Nanocrystalline Diamond Coatings

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Abstract
This entry describes the common chemical vapor deposition techniques to produce (ultra) nanocrystalline diamond (UNCD/NCD) coatings and discusses the associated mechanisms including the roles of hydrogen and argon in the processes. UNCD/NCD coatings are commonly doped with boron and nitrogen, and the corresponding electronic, electrochemical, and optical properties are discussed. The surface properties of the materials can be tailored using different surface modification techniques, and the use of UNCD/NCD coatings in micro-electromechanical systems and electron emission devices is described.

INTRODUCTION
Owing to the unique combination of physical, chemical, and mechanical properties such as high thermal conductivity, high hardness, large band gap, optical transparency, stability against chemical reagents, high mechanical stability, and corrosion resistance, diamond films have attracted considerable scientific and technological interests. However, conventional diamond coatings are too rough and the variable surface morphology has hampered wider industrial, biomedical, and consumer product applications. In this respect, smoother films with decreased crystal size are technologically better.

Nanocrystalline diamond (NCD) coatings are typically produced in a hydrogen (H₂)-rich chemical vapor deposition (CVD) environment. The materials have grain sizes ranging from a few nanometers to a hundred nanometers, which tend to increase with film thickness, and very small amounts (<5%) of sp²-bonded carbon in the form of defects or grain boundaries. Ultra nanocrystalline diamond (UNCD) coatings were first fabricated by CVD under H₂-poor and argon (Ar)-rich conditions by Gruen and coworkers in 1994. UNCD is generally characterized by crystalline grains 2–5 nm in size (independent of film thickness) surrounded by a layer of nondiamond carbon connecting the grains and possesses a significant sp²-bonded carbon content of around 10%. Gruen observed that when the crystalline size was reduced, the percentage of carbon atoms located in the grain boundaries increased drastically, thus affecting the mechanical and electrical properties of the NCD coatings. Therefore, in addition to possessing the robust chemical, mechanical, and thermal properties typical of conventional CVD microcrystalline diamond coatings, NCD and UNCD coatings have other distinctive properties including the smaller grain size, smoother and more uniform surface morphology, lower threshold for field emission, and smaller macroscopic friction coefficients. UNCD coatings are also electrically conductive due to the nondiamond matrix. Both NCD and UNCD can be readily doped with nitrogen or boron to produce high conductivity and have applications in nano/micro-electromechanical systems (N/MEMS), tribology, biotechnology, electrical and electrochemical devices, and optical devices. This entry presents a concise review encompassing CVD deposition, doping, modification, properties, and applications of NCD coatings. The burgeoning materials and field have attracted much research interests, and readers are referred to other reviews including the deposition techniques, growth mechanism, and mechanical properties for more information.

COATING DEPOSITION

Techniques
Diamond coatings are typically deposited by CVD. The plasma necessary for the deposition is activated by hot filaments (HFs) heated to 2,200–2,800°C [1–6] direct current (DC) [7,8] or microwave (MW) [9–13] MWCVD and HFCVD are the most commonly used to grow diamond thin films. While MWCDV offers more versatility in the gas choice and process control, HFCVD is more attractive economically and easier to operate and maintain.
In addition, HFCVD can be readily upscaled to substrates larger than 400 mm but it is difficult for MWCVD systems. In HFCVD, the chemical stability of the substrate, deposition parameters as well as precursor gases determines the growth rate and quality of the diamond layers.\(^{14}\) In MWCVD, NCD deposition is typically conducted in a methane (\(\text{CH}_4\))/\(\text{H}_2\) mixture.\(^ {15-17}\) \(\text{H}_2\) can be replaced partially or completely by \(\text{Ar}\)\(^ {18}\) or \(\text{N}_2\)\(^ {19,20}\) by reducing the pressure,\(^ {21}\) MW power, or substrate temperature\(^ {22-24}\) or by applying a bias voltage during deposition.\(^ {25,26}\) The various CVD techniques have been reviewed.\(^ {21,27-29}\) In addition, compact NCD coatings have been prepared by a high-pressure high-temperature (HPHT) process similar to the one used in the commercial production of synthetic diamond.\(^ {30-34}\) In this entry, diamond coatings produced by CVD techniques are described.

