Ultrananocrystalline Diamond

Properties and Applications in Biomedical Devices

John A. Carlisle and Orlando Auciello

D iamond is nature's extreme material. In addition to being the hardest and strongest known substance, diamond is also the best known thermal conductor and possesses very high electron carrier mobility and breakdown fields when in single crystal form.[1] Diamond also exhibits exceptional optical (high refractive index, wide band gap), tribological (low friction), and electrochemical properties that set it apart from other materials either natural or man-made.[2]

Capturing the extreme properties of diamond in a carbon-based thin film has long been an overarching goal of researchers in this area. This is necessary if this material is to be used in microelectronics applications or as hard coatings, for example. Unfortunately, it has proved very difficult to render the full range of extreme properties to diamond in thin film form. A number of thin film deposition techniques have been developed, including physical (ion sputtering, laser ablation, etc.) and chemical (hot filament, plasma, etc.) vapor deposition, for the synthesis of diamond films. For instance, the filtered cathodic arc approach is currently used to coat nearly all razor blades sold in the U.S. However, these films, commonly referred to as diamond-like carbon (DLC), do not fully capture the properties of natural diamond.

What makes diamond special is its local bonding structure. The carbon atoms in diamond are tetrahedrally coordinated: each carbon atom is bonded to four others in the diamond lattice. In chemistry textbooks this bonding is referred to as sp^3 bonding. It is the strength of these bonds and their tetrahedral configuration that gives diamond its fundamental materials properties. Graphite (a different allotrope of carbon), consists entirely of 3-fold coordinated carbon atoms bonded in a planar, triangular geometry, and consequently has very different materials properties compared with diamond. The bonding found in graphite is commonly referred to as sp^2 bonding.

The sp^2 bonds in graphite are slightly stronger than the sp^3 bonds in diamond, and when configured differently, such as in fullerenes and carbon nanotubes, give rise to yet more allotropes of carbon with properties distinct from either diamond or graphite. Carbon films are very often characterized by the relative amount of sp^3 and sp^2 bonding and the long range ordering of these bonds, with single crystal diamond representing one extreme (100% sp^3 bonded, very well-ordered) and amorphous graphitic carbon the other extreme (100% sp^2 bonded, completely disordered).

DLC films consist of at most only 80% sp^3 bonded carbon and are amorphous.[3] Thus, as the name implies, DLC films are *like* diamond, so they have some but not all of the extreme properties of this material. DLC films work quite well for razor-blades and as scratch-resistance coatings in various applications, but fall short when the unique properties of natural diamond are critically needed.

The main technique for depositing diamond thin films involves microwave plasma chemical vapor deposition (MPCVD), using mixtures of small amounts (~1%) of a carbon source gas, typically methane (CH_4), mixed with the balance of hydrogen (H_2).[4] In a CH_4/H_2 plasma discharge, methyl radicals (CH_3^-) and atomic hydrogen (H^+) lead, through surface chemical reactions (hydrogen abstraction), to the growth of microcrystalline diamond (MCD) films, which can be more than 99% sp^3 bonded carbon, and do possess many of the properties of natural diamond. Unfortunately, MCD films have several drawbacks, including the following: (1) The films are very rough, due to their large grain sizes; (2) They consist of low-energy grain boundaries; (3) The films must be grown at high temperatures (700-
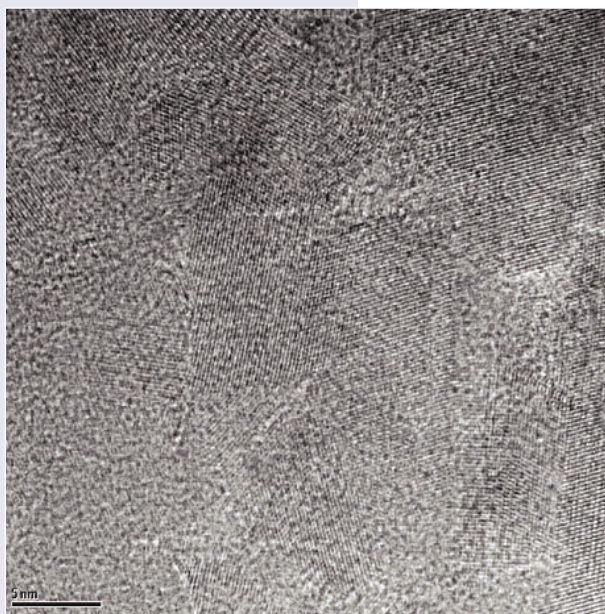
FIG. 1. High-resolution transmission electron micrograph, showing the structure of ultrananocrystalline diamond at the nanometer scale. UNCD consists of 2-5 nm grains of pure sp^3 bonded carbon, separated by atomically abrupt (one atom wide) grain boundaries that consist of a disordered mixture of sp^3 (diamond) and sp^2 (graphitic) bonding.

