoparticles mask, (2) oxide nanoparticles mask, and (3) diamond nanoparticles mask. However, the size and density of the developed DNWs depends on the nanoparticles that are used in masks, in which the size of those nanoparticles may lie in few nanometers.

(A) RIE with metal mask: After Shiomi's report [26] on DNW growth by using Al mask and oxygen plasma RIE, various columnar diamond nanowires with 300-nm length and 10-nm width have been constructed through etching CVD polycrystalline diamond films in O_2 plasma [27, 28]. In this light, Liao et al. effectively developed the single-crystal diamond pillar like DNWs by Al-masked RIE technique [29]. However, Al-masked RIE method led to provide polycrystalline DNWs, hence having the disadvantages such as the presence of grain boundaries, impurities and large stresses in the films. Apart from Al-mask, other kinds of metals such as Mo, Ni, Fe and Au were also been utilized to develop doped or undoped DNWs [30–32]. Li and Hatta explored the effect of those metal masks, for the development of DNWs [33].

(B) RIE with oxide nanoparticles mask: Fujishima et al. successfully developed the DNWs through reactive-ion etching supported by oxygen plasma consisting of two-dimensional

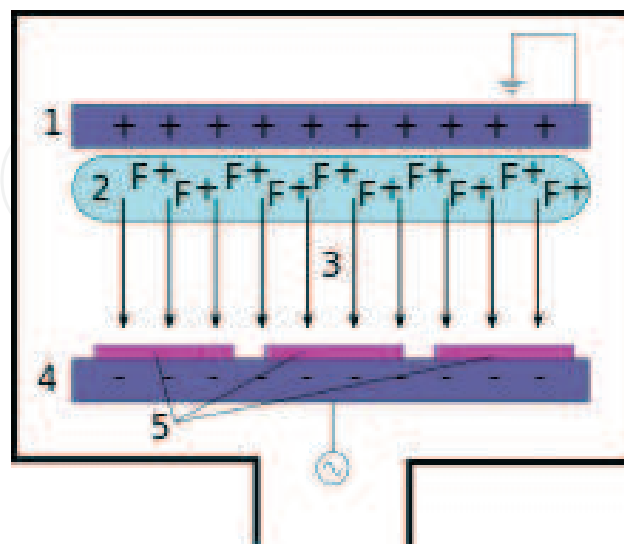


Figure 1. A diagram of a common RIE setup. An RIE consists of two electrodes (1 and 4) that create an electric field (3) meant to accelerate ions (2) toward the surface of the samples (5) (https://en.wikipedia.org/wiki/Reactive-ion_etching).

(2D) arrays of monodisperse solid SiO_2 particles as masks [34]. Wherein, on the planar diamond surface, fine SiO_2 particles are packed at high density [35] and oriented layers over a wide surface area by water evaporation and lateral capillary forces [36]. Then, reactive-ion etching (RIE) was carried out with oxygen plasma through the SiO_2 arrays for 5–120 min in a plasma-etching machine with a radio frequency (RF) generator. Lastly, the SiO_2 particles were detached from the diamond by HF-HNO_3 treatment, which afford the DNW arrays. After this report, Hausmann et al. also elaborate the DNW synthesis by Al_2O_3 mask [37], which found to be the most etch resistant. Hence, these flowable oxide masks are demonstrated to be a suitable etching mask for the construction of ordered arrays of DNWs.

(C) RIE with diamond nanoparticles: As shown in **Figure 2**, by using diamond nanoparticles as a mask, Yang et al. described the vertically aligned DNW synthesis from boron-doped single-crystalline CVD diamond films [38]. Initially, a microwave-assisted CVD technique is used to grow the boron-doped (P-type) diamonds with smooth surfaces by homoepitaxy on Ib diamond substrates. Next, diamond nanoparticles etching mask with well-defined size and quality is deposited. The size of those diamond nanoparticles (dissolved in water by ultrasonication to form a pseudostable suspension) lies between 8 and 10 nm. Thereafter, to seed diamond nanoparticles on the surface of a diamond substrate, the planar diamond film is immersed into the suspension and sonicated. After deposition, RIE in an O_2 (97%)/ CF_4 (3%) gas mixture is applied to afford the vertically aligned DNWs, which has been utilized in DNA sensing [39].

2.1.2. Maskless RIE for DNW growth

The above mask methods have certain limitations and hence become unfavorable for large-scale fabrication. Therefore, researchers tend to develop uncomplicated methods to remove some masks by additional chemical or physical processes that can grow the DNWs. In this way, Fujishima et al. described the synthesis of heavily B-doped DNWs (the boron doping level is $2.1 \times 10^{21} \text{ B cm}^{-3}$) through oxygen plasma without any additional mask [40]. Here, boron atoms on the diamond act as the mask during plasma etching, hence avoiding the deposition or removal of mask by additional steps. In detail, during the etching step, those boron oxide species are removed collectively with carbon atoms, and then they appear to redeposit near the tops of the DNWs, which may serve as an etching mask. This straightforward maskless method has been widely used for the synthesis of DNWs in recent times.