**Nucleation**

Diamond nucleation on nondiamond surfaces without pretreatment is usually very difficult and slow. Small nucleation densities typically lead to poor film properties especially thermal conductivity and roughness.\(^ {22,35,36}\) Nucleation in the early growth stages is vital to film growth and morphology.\(^ {37-43}\) One important pretreatment is substrate activation performed by scratching with diamond powder.\(^ {44,45}\) The process embeds small residual diamond particles into the substrate resulting in higher nucleation densities and better uniformity.\(^ {46-48}\) possibly due to the larger surface-to-volume fraction of fine scratches. Alternatively, denser nucleation can be achieved by immersing the substrate into a suspension of diamond particles followed by ultrasonic treatment.\(^ {37,39,41}\) This yields more uniform film growth and smoother films. The nucleation mechanism is similar to the abrasion process in which the ultrasound causes similar damage to the substrate as the embedded diamond fragments. Contrary to abrasion techniques, the nucleation density actually increases with particle size because the very small diamond particles have insufficient momentum to damage the substrate or embed the diamond fragments.\(^ {137}\) Another approach to enhance the diamond nucleation density is to coat the substrate with many diamond particles as possible. They act as seeds for subsequent epitaxial growth and the basic mechanism is electrostatic attraction of fine particles to the substrate. The last technique has advantages such as no substrate damage, 3-D possibilities, and simple up-scaling. It has been shown that the nucleation density increases with decreasing dimensions of the seeding materials.\(^ {40,49}\)

Carbon-derived interlayers have been shown to increase the local nucleation density due to the higher surface sticking coefficient, larger carbon content, or higher carbon growth species surface mobility.\(^ {50,51}\) that is, a mechanism which enhances the surface carbon concentration or provides a carbon diffusion barrier should be beneficial.\(^ {38,51-55}\) Furthermore, the more sp\(^ 3\) content the interlayer has, the better is nucleation.\(^ {56}\)

A special nucleation technique called bias-enhanced nucleation (BEN) can be applied to conductive substrates. In this method, the substrate is negatively biased to 100–250 V DC with respect to the chamber or a second internal electrode.\(^ {57-62}\) According to the report by Lee et al.,\(^ {57}\) the bias voltage shows more pronounced effects on improving the electron field emission capacity of diamond than doping with boron. It can be ascribed to the increased grain boundaries which are highly conductive and good emission sites. Sharda et al.\(^ {58}\) and Jiang et al.\(^ {59}\) have extended the use of the bias voltage over the growth period to enhance secondary nucleation of diamonds that leads to the formation of NCD.\(^ {57}\)

Larger nucleation densities can be accomplished by combining the aforementioned techniques.\(^ {62-67}\) For example, Rotter et al. have developed multistage nucleation starting with a short growth step on the mirror silicon (Si) surface to produce a thin carbon layer followed by treatment in an ultrasonic bath containing a suspension of nanodiamond particles.\(^ {62}\) This process embeds diamond fragments into the carbon layer, and subsequently, the carbon layer becomes a high concentration source of carbon for particle growth and is completely removed during the early stages of growth. Sumant et al. have reported a similar approach by first exposing the substrate to a hydrocarbon plasma for a short time to induce the formation of silicon carbide at the diamond/Si interface along with a thin, uniform layer of hydrogenated amorphous carbon on top. This amorphous carbon layer enables the formation of a uniform and dense layer of nanodiamond seed particles spread over the substrate in the second step.\(^ {60}\) Lee et al. have shown that a 50-nm thick Si overlying layer on the nucleated substrate can increase the nucleation density by almost two orders of magnitude.\(^ {67}\) The nucleation kinetics of diamond on the Mo-coated Si followed by an ultrasonic seeding step with nanosized detonation diamond powders is increased 10 times compared to blank Si.\(^ {68}\) Naguib et al. have reported that thin layers of tungsten can enhance the nucleation density on account of the formation of carbide at the interface impeding carbon diffusion into the substrate,\(^ {65}\) although this metal interlayer may be undesirable in optical coatings.\(^ {69}\)

**Growth Mechanism**

Most research activities have hitherto focused on the use of \(\text{Ar}/\text{CH}_4\) (with or without \(\text{H}_2\)) to deposit NCD and UNCD.\(^ {70-74}\) Alternatively, NCD can be produced using high concentrations of \(\text{CH}_4\) in \(\text{H}_2\)\(^ {75}\) or \(\text{CH}_4/\text{H}_2\) containing \(\text{N}_2\)\(^ {76,77}\) and/or \(\text{O}_2\).\(^ {78}\) In all these cases, \(\text{H}_2\) is the carrier gas, \(\text{CH}_4\) is the carbon source, and the other gases supply the dopants.\(^ {77-79}\) The role played by \(\text{O}_2\), \(\text{N}_2\), \(\text{halogen,}\)\(^ {82}\) and other chemistries\(^ {83,84}\) may not be critical to the basic understanding of diamond growth. It is generally...
regarded as perturbation of the CH$_4$/H$_2$ chemistry. In this section, we will discuss the Ar/CH$_4$/H$_2$ chemistry and consider diamond growth on existing diamond surfaces.

