1 Fundamentals on Synthesis and Properties of Ultrananocrystalline Diamond (UNCD™) Coatings

Orlando Auciello, Jesus J. Alcantar-Peña, and Elida de Obaldia

1.1 Background on UNCD Film Synthesis, Properties, and Applications

This chapter serves as the introduction of the focus of this book on the science and technological applications of a new material paradigm provided by a novel material in thin-film (coating) form named ultrananocrystalline diamond (UNCD™), which has enabled new generations of industrial, high-tech, and electronic-related products. In this respect, this chapter focuses on presenting a review of the status of the synthesis and properties of the UNCD film technology, originally developed and patented by a group of scientists (O. Auciello, D. M. Gruen, A. R. Krauss, and J. A. Carlisle), with a view to industrial and high-tech applications, and subsequently under R&D by Auciello’s group for biotechnological and medical devices/prostheses and medical treatment applications, which is the main topic of this book.

Early research on the growth and characterization of properties of diamond films provided valuable information for understanding the underlying physical [1, 2], chemical [1, 3], and structural [1, 4, 5] properties of the various diamond films, from single crystalline diamond (SCD) to microcrystalline diamond (MCD; ≥1 μm grain sizes) to nanocrystalline diamond (NCD; ~10–1000 nm grain sizes) films, which were synthesized by various different processes reported by several different groups [6–15].

The technique used to grow the SCD, MCD, and NCD films involved mainly the microwave plasma chemical vapor deposition (MPCVD) process, whereby a mixture of H₂ (99%) and CH₄ (1%) gases were flown in a chamber evacuated from air to relatively high vacuum (around ≤10⁻⁶ Torr), followed by coupling of microwave power to the gas mixture to create a plasma, producing CHₓⁿ and CHₓ⁺⁺ (x = 1, 2, 3), C⁺ and C⁰ species, and electrically neutral atomic H⁰ atoms and electrically charged H⁺ ions, which, interacting on the surfaces of substrates, produced the SCD, MCD, and NCD films. The large quantity of H inserted into the gas mixture was to produce neutral H⁰ atoms and H⁺ ions, which may also induce chemical etching of diamond nanograins (≤10 nm grain size), which are nucleated in the initial phase of MCD and NCD film growth,
thus eliminating the possibility of growing polycrystalline diamond films with grain sizes ≤10 nm.

The next materials science breakthrough in relation to growing polycrystalline diamond films happened with the discovery of a new process to grow polycrystalline diamond films with grain sizes ≤10 nm. Gruen et al. [16–18] demonstrated that by flowing Ar gas through an oven heated to ~900 °C to evaporate C60 fullerene molecules from powder, the Ar gas induced flow of C60 fullerene molecules (Figure 1.1) into an evacuated MPCVD chamber, where coupling of microwave power to the Ar/C60 fullerene molecules mixture induced cracking of the C60 fullerene molecules, releasing C atoms that upon landing on the surfaces of substrates produced the growth of polycrystalline diamond films with ≤10 nm grain size. The C60 fullerene molecule had been discovered previously in 1985 by H. W. Kroto, R. E. Smalley, and R. F. Curl, Jr. (1996 Nobel Prize Winners in Chemistry for this discovery, see review in [19]).

Although the use of C60 fullerene molecules produced the growth of polycrystalline diamond films with ≤10 nm grain size, this process was too expensive to produce polycrystalline diamond films for industrial applications, and in addition the need for an oven producing the gas-phase C60 fullerene molecules induced the formation of substantial amounts of carbon soot, which was not appropriate for being interconnected with a clean vacuum system, where the films were grown.