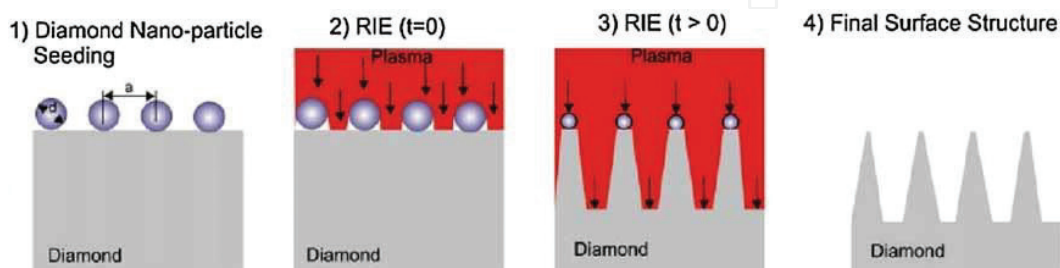


Figure 2. Schematic illumination of the fabrication of vertically aligned diamond nanowires using a top-down technology and using diamond nanoparticles as the etching mask. Reproduced with permission from [38].

2.2. Chemical vapor deposition (CVD) for DNW synthesis

Among the available effective methods for DNW synthesis, CVD technique is one of the promising processes utilized extensively [41]. This simple evaporation technique has been used to grow the elemental or oxide nanowires in an appropriate atmosphere. However, CVD process can be applied by means of template assistance or template-free ones as follows.

2.2.1. Template-assisted CVD methods for DNW growth

This is a convenient method to generate the 1D nanostructures and capable of producing nanostructures with exclusive structures, morphologies and properties [42–44]. Wherein, the template assists as a scaffold on which other materials with similar morphologies are produced. Moreover, they can be at nanoscale within mesoporous alumina or polycarbonate membranes. The following templates were applied so far to grow DNWs: (A) nanowires templated with CVD and (B) anodic aluminum oxide (AAO) templated CVD.

(A) Nanowires templated CVD for DNW growth: This method has two steps such as (1) synthesis of various nanowire templates and (2) conformal coating of nanowires templates with nanodiamond, which may lead to form the DNWs by CVD technique. Firstly, May et al. explored the microdiamond coatings into tungsten wires through CVD to construct the DNWs [45]. Afterward, several researchers applied this technique by using silicon, carbide, tungsten, titanium and copper nanowires as a template for DNW synthesis. **Figure 3** illustrates such B-doped DNW growth by Si nanowires template [46].

(B) Anodic aluminum oxide (AAO) templated CVD: Masuda and coworkers illustrated the growth of polycrystalline DNWs and diamond-like carbon (DLC) nanotubes by means of anodic aluminum oxide templates in microwave plasma-assisted CVD [47], in which those alumina templates [48] were prepared by electrochemical anodization of an aluminum sheet. Alumina templates possessing the holey nanoporous membranes and nucleated with 50- and 5-nm diamond particles led to the formation of DNWs. In this process, the deposition of diamond through the alumina pores yields a continuous film and supports the formation of nanostructures. Finally, by immersing in concentrated phosphoric acid at 250°C, those nanostructures can be released from the alumina.

2.2.2. Template-free CVD techniques for DNW growth

More recently, template-free CVD methods for DNW synthesis attracted the scientific community. Those template-free CVD techniques are (A) microwave plasma-enhanced CVD

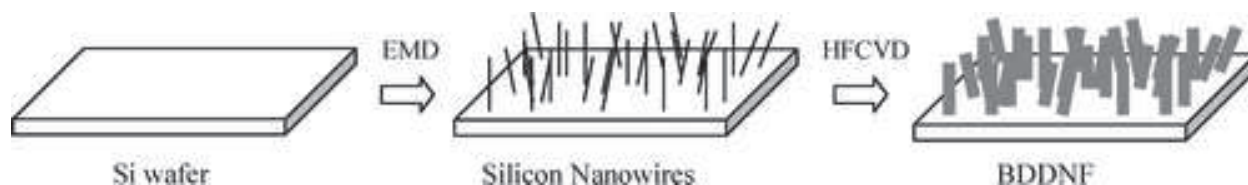


Figure 3. Fabrication of B-doped DNWs by Si-nanowires templates with CVD. Reproduced with permission from [46].

(MPCVD), (B) hot cathode direct current plasma CVD (HCDC-PCVD), and (C) catalyst-assisted atmospheric pressure CVD. Detailed information of the above CVD methods is presented subsequently.