1000°C) to achieve technologically relevant growth rates, limiting the range of substrate materials MCD can be deposited on; and (4) The as-deposited films exhibit high stress, leading to substrate deformation and even film delamination.

All these shortcomings limit the application of MCD films in microelectro-mechanical systems (MEMS) devices, a key application area. MCD films are used however as IR windows for heat-seeking missiles and heat spreaders for microelectronic circuits, and are being developed for high-voltage, high-temperature microelectronics and particle detectors.

A microwave plasma chemical vapor deposition (MPCVD) technique developed at Argonne National Laboratory (ANL)[5,6] over the past several years produces a new form of diamond film called ultrananocrystalline diamond (UNCD). This new technique involves a novel chemistry based on using a mixture of CH_4 (~1%) with inert gases (*e.g.,* Ar, Kr, or Xe) that yields carbon films with a unique nanoscale structure. The new

FIG. 2. Molecular dynamics simulation of a high-energy grain boundary found in UNCD. These high-energy grain boundaries contain a mixture of sp^3, sp^2, and other types of bonding, and are much more stable compared to low-energy grain boundaries found in MCD or perhaps even the perfect crystal.

microwave plasma process results in the formation of carbon dimers (C_2) that constitute the growth species. UNCD films grow via direct insertion of C_2 dimers into the diamond lattice, and consist of 95% sp^3-bonded carbon, along with sp^2 and other types of bonding. These films are therefore not truly phase-pure diamond films but can be thought of as composite or hybrid sp^3/sp^2 films. The nanometer-scale structure of UNCD is truly unique. UNCD consists of crystalline grains of pure sp^3 bonded carbon that are 3-5 nm in size, separated by atomically abrupt (0.5 nm wide), high-energy, grain boundaries. A high-resolution transmission electron micrograph (HRTEM) of this material is shown in Fig. 1. The grain boundaries (Fig. 2) have been studied in detail[7] and consist of a mixture of sp^3, sp^2, and other types of bonding, and because of their local structure, these high-energy grain boundaries are much more mechanically stable compared to the low-energy boundaries found in MCD. The combination of large amounts of sp^3 bonded carbon and the local order of these bonds give UNCD its unique materials properties, which are discussed in detail below.

UNCD films grown at ANL, and elsewhere, are usually synthesized using MPCVD, although other methods, including the hot-filament technique, have been successfully used. MPCVD, however, offers the best pathway for scale-up to large area plasmas and more precise control of plasma chemistry. Recent advances in reactor design have made this possible. The system we are currently using in our laboratory is shown in Fig. 3, in which we can grow highly uniform UNCD films on 100 mm silicon wafers. Argon-rich plasmas offer several distinct advantages over traditional hydrogen-rich plasmas, including low-power consumption and safer operation (hydrogen gas is extremely explosive). The CH_4/Ar gas plasmas containing C_2 exhibit a beautiful emerald green color (Fig. 3), which results from light emission due to electronic transitions within the C_2 molecules (swan bands).[8]

UNCD films are typically grown at pressures around 100 Torr, using 99% Ar/1% CH_4 gas mixtures. We have grown these films at temperatures ranging from 200 to 900°C, on a wide variety of substrate materials, including silicon, SiO_2 (glass), transition metals (Ti, W, Mo), carbides (SiC, WC), and others materials such as Al and Pt. Most frequently, films are grown on flat substrates (such as silicon wafers used in microelectronics), but small, three-dimensional objects can be coated as well, including wires and small parts (cutting tools).