The next breakthrough in growing polycrystalline diamond films with grain sizes <10 nm happened through the discovery led by Gruen, Krauss, and Auciello [20], which was based on replacing the H2 gas in the H2/CH4 gas mixture, used previously to grow from SCD to NCD films [6–15], with Ar gas (the less expensive inert gas on the market today) to produce an Ar (vol. 99%)/CH4 (vol. 1%) gas mixture in the
MPCVD system, which resulted in the growth of polycrystalline diamond films with grain size in the range 3–5 nm, the smallest grain size of any polycrystalline diamond film today (see [20], patent [21], and reviews [22, 23], and Figure 1.4a,b). The R&D described in [20–23] superseded prior work that showed that diamond films grown by MPCVD, using mixtures of Ar (80–97%)/CH\textsubscript{4} (1%)/H\textsubscript{2} (19 to 2%), produced diamond films with grain sizes in the range 50–10 nm [24], respectively, as the H\textsubscript{2} flux volume was reduced. Gruen, Krauss, and Auciello coined the name ultrananocrystalline diamond (UNCD) to designate the new polycrystalline diamond film with a grain size of 3–5 nm.

Auciello and Carlisle trademarked the name UNCD\textsuperscript{TM} when founding Advanced Diamond Technologies, Inc. (founded in 2003, profitable in 2014, and sold for profit to a large company in 2019) [25]), the first and only company worldwide marketing UNCD-coated industrial products, as described below.

Auciello then led the founding of Original Biomedical Implants (OBI-USA 2013–present [26] and OBI-México 2016–present), which are currently developing revolutionary new generations of external and implantable medical devices (new long-life Li-ion batteries for a new generation of defibrillators/pacemakers with >10 times longer life and safer than the current technology – see Chapter 7), prostheses (UNCD-coated dental implants, hips, knees, and more – see Chapter 8) with superior performance to current metal-based devices and prostheses, which are corroded by body fluids sooner or later, resulting in the need for replacement earlier than desired, and other devices for medical applications, as reviewed in various chapters in this book. The UNCD coating provides the best biocompatible material for insertion in the human body, since UNCD is made of C atoms (the element of life in the DNA, cells, and molecules of every human body), and it exhibits the strongest resistance to mechanical wear [27] and chemical attack by body fluids [28], and the lowest coefficient of friction compared to any biocompatible material [27], a condition very favorable for operation of any prostheses involving friction (hips, knees, and others).

Other breakthroughs in material-related science and development of the UNCD film technology include the following:

1. The discovery that incorporation of nitrogen atoms in grain boundaries of UNCD films, grown flowing a mixture of Ar/CH\textsubscript{4}/N\textsubscript{2} gases for the MPCVD process, produced the first electrically conductive diamond film, via N atoms’ incorporation in UNCD grain boundaries, satisfying C atoms’ dangling bonds and providing electrons for electrical conduction through the large grain boundary network of the structure of the as defined N-UNCD film [29, 30].

2. The discovery that B atoms replacing C atoms in the UNCD lattice of the nanograins provides electrons to the electron energy conduction band, inducing true semiconductor-type doping, which yielded high electrical conductivity B-UNCD films that were inserted as a corrosion-resistant coating on metal electrodes in the first worldwide transformational electrolysis-based/ozone-generation/water purification system (DIAMONOX-Advanced Diamond Technologies) marketed by ADT [25]. The B-doping of UNCD coatings done by ADT, including the recent
demonstration of the first process for low-temperature (460–600 °C) growth of B-UNCD by hot filament chemical vapor deposition (HFCVD) [31], a world-first for UNCD coatings, was recently reproduced by independent groups using the MPCVD process [32]. The development of the B-UNCD films followed the early R&D on B-doping of crystalline and MCD and NCD films using MPCVD and HFCVD processes, based on H₂/CH₄ gas mixture chemistry (see [33–36] and a recent review [37]). The problem with all MPCVD and HFCVD growth processes used to produce B-UNCD or B-SCD, B-MCD, B-NCD films is that the B-containing molecular precursors flown into the vacuum systems during diamond film growth result in contamination of expensive systems used for growing any type of diamond films, thus limiting those systems to growing only B-doped diamond films. In relation to this issue, Auciello’s group recently developed a post-grow dedicated rapid thermal annealing system, which produces B-UNCD films or any other B-diamond doped films with similar quality and high electrical conductivity as the B-doped diamond films produced by MPCVD and HFCVD growth processes, by simply inserting the diamond film with a spin-on-dopant (SOD) solution (Borofilm 100®) dispersed on the UNCD surface via a spinning speed of 3000 rpm and a process time of 20 s, and subjecting the surface-doped UNCD film to a rapid thermal annealing (RTA) process for ~10 s, which diffuses the B atoms into the UNCD film lattice to produce B-doped B-UNCD films [38].