**Role of CH$_4$**

There are two main procedures and mechanisms pertaining to the preparation of NCD coatings. The C$_2$ insertion mechanism was proposed by Gruen and coworkers. There have been follow-up studies about this mechanism and the role of Ar in the growth process will be discussed later. It has been proposed that NCD films can be synthesized by substrate BEN in conventional CH$_4$/H$_2$ plasma CVD. When the substrate is biased negatively, cations such as H and CH$_x$ play an important role in the subplantation model, and it will be discussed later in this entry in the section discussing about the role of H$_2$ in diamond fabrication.

CH$_4$ in the precursor mixture has a profound effect on the morphology and properties of the diamond coatings. The nucleation density, nucleation rate, and adhesion strength of the diamond coatings can be enhanced by increasing the CH$_4$ concentration. Fig. 1a and 1b shows the synchrotron near edge extended X-ray absorption fine structure spectroscopy of NCD films prepared using different CH$_4$ concentrations from 1% to 100%. It was calculated that the sp$^2$ carbon concentration of the samples increases the steadily from 2% to 25% in the surface (based on TEY) and from 1% to 23% in the bulk (based on FY) when the CH$_4$ concentration increases from 1% to 100%.

**Role of H$_2$**

H$_2$ plays a vital role in the CVD processes. In particular, atomic hydrogen is an essential ingredient of the vapor used to produce the films and a small amount of H$_2$ improves aggregation of the NCD films. The transition between microcrystalline diamond and UNCD can be controlled by varying the amount of H$_2$ in the plasma. Fig. 2 illustrates the microstructure of the diamond films during the transition from the microcrystalline structure to the nanocrystalline one as the H$_2$ concentration increases from 0.5% to 1.5%. At H$_2$ concentrations of 1% and 1.5%, the film appeared as UNCD. However, there is a sharp transition between 1% and 0.5% H$_2$, where not only diamond but also a noncrystalline carbonaceous structure was grown.

According to the conventional CVD diamond model, H atoms created during the activation process react with the hydrocarbon precursor creating a complex mixture of hydrocarbon species including reactive carbon-containing radicals. The H atoms also abstract H$_2$ from the surface of CH bonds thereby creating surface radical sites. These radical sites occasionally react with gas-phase carbon-containing radicals creating adsorbed carbon species. Finally, the atomic hydrogen and, to a lesser extent, other gaseous species react with sp or sp$^2$ carbon sites on the surface, converting them into sp$^3$-bonded carbon. However, the sp$^2$ carbon atoms are etched back into the gas phase at a high rate by the H$_2$-rich plasma during NCD growth, and this explains why the sp$^2$ content in the film is rather small (<5%). The grain size, surface morphology, and surface roughness of the NCD films prepared in H$_2$-rich plasmas depend on the film thickness. Furthermore, plasma with a small H$_2$ concentration produces UNCD films with about 10% grain boundaries. By reducing the atomic H$_2$ concentration, etching of sp$^2$ carbon atoms is retarded giving rise to nonepitaxial crystallites, re-nucleation as well as smaller grain size. However, if the H$_2$ concentration is reduced while the hydrocarbon...
content in the plasma is increased, nondiamond phases are formed and it may eventually lead to complete absence of the diamond phase. Zhou et al. have reported diamond growth based on the C₂ insertion mechanism. Role of Ar