(A) Microwave plasma-enhanced CVD (MPCVD): At first, Valsov et al. presented the synthesis of hybrid graphite-diamond nanowires (G-DNWs) over an ultrananocrystalline diamond (UNCD) film by using MPCVD technique [49]. Afterward, Shang and coworkers described the development of ultrathin diamond nanorods (UDNRs) by this method [50]. However, the incorporation of N_2 becomes essential as demonstrated by recent reports [51, 52], wherein the incorporation of N_2 enhances the electrical conductivity through tuning the sp^2/sp^3 carbon ratio. Hypothetically, the introduction of nitrogen into plasma may motivate the formation of molecular CN species, thereby generating favorable conditions for an increase in the grain size as well as the formation of 1D diamond nanostructures. In general, DNWs synthesized through MPCVD technique show good electrochemical properties due to the rise of sp^2 content, new C-N bonds at the grains and an escalation in the electrical conductivity at the grain boundaries [53].

(B) Hot cathode direct current plasma CVD (HCDC-PCVD): This is an innovative technique for the deposition of nano- and micro-crystalline diamond films with uniformity over a large area and with a high growth rate. Here, the cathode made up of a tantalum disc linked to a water-cooled cylindrical copper block, water-cooled copper block anode and a nonpulsed-type dc power source is used. From this technique, Zeng et al. explored the formation of DNWs along with (111) diamond microcrystals and (100) diamond microcrystals on Si substrates [54].

(C) Catalyst-assisted atmospheric pressure CVD: Apart from the previously mentioned high-temperature methods assisted by plasma or energy radiation, the production of long single-crystalline DNWs by conventional thermal CVD methods has become essential because of their potential benefits. In this light, Hsu et al. described the growth of DNWs by means of CVD without plasma or energy sources and at atmospheric pressure [55]. Here, methane and hydrogen were flowed into the Fe catalyst solution, which was dispersed on an Si substrate at 900°C . Then, pure hydrogen was run through the quartz tube chamber (at 200 sccm as rate) without pumping the residual methane. Subsequently, the temperature lowers down to an ambient condition at a rate of $1.2^\circ\text{C min}^{-1}$ for 12 h. This method will produce the uniform long and thin DNWs with a diameter of 60–90 nm. Importantly, in this process, hydrogen plays a vital role in the formation of DNWs via sp - and sp^2 -hybridized bonds transformation into sp^3 -hybridized atoms [56]. **Figure 4** demonstrates the possible vapor-liquid-solid (VLS) mechanism for the growth of DNWs by this method [57]. This technique supports the exceptional utilization CVD with the support of transition metal catalyst such as Fe and also envisioned the applicability of CVD at atmospheric pressure.

2.3. DNW growth from sp^2 carbon and sp^3 diamondoids

Attributed to the importance, the conversion of sp^2 graphite carbon to sp^3 diamond crystals remains to be a challenging task over many years for which high pressures and high temperatures are required. Recently, researchers developed few methods for such transformation;

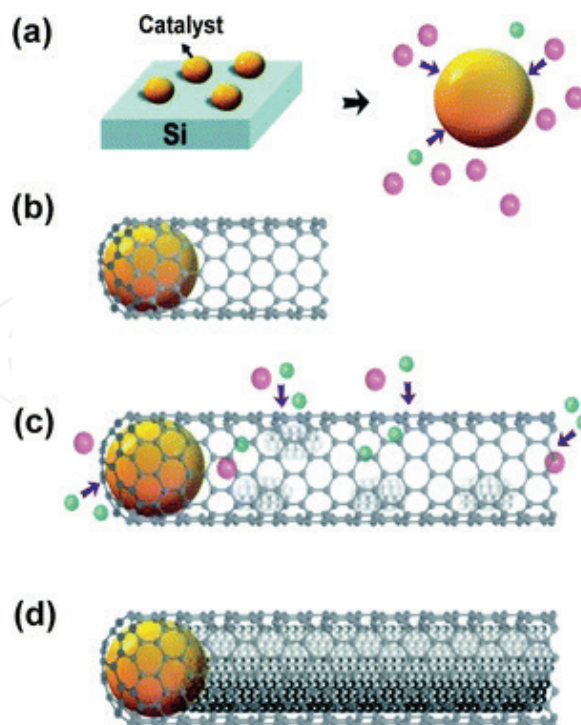


Figure 4. Schematic diagram showing a possible formation process of diamond nanowires: (a) catalytic particles are formed from the evaporated or deposited thin film on the substrate as the temperature rises; (b) carbon-containing radicals reach the surface of the catalysts, leading to the growth of either a diamond stud or a graphitic tube via the VLS mechanism. The size is determined by the catalyst. (c) Hydrogen assists in the growth process by either preferentially etching sp^2 and sp^3 bonds or transforming them into sp^3 bonds. With the higher capillary pressure at smaller diameters, the diamond phase could be more stable but the capillary pressure rapidly decreases with diameter, leaving the shell more stable in the graphitic phase. (d) The grain growth, boundary healing and structural reorganization take place in the slow-cooling period in the presence of a pure hydrogen flow. Reproduced with permission from [57].

however, it is still a challenging task. The following are few examples of transformation of sp^2 graphite carbon to sp^3 carbon, which led to the formation of DNWs: (A) DNW synthesis by hydrogen plasma post-treatment of multiwalled carbon nanotubes, (B) DNW growth from fullerenes and (C) DNWs from diamondoids.