3. Development of a new process to grow UNCD films at the lowest temperature (~350–400 °C) [39, 40] demonstrated for any diamond films at that time (early 2000s) and today, to enable integration with microelectronic devices based on complementary metal-oxide semiconductors (CMOS) technology requiring a thermal budget processing ≤425 °C. The integration of UNCD films with Si-based microchips was demonstrated by developing a hermetic/biocompatible/humor eye corrosion-resistant UNCD coating to encapsulate an Si-based microchip implantable in the eye as the main component of an artificial retina to restore partial vision to people blinded by genetically induced degeneration of photoreceptors (see [28] and Chapter 2).

4. Discovery of basic materials/chemistry/physical processes to integrate dissimilar materials like high-dielectric constant (k) dielectrics and UNCD and MCD (e.g., UNCD or MCD/HfO₂ [41]), ferroelectric/piezoelectric oxides/UNCD (e.g., PbZrₓTi₁₋ₓO₃/UNCD [42]; piezoelectric nitrides/UNCD (e.g., AlN/UNCD [43]), all enabling new generations of micro/nanoelectronic and microelectromechanical systems/nanoelectromechanical systems (MEMS/NEMS) devices, as described below.

The fundamental and applied material science on UNCD films, reviewed above, provides valuable information revealing that UNCD films exhibit a remarkable synergistic combination of exceptional mechanical, tribological, chemical, electrical, thermal, electron emission, and biocompatibility properties, which are being used to enable a new generation of multifunctional devices from the macro- to nanoscale:
1. The outstanding mechanical properties of UNCD films enable their application to produce a new generation of MEMS devices [44, 45], including the first demonstrated UNCD/piezoelectric oxide films integration to produce piezoelectrically actuated UNCD-based MEMS actuators and sensors [42]; see also a review [46].

2. The chemistry and atoms bonding configuration of UNCD coating surfaces induce unique nanotribological properties resulting in outstanding resistance to mechanical wear and the lowest coefficient of friction demonstrated today in commercial products requiring low wear and friction, such as UNCD-coated mechanical pump seals and bearings and AFM tips (NaDiaProbes™), providing practically wear-free/high-resolution AFM nanolithography and imaging capabilities, which are currently on the market commercialized by Advanced Diamond Technologies [25].

3. R&D has demonstrated that UNCD films exhibit excellent dielectric properties (as dielectric layers for RF MEMS switches [45]), which enable for the first time RF MEMS switches without failure as occurred in prior switch technologies involving dielectric layers made of SiO₂ or Si₃N₃, which failed due to electrical charging (~80 µs) of the oxides and nitrides and long discharging times (hundreds of seconds), leading to sticking of the movable switch membrane to the dielectric layer on top of the bottom electrode, and thus failure [45]. In the case of the UNCD dielectric layer used in RF MEMS switches there is fast charging and discharging, both in ~80 µs, due to the large grain boundary network of the UNCD layer, thus eliminating the electrical charging failure [45].

4. The outstanding electrical conductivity properties of nitrogen grain boundary incorporated UNCD (named N-UNCD) films [22, 29, 30] enables a new generation of metal electrodes for the new generation of implantable neural stimulation and Li-ion batteries (LIBs) with /C²₁₀ times longer life and which are safer than current LIBs due to the corrosion-resistant N-UNCD coating of anodes and cathodes [47–48]. Alternatively to electrical conduction by nitrogen incorporation into the grain boundaries, highly conductive UNCD films have been achieved by doping of UNCD films, in the true sense of semiconductor doping, by inserting boron (B) atoms to replace C atoms in the diamond lattice, providing electrons to the conduction band as discussed above.

5. Excellent electric field-induced electron emission properties based on electric field-induced electron emission from UNCD film surfaces [49, 50–52] enables field emitter cold cathodes [53] and field emitter flat panel displays [54].