In Ar-rich plasma systems, Ar atoms play an important role in the production of C₂ which is generally regarded as the growth species of NCD. In C₂H₂/H₂/Ar plasmas, the major production channel of C₂ is the direct dissociation of C₂H₂ to form C₂H₂ + Ar → C₂ + H₂ + Ar. In CH₄/H₂/Ar plasmas, the dissociation of CH₄ from collisions with metastable Ar results in the formation of a significant amount of CH₄ (x = 0–3) radicals that eventually produce C₂H₂ by recombination. Subsequent dissociation due to collisions with Ar finally produces C₂ dimers in the same manner. The intensity of C₂ relative to H in C₂H₂/H₂/Ar plasmas was 2 to 3 times higher than that in CH₄/H₂/Ar plasmas for the equivalent composition. Boron is one of the common dopants used to produce conducting NCD electrodes. Boron atoms having a covalent radius close to that of carbon are substitutional in the diamond lattice. The Bohr's radius (3.1 × 10⁻¹⁰ m) of boron is comparable with the lattice constant of diamond (3.56 × 10⁻¹⁰ m) and so it behaves like a typical shallow acceptor. The electrical properties of doped NCD are influenced in a complex manner by the boron concentration, lattice H₂, nondiamond sp² impurities, and defect density. Doping with boron leads to conventional valence band conduction, and excellent electrical conduction can be attained at high boron levels. Bulk boron doping of NCD can in fact yield superconductivity, if metallic doping is achieved. Boron-doped NCD coatings exhibit superior electrochemical properties over other conventional electrode materials including low-capacitative background currents, wide potential window in aqueous media, and good corrosion resistance in harsh environments. As shown in Fig. 4 boron-doped NCD films exhibit excellent electrochemical properties boasting a wide working potential window, low-voltammetric background current, and good response to Fe(CN)₆³⁻/⁴⁻, Ru(NH₃)₆²⁺/³⁺, IrCl₆²⁻/³⁻, and methyl viologen without pretreatment. The voltammetry curves obtained from all the couples are quasi-reversible indicating that boron-doped NCD has a sufficient density of electronic states over the wide potential range to support rapid electron transfer. Other studies have shown that boron as well as sp² carbon phases in the grain boundaries governs the optical absorption process. Hence, while the electronic properties depend
on boron, the optical properties are mainly determined by grain boundaries.

In comparison, UNCD films exhibit different conductivity behavior due to the significant sp$^2$ concentration. When doped with nitrogen, the conductivity increases dramatically due to an increase in the density of states associated with π-bonding.$^{[108]}$ The π-states have been theoretically predicted to be symmetrical around the Fermi energy but with significantly lower energy than the σ-states due to sp$^3$ bonding.$^{[108,109]}$ In UNCD coatings, nitrogen does not act as a donor (nitrogen is a deep n-type dopant at 1.7 eV from the conduction band minimum) and thus

![Cyclic voltammetric i–E curves for various redox couples.](image)

**Fig. 4** Cyclic voltammetric i–E curves for (a) Fe(CN)$_6^{3–/4–}$, (b) Ru(NH$_3$)$_6^{2+/3+}$, (c) IrCl$_6^{2–/3–}$, (d) methyl viologen (MV$^{+2/+}$) in potassium chloride, (e) 4-tert-butylcatechol, and (f) Fe$^{2+/3+}$ in perchloric acid for a NCD electrode (scanning rate = 100 mV/s; electrode geometric area = 0.2 cm$^2$).

**Source:** From Show, Witek, et al.$^{[108]}$ ©2003 American Chemical Society. Reprinted with permission.
does not significantly influence the conductivity of the UNCD films. Instead, a large concentration of nitrogen in UNCD enhances the transport path related to a highly conductive subsystem of π-states located in the grain boundaries.[109] Therefore, nitrogen affects the conductivity indirectly and it is more related to structural changes rather than doping. Nitrogen-doped NCD coatings possess semimetallic electronic properties over a potential range from at least \(-1.5\) to \(1.0\) V vs. saturated calomel electrode (SCE).[110] The electrodes, like boron-doped NCD, exhibit a wide working potential window, low background current, and high degree of electrochemical activity in redox systems such as \(\text{Fe(CN)}_6^{3-/4-}\), \(\text{Ru(NH}_3\text{)}_6^{2+/3+}\), \(\text{IrCl}_6^{2-/3-}\), and methyl viologen. It has also been found that doping with nitrogen can improve the emission properties[111] and has a profound influence on the optical transparency of the films, as shown in Fig. 5.[112] Nitrogen-doped UNCD shows the largest absorption coefficient because the addition of nitrogen increases the gain boundary volume fraction, and the grain boundaries have a large influence on the optical properties of the NCD films.

SURFACE MODIFICATION OF NCD COATINGS

Because the surface properties of materials depend on surface termination, NCD can be modified to tailor the surface properties. The common surface modification techniques are described in this section.