(A) DNW synthesis by hydrogen plasma post-treatment of multiwalled carbon nanotubes (MWCNTs): In 2005, Sun and coworkers presented this simple method for the growth of DNWs from carbon nanotubes (CNTs) via hydrogen plasma post treatment [58]. Impressively, upon extended hydrogen plasma treatment, the DNWs with the diameters of 4–8 nm and with the lengths up to several hundreds were obtained. This work also revealed the TEM of single-crystal DNWs from the MWCNTs after treatment in hydrogen plasma at 1000 K for 20 h. The author proposed the mechanism as clustering, crystallization, growth and faceting, which is similar to the report by Singh et al. [59]. It is also established that the presence of amorphous carbon sheath over diamond nanoparticles and DNWs is responsible for this kind of transformation.

(B) DNW growth from fullerenes: In 2005, Dubrovinskaia and coworkers synthesized a bulk sample of nanocrystalline cubic diamond from fullerene C_{60} , which have the crystallite sizes of 5–12 nm and a hardlike single-crystal diamond [60]. **Figure 5** represents the TEM of those ADNRs. These nanocrystalline diamonds seem to be highly stable at an elevated temperature

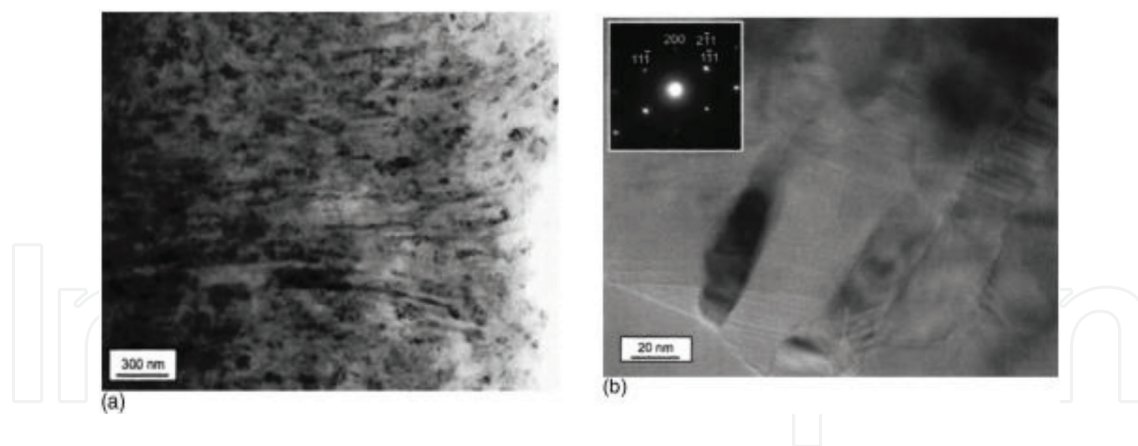


Figure 5. (a) Bright-field TEM image of a nanocrystalline aggregate with needle-shaped, elongated crystals diamond nanorods. The crystals can be longer than $1\ \mu\text{m}$, whereby the needle width is only about $20\ \text{nm}$ or less; (b) bright-field image shows a close-up of the elongated crystals. The long edges of the crystals are parallel to the (111) plane, and the needle axes are approximately parallel (211)*. Reproduced with permission from [60].

and an ambient pressure. In the meantime, they developed the aggregated diamond nanorods (ADNRs) from C_{60} by multi-anvil apparatus [61]. Those ADNRs have the diameter of $5\text{--}20\ \text{nm}$ and have the length of more than $1\ \mu\text{m}$.

(C) DNWs from diamondoids: Similar to carbon nanotubes and fullerenes, diamondoids may also lead to the formation of DNWs. The 1D diamondoid aggregates confined in CNTs directed to form the DNWs via ‘face-fused’ reaction. However, these transformations of adamantane into DNWs seem to be energetically not feasible. Contrarily, Zhang et al. explored the theoretical and experimental proof for these fusion reactions by diamantane-4,9-dicarboxylic acid transformation to 1D diamond nanowires inside CNTs [62]. In which, the fusion of diamantane-4,9-dicarboxylic acid under the confinement of CNTs yields the DNWs.