6. Excellent chemical properties, demonstrated via surface functionalization of the UNCD films by electrochemical reduction of aryl-diazonium salts to enable growth of biomolecules on the UNCD surface [55].

7. Excellent biological properties, demonstrated by DNA-induced modification of UNCD thin-film surfaces [56] that provide stable, biologically active scaffolds for biological cell growth and differentiation [57, 58].

8. Excellent biocompatibility, demonstrated in the application of UNCD coatings for encapsulation of a microchip implantable in the eye to restore partial vision to...
people blinded by genetically induced death of photoreceptors [28], and application to a new generation of implantable medical devices such as dental implants, artificial hips and knees, and many more prostheses that are implantable in the human body [59].

All applications of the UNCD film (coating) technology require growing the films with the appropriate nanostructure mentioned above and described in detail in the following sections, which discuss the two main growth techniques: MPCVD and HFCVD.

1.2 Fundamentals of UNCD Film Synthesis via MPCVD and Properties

To grow diamond films on nondiamond substrates using MPCVD or HFCVD, or any other CVD method, it is necessary to induce a nucleation step. Two main methods have been developed and used over the years to condition the surface of substrates to grow diamond films:

1. Surface “seeding,” embedding diamond particles (with micro- or nanoscale dimensions) on the substrate surface via polishing with diamond-based polishing material or immersing the substrate in a container with a solution of micro- or nano-size diamond particles in methanol in an ultrasound wave-generating system such that the sound waves shake the diamond particles, embedding them on the substrate surface as “seeds” to induce the nucleation and subsequent growth of diamond films [1–18, 20–24]. Following the seeding process, standard thin-film deposition methods based on MPCVD and HFCVD processes have been and are still used to grow diamond films, as discussed below.

2. The other process to nucleate and grow diamond films, which has been used more recently and is still being optimized to nucleate and grow films without using the wet chemical process, is the so-called bias enhanced nucleation-bias enhanced growth (BEN-BEG) process, whereby a negative voltage is applied to an electrically conductive substrate to attract positive ions of C⁺, CHx⁺, and other species that interact jointly on the substrate’s surface, inducing nucleation and growth of diamond films. A review of the synthesis of diamond films using MPCVD and HFCVD processes with both the chemical seeding and the BEN-BEG processes is discussed in this chapter.

1.2.1 Fundamentals on the Synthesis of MCD, NCD, and UNCD Thin Films via MPCVD with the Chemical Seeding Process

1.2.1.1 MPCVD Growth Process for MCD and NCD Films with the Wet Seeding Process

Growth of diamond films, using conventional wet seeding process, plus film growth using the MPCVD technique, involves several gas flow chemistries, resulting in different grain sizes of the diamond films. The hydrogen-rich chemistry (H₂ (99.9 to
96%)/CH₄(1%) [15, 60, 61] results in MCD (1–5 µm grains with columnar microstructure for ~1% CH₄/2% Ar/97% H₂ – see Figure 1.2a; and 0.5–1 µm grains for 1% CH₄/80% Ar/19% H₂ – see Figure 1.2b) and NCD films (50–100s nm grains for ~1% CH₄/90% Ar/9% H₂ – see Figure 1.2c; and 10–50–nm grains for 1% CH₄/97% Ar/2% H₂ – see Figure 1.2d).