Plasma Treatment

Generally, the as-deposited NCD possesses an H2-terminated surface. This is because CVD processes normally end with an H2 plasma treatment or are carried out in an H2-containing atmosphere.[113] H2 induces a hydrophobic behavior[114] and negative electron affinity \(\chi\) of \(-0.7\) to \(-1.3\) eV for a NCD sample.[115] H2 also produces subsurface carriers which render the diamond surface semiconducting.[116] Fig. 6a[117] shows the high-resolution X-ray photoelectron spectroscopy C 1s spectra of NCD after H2 plasma treatment, and π-bonded carbon and C–H bond can be observed. H2 termination is normally very stable in air for months, although gradual replacement of H2 by oxygen (O) from air has been reported.[118]
O plasma treatment produces O-containing functional groups such as –OH, –O–C–O–, –C=O, and –COOH on the NCD surface. These O-containing functional groups are hydrophilic enabling biologically active species to link relatively easily. In particular, carboxyl and hydroxyl termination can provide a flexible platform for surface functionalization via linker molecules leading to diverse functional termination in advanced surface engineering. Fig. 7a depicts the scheme for immobilization of aptamer probes based on carboxyl termination in biosensor applications. However, an oxidized surface has positive electron affinity and it is nonconductive due to high work function, thus limiting electronic applications. After longer O plasma treatment, plasma etching of the NCD surface can be achieved. This has been utilized to produce a patterned diamond surface for use as a porous mask.

Fluorination of NCD has been performed in the presence of cold plasma containing fluorine-containing gases such as octafluoropropane (C₃F₈), tetrafluoromethane (CF₄), or sulfur hexafluoride (SF₆). As shown in Fig. 6d, a fluorine-terminated NCD surface with extraordinary hydrophobic properties can be produced. The termination can react with Grignard reagents and amine-forming alkylated and aminated NCD, respectively. According to the report by Mangene et al., fluorinated NCD can be used to obtain alkyl, amino, and amino acid NCD derivatives by nucleophilic displacement of fluorine. Moreover, fluorinated diamond electrodes are promising in reactions requiring very negative potentials, for example, deposition of some metals and nitrate reduction. Amine-terminated surfaces can be obtained by NH₃ plasma treatment of H₂-terminated diamond. Plasma treatment can also be employed to graft specific functionalities such as halogen-containing molecules and organic films containing specific functional groups as shown in Fig. 7b.

![Fig. 7 Schematic showing the various steps: (i) initialization of NCD-biosensing surface with probe aptamers by functionalization of COOH and NH₂ on (A) carboxylated and (B) aminated surface, respectively; (ii) immobilization of PDGF-binding aptamers onto the NCD surface; (iii) specific conjugation between introduced PDGF proteins and immobilized aptamer probes; and (iv) attachment of Cy5-tagged signaling aptamer onto PDGF proteins.](image)

Ion Implantation

Ion implantation is a good modification technique for NCD. Implanting nitrogen into NCD at room temperature at 100 kV (ion implant fluence of $10^{16}$ cm$^{-2}$) produces super hydrophobic properties and ultra-low friction coefficients contrary to the as-deposited coatings. At a small load of 10 mN, a large friction coefficient is observed due to ploughing, fracture of the ball counter body, and absence of carbonaceous transfer layer. High-fluence nitrogen ion implantation into NCD reduces the diamond crystallinity leading to swelling of the crystal lattice. The cubic diamond grains in the film are converted into round grains due to sputtering by the nitrogen ions. The NCD morphology changes from “cauliflower-like” to a smoother one after nitrogen plasma ion immersion. The implanted NCD films exhibit improved electrical conductivity while the electron transfer kinetics decreases after nitrogen implantation for 15 and 30 minutes. After nitrogen ion implantation, the field emission characteristics are improved due to breaking of sp$^3$ bonds, creation of amorphous regions, and formation of defects. The electrical conductivity increases based on the electrochemical response observed from the treated NCD electrodes and the reduction of the work potential window for H$_2$ evolution in the acidic solution. Modification of NCD by B ion implantation yields good electronic properties (refer to the section on boron doping). Hu et al. have performed oxygen ion implantation into NCD at room temperature at 90 kV (implant fluence of $1 \times 10^{14}$ cm$^{-2}$) and found that the oxygen-implanted NCD exhibits n-type conductivity when the annealing temperature is above 800°C. In addition, 30 kV-focused Ga$^+$ ions are implanted into NCD to investigate the fluence dependence. Vanadium has been suggested as a dopant in the n-type diamond semiconductor based on theoretical calculation. Experimental results indicate that implanting an element with a larger atomic volume into the NCD may be a feasible means to synthesize otherwise difficult-to-dope semiconductors.