2.4. Wet chemical route to synthesis DNWs

Attributed to the applications of DNWs, numerous efforts have been made by the researchers to synthesize them. Among them, wet chemical route seems to be impressive with respect to cost-effectiveness than that of RIE and CVD techniques. But it is also essential to make them with reproducibility and uniformity. To this footpath, recently, our group report the pH-induced electrostatic self-assembly of novel cysteamine functionalized diamond nanoparticles (ND-Cys) to evidence hybrid G-DNW growth [63]. Those G-DNWs are highly stable in respective pH buffers, but if more amount of DI-water is added, the longer nanowires (initially at $\sim 100\ \mu\text{m}$) break into small wires/rods (few microns). At pH 6, the width of G-DNWs ranges between 20 and $800\ \text{nm}$ and the length lies between $200\ \text{nm}$ and hundreds of microns with respect to dispersion concentration. Wherein, the DNW formation was initiated through electrostatic forces within the partially graphitized ND-Cys particles. Next, those partially graphitized ND-Cys particles and defects/impurity channels were further promoted to form the graphene shells on the surface of DNP and sandwiched between the diamond cores. These G-DNWs show exceptional conductivity due to the presence of defects and impurity channels. **Figure 6** illustrates the TEM image of those nanowires with defect or impurity channels.

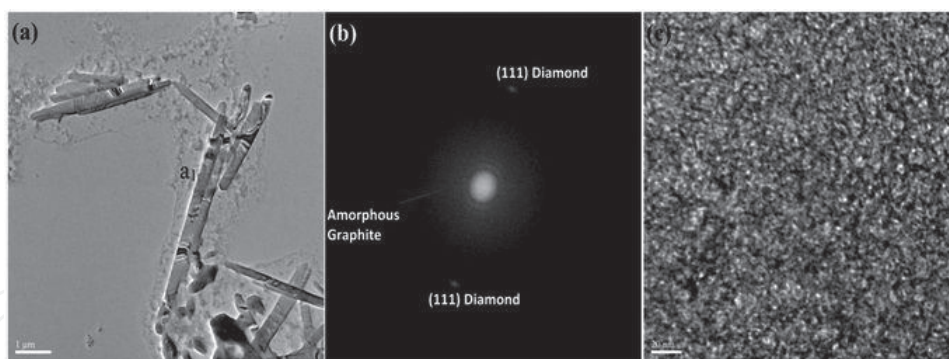


Figure 6. (a) HR-TEM image of G-DNWs, (b) FT pattern of selected area a_1 representing amorphous graphite along with diamond (111) diffraction pattern and (c) high magnification image of a_1 region representing less perfect graphite layer along with defects or impurity channels. Reproduced with permission from [63].

In this way, with respect to Berman et al. report on metal-induced graphitization of diamond particles [64], metal ions induced G-DNWs formation is also seem to be highly feasible. However, the reproducibility and percentage formation of G-DNWs by this path is still a challenging task. Currently, our group is working on this research to grow the G-DNWs with good reproducibility.

3. Structures and properties of DNWs

In order to establish the diverse applications of DNWs, the structure and properties should be elucidated. The properties such as structural stability, mechanical properties, density and compressibility, photon optical mode and electronic structure, thermal conductivity and electrochemical properties play vital role in their applications. Hence, researchers described the experimental and theoretical investigations on the structure and properties of DNWs as follows.

3.1. Structural stability of DNWs

From theoretical investigations, it has been found that dehydrogenated C(111) octahedral nanodiamond surfaces are structurally unstable. However, cuboctahedral structures of nanodiamond may increase the C(100) surface area and become more stable, which also reduce the surface graphitization. In this light, Barnard et al. investigated three kinds of DNWs including dodecahedral, cubic and cylindrical nanowires and found that nanocrystalline diamonds are structurally stable at one dimension [65]. Moreover, they also demonstrate that stability depends on the surface morphology and crystallographic direction of the principal axis of DNWs. In a similar fashion, Tanskanen and coworkers established the structures of polyicosahedral DNWs derived from diamondoids, $C_{20}H_{20}$, $C_{20}@C_{80}H_{60}$, and $C_{20}@C_{80}@C_{180}H_{120}$. For which they have summarized the HOMO-LUMO gaps, and band gaps via B3LYP calculations [66]. Wherein, the $C_{20}@C_{80}@C_{180}H_{120}$ structures are energetically favored and the DNWs at 110 direction have the lowest strain energies leading to more stability. This has been experimentally

proved by the stability of DNRs (at 110 direction) synthesized through hydrogen plasma post-treatment of multiwalled CNTs [58], whereas the DNWs at 100 direction seem to be unstable as reported earlier [67].

3.2. Mechanical properties of DNWs

Tanskanen et al. described the mechanical properties of DNWs through Poisson's ratios, Young's moduli and shear moduli interrogations [66], which proved that (111) DNWs have the highest Young's moduli than the (110) and (111) DNWs. In this report, they suggest that polyicosahedral DNWs have more strain than that of conventional DNWs. In this way, Guo and coworkers presented the mechanical properties of (001) DNWs by means of molecular dynamics simulations [68] and specified that Young's modulus of those DNWs is lower than those of bulk diamond. Similarly, Jiang et al. explored Young's modulus of DNWs in different crystallographic orientations as a function of cross-sectional area [69]. Wherein, Young's modulus has the sequence of (100), (110), (111) and (112) directions and indicated that those values are lower than the bulk value and increase with its cross-sectional area.