High-quality NCD films can also be grown with relatively low methane percentages (0.3%) [61]. The MCD and NCD films grown on surfaces seeded with conventional solutions of diamond micro- or nanoparticles, without proper functionalization to reduce agglomeration, experience the drawback of relatively low initial nucleation density (<10¹¹/cm²). The MCD film surface coarsens with thickness, exhibiting a rough, highly faceted surface morphology with a root mean square (RMS) roughness generally ~10% of the film thickness. When an optimized seeding process and CH₄ (0.3%) is used in the H₂/CH₄ gas mixture, at substrate temperatures in the range of 450–900 °C, very high nucleation densities are achieved (>10¹³/cm²) jointly with relatively smooth, high-quality NCD structure of film with various thicknesses [60]. In any case, there is no report in the literature of successful integration of NCD films with CMOS devices, which is a critical proof of low-temperature growth of diamond films, as demonstrated for UNCD films encapsulating an Si microchip implanted inside the...
eye as the main component of the Argus II device, which returns partial vision to people blinded by retinitis pigmentosa [28]. The growth process related to the $\text{H}_2/\text{CH}_4$ chemistry is driven by $\text{CH}_3^-$ radicals interacting on the substrate surface, involving hydrogen extraction from the radicals and ultimately resulting in C atoms’ chemical reaction with the surface to induce the growth of the NCD films. The atomic neutral $\text{H}^0$ atoms and $\text{H}^+$ ions generated in the plasma induce preferential etching of a graphitic phase that co-deposits with the diamond phase. Unfortunately, the $\text{H}^0$ atoms and $\text{H}^+$ ions also induce chemical etching of the diamond phase, specifically nano-grains that try to continually nucleate. However, the etching of the diamond nano-grains by the $\text{H}^0$ atoms and $\text{H}^+$ ions occurs at a much lower rate (~50 times) than for graphite, resulting in the formation of intergranular voids and columnar morphology with large grains ($\geq 1 \mu$m). The grains of MCD (1–5 µm) and NCD (10–100s nm) films are much and a medium step larger, respectively, than those of the UNCD films (3–5 nm), which are the main topic of this chapter (compare Figures. 1.2a–d and Figure 1.4).

The MCD films produced by the MPCVD process exhibit high residual compressive stress, poor intergranular adhesion, and very rough surfaces (see Figures 1.2a,b). Consequently, MCD films are not well suited, for example, to producing MEMS/NEMS structures with smooth surfaces and sharply defined geometries. In addition, MCD films exhibit high coefficient of friction due to high roughness, which makes them inappropriate for applications such as coating of prostheses (e.g., hips, knees, and others), which requires a low coefficient of friction. The grain size can be reduced to 10–100 nm, characteristic of films typically known as nanocrystalline diamond, by inserting Ar gas into the mixture and reducing the $\text{H}_2$ percentage, thus increasing the $\text{CH}_4/\text{H}_2$ ratio in the plasma. This process produces a smoother surface than for MCD films, but at the cost of increased nondiamond components at the grain boundaries [62]. There is also another class of NCD film with high sp$^3$ content which is grown with the $\text{CH}_4/\text{H}_2$ gas chemistry with relatively low $\text{CH}_4$ content (0.3%) using a special diamond seeding/nucleation process [63], but these films exhibit the NCD structure only when the film thickness is limited to $< 100$ nm [64], while for thicker films grain coarsening dominates due to practically no renucleation and film growth with columnar structure, resulting in increasing grain size and roughness as the film thickness increases.

1.2.1.2 MPCVD Growth Process for UNCD Films with the Conventional Wet Seeding Process

$\text{Growth, Structure, and Chemical Characterization of Insulating UNCD Films}$

$\text{Growth Process.}$ Contrary to the growth process for MCD and NCD films described above, the UNCD films, discussed in this chapter, were first produced by the MPCVD process, but in recent years the HFCVD process was also developed to produce high-quality UNCD films, as discussed in this chapter. The original MPCVD process used to grow UNCD films was based on gas mixture flowing into an air evacuated chamber, and involved – and still involves – a novel Ar-rich chemistry (Ar [99%]/CH4 [1%]) with no $\text{H}_2$ gas flow in the system [20–23, 50] and in more recent years including also
extremely small H₂ gas flow (≤1%). In both cases, it was determined, using in situ real-time optical emission spectroscopy imaging of the MPCVD plasma, generated with the Ar/CH₄ chemistry, that carbon dimers (C₂) are produced in the plasma (inducing a green color to the plasma from the light emission from the excited C₂ dimers) generated by the MPCVD process, from methane decomposition, via reactions (1.1) and (1.2):

\[
\begin{align*}
2\text{CH}_4 & \rightarrow \text{C}_2\text{H}_2 + 3\text{H}_2, \quad (1.1) \\
\text{C}_2\text{H}_2 & \rightarrow \text{C}_2 + \text{H}_2. \quad (1.2)
\end{align*}
\]