Photochemical Functionalization

Photochemical functionalization is another to surface modification technique for diamond. The photochemical reaction of alkenes and H-NCD is a common method for diamond functionalization. An H$_2$-terminated diamond surface is obtained as grown or employing the aforementioned plasma chemistry. Photochemical modification is achieved with a long alkene chain illuminated with ultraviolet light at a wavelength of 254 nm under dry nitrogen. UV exposure (254 nm) of the H-NCD surface in the presence of terminal olefin molecules such as undecylenic acid produces alkanes that are bound to the diamond surface by C–C bonds. The reaction can be accelerated in the presence of electron-accepting groups such as CF$_3$ in the molecule. Photoysis of perfluorooctanoate in the presence of NCD modifies the surface by adding perfluorooctyl functional groups. Amine-terminated diamond surfaces have been produced in this manner. Yang et al. and Hartl et al. have modified H-NCD by a photochemical process to generate a surface layer with amino groups. The amine-NCD can immobilize biomolecules such as proteins and DNA molecules in biotechnological applications. Wang et al. described a photochemical technique to graft different functionalities including carboxyl, hydroxyl, amine, and fluoride, as shown in Fig. 6b and 6c. Biosensors produced on directly carboxylated and aminated NCD deliver high performance in terms of sensitivity, selectivity, long-term stability, and regeneration ability, demonstrating that directly functionalized NCD films have large potential in sensing platforms.

Chemical/Electrochemical Reactions

Chemical and electrochemical surface modification of NCD using organic substances has also been performed by taking advantage of the carbon chemistry in the design of chemically modified surfaces. A variety of functional groups has been introduced using primary alcohol groups on hydroxylated nanodiamond using a chemical approach. The reactivity of the terminal alcohol groups is then exploited to create different functionalities on the diamond surface (halides, amines, cyanide, azide, and thiols). Silane-grafted nanodiamond particles are synthesized by functionalization of the hydroxylated diamond samples and successfully applied as a novel solid phase in peptide synthesis. Alternatively, long-chain carboxylic acid chlorides are reacted with hydroxylated diamond to introduce long alkyl groups in place of silane functional groups. To graft oligomers with various functionalities including C(=O)OCH$_3$, COOH, NH$_2$, or aliphatic moieties, Chang et al. have used a graphitized surface on H-UNCD. It is also possible to chemically graft (without electrochemical activation) diazonium salts by dipping the freshly hydrogenated diamond surface in a saturated solution of the diazonium for 72 hours. Diazonium chemistry is used to introduce brominated aryl groups onto the diamond nanoparticles. The reaction leads to a radical polymerization reaction of tert-butyl methacrylate and subsequent hydrolysis of the polymer brushes into poly (methacrylic acid) allows bovine serum albumin covalent immobilization. Electrochemical reduction of diazonium derivatives is an important route for surface functionalization of doped diamond and other substrates. Covalent functionalization of diamond surfaces through C–C bonds can be achieved by using aryldiazonium salts under rigorous ultrasonication. Modification of NCD by alkenes followed by electrochemical reduction of diazonium salts has been utilized to functionalize boron-doped UNCD diamond with amine groups. Electroless grafting onto nanodiamond particles is an interesting alternative to
electrochemical reduction of diazonium salts\textsuperscript{161} because nanoparticles cannot be grafted by electrochemical treatment when they are suspended in a liquid medium. Using a $\text{F}_2/\text{H}_2$ mixture at temperature varying from 150°C to 470°C, Liu et al. have fluorinated nanodiamond.\textsuperscript{149} 

Reflexing of the diamond in sulfuric acid and nitric acid is a common method to introduce polar functional groups such as hydroxyl, carboxylate, ester, and ether moieties onto the diamond surfaces.\textsuperscript{151,162} The surface functionalities of acid refluxed diamond can be further converted into other functional groups by converting the carboxylic acid moieties into acid halides, followed by atom transfer radical polymerization (ATRP) in the presence of monomers and a radical initiator under deoxygenated conditions for a long reaction time (>20 h). Polymethacrylate brushes have been attached to nanodiamond by the so-called “grafting from” method of ATRP. Although several steps are necessary to attach the ATRP initiators to the surface, the diamond polymer hybrids show controlled dispersing properties.\textsuperscript{149}