3.3. Density and compressibility of DNWs

Initially, Dubrovinskaia and Dubrovinsky reported the density of the aggregated diamond nanorods (ADNRs), which were developed from fullerene C_{60} by multi-anvil apparatus [61]. The X-ray density of ADNRs is about 0.2–0.4% greater than the bulk diamond, which also corresponds to the measured density of $3.532(5) \text{ g cm}^{-3}$. The higher density of ADNRs may arise from the outerlayer contraction leading to shortening of the C-C bonds inside the diamond. In this work, they have also evaluated the compressibility of ADNRs by using the third-order Birch-Murnaghan equation of state, wherein they established the >11% lesser compressibility of ADNRs than that of usual diamond.

3.4. Phonon optical modes and electronic properties of DNWs

Trejo and coworkers reported the optical phonons and Raman-scattering properties of DNWs by using a local bond polarization model based on the displacement–displacement Green's function and the Born potential [70]. Further, they have also studied the electronic band structure of DNWs through a semiempirical tight-binding approach and compared with density functional theory (DFT) studies. From the calculations, they have concluded that phonons and electrons tend to show a clear quantum confinement signature. Moreover, this study also establishes that during the DNWs width increase, the Raman peak shifts to lower frequencies due to the phonon confinement, as reported by our group [71]. Subsequently, the band gap also decreases as the width of the DNWs increases.

3.5. Thermal conductivity and electrochemical properties of DNWs

In general, it is recognized that the thermal conductivity of DNWs may not be incredibly affected by surface functionalization. However, at nanometer scale, dimensions of DNWs may reduce the thermal conductivity than that of bulk diamond as demonstrated by Novikov et al. [72]. In this way, Moreland and coworkers explored that the conductivity of DNW is lower

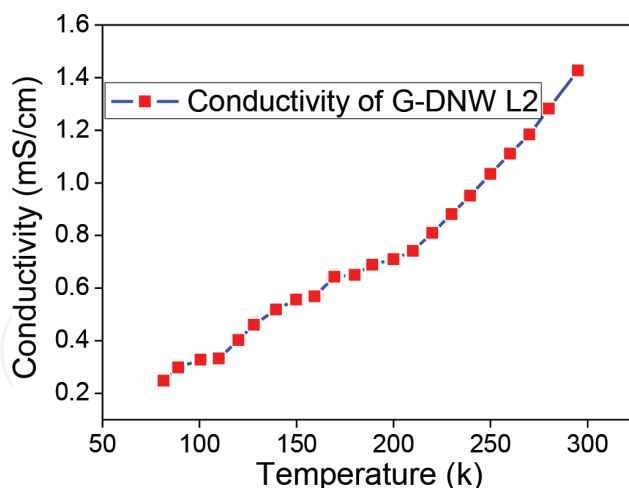


Figure 7. Temperature-dependent conductivity of DNW L2. Reproduced with permission from [63].

than the CNT and depends on the choice of thermostat [73]. Similarly, Guo et al. described that the thermal conductivity of DNWs may rise with respect to the increase in length and cross-sectional areas [74]. Recently, as seen in **Figure 7**, our group also proved the downfall in the conductivity of a single G-DNW with respect to a decrease in temperature [63]. Overall, it has been concluded that between 0 and 1000 K, DNW's thermal conductivities firstly upsurge with an increasing temperature and then dropdown.

Next, coming to the electrochemical properties, it is well recognized that the planar boron-doped diamond (BDD) materials have the unique physical properties and were already been effectively applied as electrodes in many sensing studies. Wherein, compared to glassy carbon electrode, the diamond electrode acts as a potential candidate due to its chemical stability and biocompatibility [75]. Moreover, BDD electrode is not fouled easily and has a low background current with a wide potential window. By altering the surface end of BDD, the electronic and chemical properties can be tuned according to the requirement. Currently, the BDD nanogross array is also involved in electron transport and electrocatalytic utilities [76, 77]. Conclusively, it is well established that the nanotextured DNW surfaces become the suitable platform for novel biosensor investigations.

4. Applications of DNWs

Among the applications of DNWs, the following five utilities have been demonstrated strongly. Those applications are (1) field emission applications of DNWs, (2) DNWs in mass analysis of small molecules, (3) DNWs as nanoelectromechanical switches, (4) DNWs as electrochemical sensors and (5) DNWs in ultrasensitive force microscopy.