Although the Ar-rich/CH₄ plasma induces the formation of a complex mixture of carbon (C₂ dimers) and hydrocarbon molecules (CHₓ, with x = 1, 2, and 3), the C₂ dimers have been proposed and demonstrated to play a critical role in the UNCD nucleation and growth process (see review in [22]). Calculations predict that C₂ dimers have low activation energy (~6 kcal/mol) for insertion into the surface of substrates to induce nucleation and subsequent growth of UNCD films, thus establishing the unique growth process of the UNCD films. However, recent modeling indicated that while the C₂ population in the plasma is high, the population near the surface may be lower, and other hydrocarbon radicals (e.g., C₂H₂) may also contribute to the growth of UNCD films [65, 66]. However, the model [66] is related to the growth of diamond films produced by MPCVD using a mixture of Ar/CH₄/H₂ gases, which, as shown in Figure 1.2, does not produce the unique UNCD structure (with 3–5 nm grains) grown by MPCVD with the Ar/CH₄ chemistry [21–23]. In addition, the model could not fully explain the low-temperature growth of UNCD films as demonstrated for UNCD film growth at ~400 °C [39, 40]. Clearly, more experimental and modeling studies are needed. Regardless of the mechanism, the distinctive characteristic of the UNCD film growth process is that the plasma contains very small quantities of hydrogen, which arise mainly from the thermal decomposition of methane to acetylene in the plasma (about 1.5%) and eventual addition of an extremely small amount of H₂ (≤1%). The MPCVD process is implemented in small research and, most importantly, industrial-type systems, like the ones operating in Auciello’s group laboratory at UTD and the company OBI-México (Figure 1.3a), which grows UNCD, NCD, and MCD films on up to 200 mm diameter substrates (Figure 1.3b) with outstanding uniformity in thickness (≤1%) and nanostructure.

A critical outcome of the nucleation and growth processes for UNCD films is that they are the only diamond films that have been demonstrated to grow at temperatures as low as 350–400 °C [39, 40], as determined not only by in situ substrate temperature measurements during growth [22, 39, 40], but most importantly by the demonstration that CMOS devices exhibit practically the same performance before and after growing UNCD film on them [28, 67]. Similar demonstration of low-temperature NCD films integration with CMOS devices has not been published in the open literature yet. The demonstrated integration of UNCD films with CMOS devices is paving the way for the integration with CMOS for the development of monolithically...
integrated UNCD-MEMS/NEMS/CMOS devices, as recently demonstrated [67], and for encapsulation of Si microchips implantable inside the eye [28] or other parts of the human body.

**Structure Characterization.** The nucleation and growth process described above produce the UNCD films with the name based on the equiaxed 3–5 nm grains dimension and 0.4 nm wide grain boundaries for undoped insulating UNCD films grown both at 800 °C (Figure 1.4a) and 400 °C (Figure 1.4b), which exhibit extremely smooth as-grown surfaces (~3–5 nm) (Figure 1.4d) when using optimized seeding techniques.

**Chemical Characterization.** The UNCD films grown by MPCVD were and are characterized by Raman analysis, to provide information on the chemical bonds of the C atoms in the grains and in the grain boundaries. Raman spectroscopy is a nondestructive chemical analysis technique that provides detailed information about the chemical bonds of atoms in a material, distinguishing the atomic bonds in a crystal-type structure such as crystalline diamond and other structures such as the noncrystalline structure of grain boundaries in polycrystalline diamond films. Raman analysis is based on the interaction of light with the chemical bonds of molecules within a material, such that light induces excitation of electrons in the electronic cloud around the atomic nuclei in molecules, producing displacement of the negatively charged electrons with respect to the positively charged nucleus, inducing molecular vibration and causing a “change in polarizability” of the molecule, such that the induced dipole emits or scatters light at the optical frequency of the incident light wave, and the scattered light detected in a detector provides the information on the chemical bonds of the atoms (see a recent review in [69]).

**Figure 1.3** (a) Industrial MPCVD system (IPLAS-Germany); (b) Si wafer (200 mm diameter) coated with outstanding uniform UNCD film.