\section*{APPLICATIONS}

Owing to its unique chemical, physical, and mechanical properties, NCD can be used in a myriad of structural, biomedical, and microelectronic applications.\textsuperscript{117,122,123,126,136,144}

\subsection*{Micro-Electromechanical Systems}

The superior physical, chemical, and tribomechanical properties of diamond make it in principle an ideal material for MEMS, particularly in a harsh environment. However, the high intrinsic stress, rough surface, and inappropriate grain morphology associated with conventional diamond films are drawbacks.\textsuperscript{163} NCD and UNCD have distinct nanostructures but complementary properties.\textsuperscript{134} Nowadays, diverse arrays of micro- and nanostructures have been developed\textsuperscript{164–166} Wang et al. have produced NCD-based phononic structures (coupled mechanical resonator arrays)\textsuperscript{167} and UNCD-based resonators. Simple cantilever beams fixed at both the ends have also been fabricated.\textsuperscript{168} These mechanical resonators have very high frequencies due to high stiffness (Young’s modulus) of NCD, and they are excellent for mass and chemical sensors,\textsuperscript{169} especially if the chemical termination of the surface can be controlled.\textsuperscript{122,123,170} The grain boundaries doped with H$_2$ render NCD and UNCD as excellent dielectric materials, and their use as insulating dielectrics in radio-frequency MEMS capacitive switches has been demonstrated.\textsuperscript{171} 

Optical resonator structures and phononic crystals\textsuperscript{172} are also possible using NCD NEMS fabrication and eventually may be integrated into mechanical resonator structures for optical transduction of the mechanical motion. The technology for fabricating monolithic UNCD AFM cantilevers with integrated tips has been developed\textsuperscript{144} and UNCD AFM probes, the first MEMS-type structures in the market based on UNCD, are commercially available. This UNCD AFM tips exhibit practically no wear after extensive scanning on different surfaces as opposed to the high wear generally observed from conventional Si- and Si$_3$N$_4$-based AFM tips.\textsuperscript{173} 

Low-voltage MEMS/NEMS actuation can be achieved using piezoelectric technology. Several piezoelectric materials such as langasite,\textsuperscript{174} gallium phosphate,\textsuperscript{175} PZT,\textsuperscript{176} ZnO\textsuperscript{177} as well as AlN\textsuperscript{178} have been combined with NCD to produce drivers for QCM, SAW, and cantilever diamond structures.\textsuperscript{179}

\subsection*{Electron Emission}

NCD can be used as electron field-emitting materials that have promising applications\textsuperscript{136,180–182} due to low threshold field and strong emission current density.\textsuperscript{181} Remarkable electron emission with turn-on fields of $\sim$ 1 V/$\mu$m and current density of $4 \times 10^{-4}$ amps/cm$^2$ at 4 V/$\mu$m has been achieved using NCD.\textsuperscript{29} Zhu et al.\textsuperscript{183} have reported ultra-low field emission from undoped nanostructured diamond and the emission behavior stems from the inherently defective structure in the nanostructured diamond and low electron affinity of the diamond surface.

Grain boundaries contain sp$^2$-bonded carbon and provide the conduction path for electrons, thus facilitating electron field emission.\textsuperscript{29} Si field emitter arrays coated with UNCD emit electrons at as low as 2.6 V/mm.\textsuperscript{184} After exposure to H$_2$, the field emission properties of the UNCD-coated Si field emitter arrays are enhanced. The significant reduction in the turn-on voltage and increase in the emission current arise from the modification of the effective work function at the localized emission sites.\textsuperscript{185} Nitrogen-doped NCD offers excellent field enhancement factors on account of the small grain size, increased and controlled sp$^2$ carbon content as well as n-type electrical conductivity and is a suitable electron-emitting material. Okano et al.\textsuperscript{186} have obtained low-field electron emission from nitrogen-doped diamond films prepared by HF CVD. The field emission properties of UNCD films are greatly improved after N ion implantation and annealing because N ions residing in grain boundaries can render the UNCD grains semiconducting by charge transfer.\textsuperscript{187}