4.1. Field emission applications of DNWs

The negative electron affinity of DNWs has been used in field emission studies. Recently, reports on the electron field emission (EFE) properties of CVD-developed ultracrystalline

diamond and hybrid diamond-graphite films were reported [78, 79]. In this way, the EFEs of DNWs were also been described by (A) planar DNWs array and (B) single DNW.

(A) Electron field emission of planar DNW array: Lee et al. demonstrated the EFE characteristics of planar diamond film array, which has been developed by CVD techniques [80]. Recently, Sankaran et al. presented the improved EFE applications of graphite-wrapped DNWs [81]. In this path, the above group determined the enhanced electron field emission of vertically aligned ultrananocrystalline diamond needles via ZnO coating to form the heterostructured nanorods [82]. Wherein, it shows a high emission current density of 5.5 mA cm^{-2} at $4.25 \text{ V } \mu\text{m}^{-1}$ and has a low turn-on field of $2.08 \text{ V } \mu\text{m}^{-1}$ than that of bare Zn-nanorods. This outstanding emission property of planar diamond film arrays seems to be impressive to apply as the electron emitters in flat display panels.

(B) Electron field emission of a single DNW: Recently, Hsu and coworkers presented the electron field emission of a single DNW [57]. Wherein, the threshold field of DNW ($1.25 \text{ V } \mu\text{m}^{-1}$) is four times lower than that of carbon nanotube ($5 \text{ V } \mu\text{m}^{-1}$). This might be due to the electron affinity of DNW and defects existence. In addition, the EFE property of DNW may be attributed to its chemical inertness, high mechanical strength and high thermal conductivity.

4.2. DNWs in mass analysis of small molecules

Firstly, Coffinier et al. described the matrix-free laser desorption/ionization (D/I) mass spectrometric utilization of boron-doped DNWs (BDD NWs) toward small molecular analysis [83], in which the S/N ratios of UDD NWs are very low than that of BDD NWs. Therefore, the potentiality of BDD NWs in mass analysis of small molecules has been proved.

4.3. DNWs as nanoelectromechanical switches

Recently, researchers tend to develop the diamond-based nanoelectromechanical (NEM) switches as an alternative silicon-based ones due to its exceptional properties such as high Young's modulus, maximum hardness, hydrophobicity, low mass density, greater thermal conductivity, extraordinary corrosion resistance and low toxicity. However, because of existed grain boundaries, impurities, large stress, low electrical conductivity and poor reproducibility, the polycrystalline or nanocrystalline film-based switches seem not to be as impressive candidates [84, 85]. In contrast, the utilization of single-crystalline DNWs as NEM is appraised by Liao and coworkers [29], in which those switches show low leakage current ($<0.1 \text{ pA}$) with a high ON/OFF ratio, hence can compete Si-NEMS structures.

4.4. DNWs as electrochemical sensors

DNWs were effectively applied in many electrochemical sensory studies. For example, Yang and Nebel utilized the vertically aligned diamond nanowires toward DNA detection *via* electrochemical approach [86]. **Figure 8** represents the schematic of biofunctionalized vertically aligned diamond nanowires for the determination of DNA in the abovementioned report.

Further, they have protracted those diamond nanowires in electrochemical gene sensors [87]. Akin to vertically aligned nanowires, BDD NWs were applied in nonenzymatic amperometric

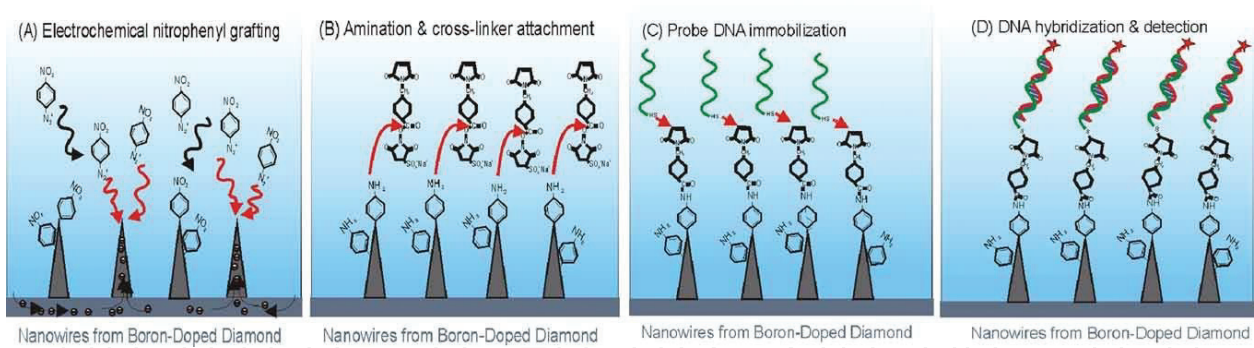


Figure 8. Schematic illumination of the biofunctionalization of vertically aligned diamond nanowires to realize a nanoscaled spacing between DNA molecules. Reproduced with permission from [86].

glucose biosensing by Zhi et al. [46]. Wherein, the selective determination of glucose has been demonstrated in the presence of ascorbic acid (AA) and uric acid (UA). Meanwhile, BDD NWs were also been efficiently used in the electrochemical identification of tryptophan by Szunerits and coworkers [88]. Alternatively, Lee and Lin collaborators developed a nitrogen incorporated DNW electrode for the amperometric detection of urea and *in situ* detection of dopamine [89]. Here, dopamine determination was well illustrated in the presence of AA and UA. More recently, Peng et al. reported the detection of CO gas by BDD NWs through electrochemical studies [90]. Wherein, the boron-doped ultrananocrystalline diamond (B-UNCD) nanowires (NWs) evidenced greater selectivity to CO gas than that of competitive species.

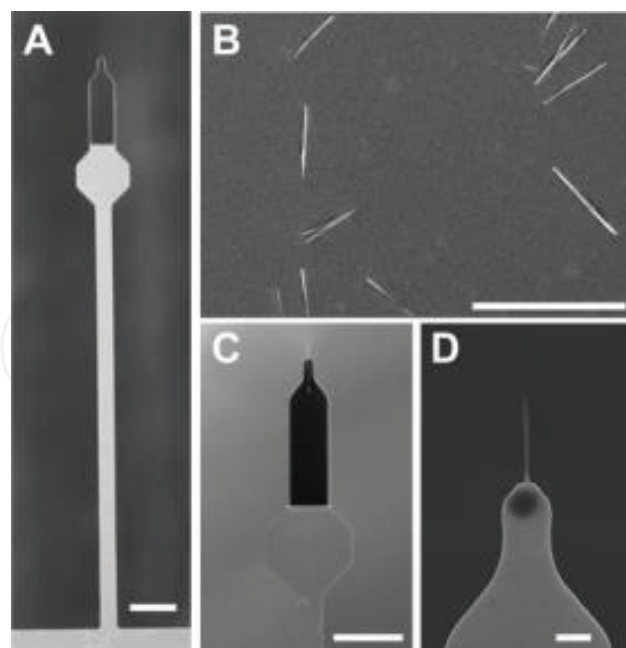


Figure 9. Integration of diamond nanowire tips on ultrasensitive silicon cantilevers. (A) Bare silicon cantilever with a nominal length of 90 μm , a shaft width of 4 μm and a thickness of 135 nm. The scale bar is 10 μm . (B) Batch of DNWs transferred onto an Si substrate for manual pickup. The scale bar is 10 μm . (C, D) zoom-in onto the end region of two different cantilevers where DNW tips had been attached. Scale bars are 10 μm in C and 1 μm in D. Reproduced with permission from [91].

4.5. DNWs in ultrasensitive force microscopy

Recently, Tao et al. described the utility of DNWs as tips for ultrasensitive force microscopy experiments [91]. Wherein, they have fabricated two types of tips using the upper and lower halves of a DNW by means of a top-down plasma etching technique and from a single-crystalline substrate. **Figure 9** demonstrates the integration of diamond nanowire tips on ultrasensitive silicon cantilevers. The typical lengths of those DNWs lie in few micrometers with diameters around 100 nm. Moreover, the tip radii were at the order of 10 nm, hence becoming suitable for scanning probe applications [32].

5. Conclusions and perspectives

Attributed to the importance of DNWs, several efforts have been driven by experts to apply in diverse semiconductor and biological applications. In this way, those DNWs were effectively developed through different methods such as reactive-ion etching, chemical vapor deposition, from sp^2 carbon and sp^3 diamondoids and wet chemical route. Among them, the template-assisted synthesis of DNWs seems to be impressive to produce highly precise nanostructures. On the other hand, the cost-effective wet chemical route still remains a challenging task in terms of reproducibility and obtaining the unique structures. From experimental and theoretical studies, it has been found that DNWs have the exceptional structural, mechanical, thermal conductivity, electronic and electrochemical properties. However, structural studies on hybrid G-DNWs require exclusive focus for future applications. Subsequently, those DNWs also possess the unique applications such as EFE device, high-performance NEM switches, conductivity and electrochemical biosensor and so on. However, with respect to practicality, those applications remain unsatisfied. For instance, the reported DNW-based electrochemical biomolecules monitoring was affected by its stability; hence, still it is a challenging task to fabricate the DNW-based device for real-time continuous determination.

So far, except the wet chemical route, the reported synthetic techniques for DNWs are costly, and hence their development is still a challenging task. Therefore, much effort needed to develop the DNWs at large scale, which can be attained by the collaboration of diverse technical fields such as electro-biochemistry, nanoelectronics and analytical techniques, etc. For example, attempts are needed to develop hybrid G-DNWs by the association of CVD and wet chemical pathways. Such investigations may direct the DNWs toward diverse opto-electronic applications.

Conflict of interest

The author declares that there is no conflict of interest.

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