\subsection*{Biotechnology}

Because of the unique chemical, physical, electrical, and biological properties, NCD has attracted much attention as a robust and stable bio-interface on implantable biosensors even under harsh operating conditions. Surface termination and dopants have been shown to be crucial to many applications. NCD electrodes modified with DNA oligonucleotides have been used in field-effect biological sensors,\textsuperscript{122} and H-terminated NCD films offer an ideal platform for enzyme-based amperometric biosensors.\textsuperscript{123} Biosensors based on carboxylated and aminated NCD films can deliver
high sensing performance in terms of sensitivity, selectivity, long-term stability, and regeneration ability, indicating that directly functionalized NCD films have big potential.[117] Enzymatic[188] and nonenzymatic[189] glucose sensors based on the boron-doped NCD electrode boast high sensitivity and reproducibility, and NCD single photon sources and biomarkers have been fabricated.[190] An optical sensor based on NCD loaded with horseradish peroxidase has been demonstrated to be highly sensitive toward hydrogen peroxide.[191]

NCD combines the virtues of surface smoothness, high corrosion resistance, and biological tolerance. These favorable features bode well for applications to medicine such as surgical tools and medical implants. NCD films induce improved proliferation and differentiation of human osteoblasts and neural stem cells compared to conventional polystyrene petri dishes.[125] NCD has better resistance to bacterial colonization than medical steel and titanium.[122,192,193] Owing to the high wear resistance and low coefficient of friction of NCD, the amount of wear debris generated during the joint functioning is reduced, thereby increasing the life span of the prosthesis.[194] NCD can be used as a template for immobilization of active molecules in biological and sensing applications.[117,122,123] The NCD surface can also be modified by linking with antibody, human immunoglobulin G, which provide biomolecular recognition capability and specificity characteristics. It can thus be used in biologically sensitive field effect transistor (Bio-FET).[195]

Electrode Applications

NCD is an outstanding material for electrochemical electrode, as it has a wide electrochemical window and low noise,[107,110] and the utilization of NCD or UNCD in this area is an extension of implemented technology.[112,118] Boron-doped NCD can be deposited on transparent substrates to produce a transparent electrochemical electrode suitable for spectro-electrochemistry.[196,197] The reported high conductivity of nitrogen-doped UNCD has spurred applications to high-power electronic devices.[4] Boron-doped NCD electrode arrays prepared by microfabrication can be used as electrochemical sensors, and they exhibit low background currents, almost theoretically steady-state limiting currents, and fast electron transfer rates close to 0.01 cm s$^{-1}$.[198] They have potential applications in electrophysiology, and boron-doped NCD electrodes have many electroanalytical applications, e.g., determination of sulfur-containing compounds,[199] post column detection of nitrogen-containing molecules, and heavy metal analysis.[200–202] The electrode can be made to be highly conducting and active in electroanalytical processes in aqueous media, thus suitable for a wide range of processes including oxidation of ferrocyanide, ascorbic acid, and nicotinamide adenine dinucleotide.[203] It has been shown that metal (gold and copper) deposition on NCD electrodes is fast and efficient. The stripping efficiency (ratio of cathodic charge for deposition to anodic charge for stripping) in these processes is close to unity under a wide range of conditions.

The pH- and ion-sensitive properties of an electrolyte-gate FET with diamond coatings have been investigated.[204,205] For instance, a pH-sensitive electrolyte–diamond–insulator–semiconductor (EDIS) sensor with NCD coatings has been reported by Christiaens et al.[206] The feasibility of using the EDIS structures with O-terminated NCD coatings in transducers for multiparameter sensing of different (bio-) chemical quantities such as pH, penicillin concentration as well as charged macromolecules has been demonstrated.[207]

CONCLUSION

NCD is typically prepared using a CH$_4$/H$_2$ mixture or by replacing partially or completely H$_2$ with Ar, N$_2$, and other gases. Mechanical pretreatment, seeding with particles, and chemical pretreatment can effectively enhance the diamond nucleation density on nondiamond substrates. The roles of CH$_4$, H$_2$, and Ar in the growth of NCD are discussed. By increasing the CH$_4$ concentration (from 1% to 100%), the growth rate, surface smoothness, and sp$^3$ carbon content in the film increase and the grain size decreases. H$_2$ plays an important role in stabilizing the sp$^3$ carbon phase and etching of the sp$^2$ carbon phase. The Ar concentration shows obvious effects on the grain size and deposition rate of NCD. Boron and nitrogen are common dopants in NCD coatings, and the doped materials possess good electronic properties, optical properties as well as electrochemical properties. The quantitative methods for functionalization of NCD surfaces are also described. Incorporation of biological species into the functionalized diamond surfaces in a controllable manner enables the fabrication of biosensing devices which can be used in the fundamental study of living cell morphology in contact with the surface structures. NCD is an important emerging material with immense potentials in different types of applications especially pertaining to MEMS, electron emission, biotechnology, and electrodes.

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