As discussed above, UNCD exhibits a unique nanometer-scale structure that sets it apart from MCD, DLC, and also the so-called nanocrystalline diamond films (NCD) that are also grown using H_2/CH_4 plasmas.[9] UNCD exhibits a fully equiaxed grain structure, with grain sizes ranging from 3-8 nm, with grain boundaries that are 0.2-0.5 nm wide. Over the past several years we have optimized and characterized the basic materials properties of UNCD. The hardness, Young's Mod-
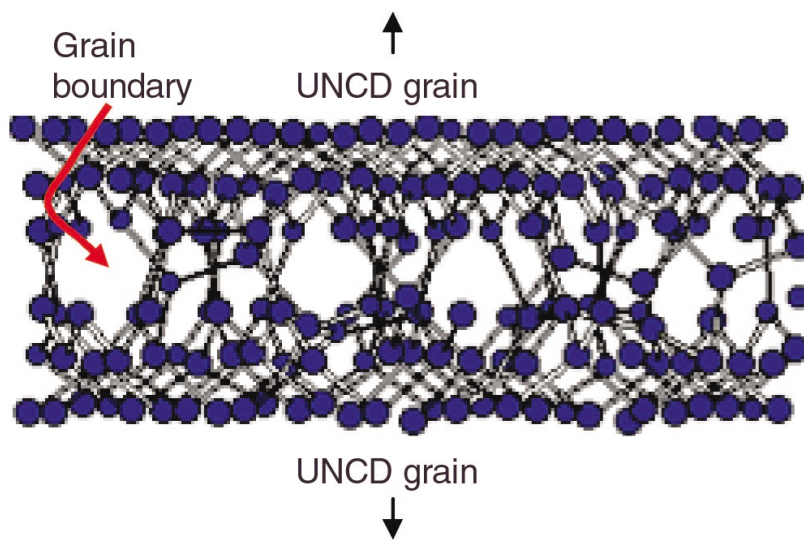

FIG. 3. Picture of the microwave plasma system used to grow UNCD thin films at Argonne National Laboratory. The emerald green color is derived from the C_2 dimers created in the plasma.

ulus, refractive index, and friction properties are all essentially equivalent to natural diamond. Several materials properties of UNCD actually exceed those of diamond. For instance, UNCD has a fracture strength of 4-5 GPa, compared to 1-2 for natural diamond.[10] By adding nitrogen gas to the Ar/CH_4 gas mixture normally used to grow UNCD, we have recently demonstrated that we can make n-type films that are highly conducting at room temperature.[11] Despite many years of research, successful n-type doping of MCD diamond films has not been achieved, limiting the use of this material in electronics. We have also demonstrated that the threshold voltage for electron field emission is very low (2-3 V/mm), even from flat UNCD surfaces. UNCD films can be grown at much lower temperatures[12] compared to other diamond film technologies (less than 350°C in our more recent unpublished work). The electrochemistry of UNCD is equivalent to that of heavily doped MCD films.[13]

As a coating technology, UNCD also offers several advantages. (1) UNCD films exhibit very low as-deposited stress (50 MPa), compared with 1-2 GPa for both MCD and DLC films. The control and minimization of film stress is important for any thin film technology, particularly for applications in film technology in microelectronics and MEMS, and in relation to materials integration issues (integrating diamond films with metal, oxide, and ceramic films), which are critical for device design and performance. (2) The as-deposited film roughness is low (~20 nm rms), which is particularly relevant for the production of MEMS components with high resolution. (3) Friction and stiction are very low (UNCD surfaces do not stick to one another since they are naturally hydrophobic), a critical property for MEMS components involving extensive surface contact.

Over the past several years we have explored numerous possible applications of UNCD films, ranging from hardness coatings for mechanical pump seals,[14] to cold cathode (field emission) electron sources (flat panel displays),[15] as both a structural material and anti-stiction coating for microelectromechanical systems (MEMS),[16] to, most recently, as a platform material for biosensors and biomedical devices.[17] It is our opinion that these latter two areas offer the most potential for this material.

There is perhaps no other application of UNCD films that could leverage as many of the unique properties of this material than in the biomaterials space, particularly BioMEMS-based biosensors. Diamond is the ultimate biocompatible material. Implantable devices must not trigger the body's immune defense systems, otherwise they are encapsulated by liposites or macrophages and rendered inoperative. The electrochemical properties of UNCD, and the fact that these properties can be modified by altering its surface chemistry (discussed below), may make UNCD an interesting biointerfacing material.

We are currently working on three specific projects in the biomedical space: (1) as hermetic coatings to encapsulate silicon chips for retinal implants (supported by DOE Biomedical Engineering Program); (2) as an electrochemical interface between biomimetic lipid layers containing membrane proteins (as part of a new initiative supported by DOE Basic Energy Sciences); and (3) on bioMEMS sensors that incorporate derivatized UNCD surfaces and MEMS structural layers. A schematic of a UNCD-based biosensor is shown in Fig. 4. In this approach, selective absorption of a particular target analyte is achieved by expressing a receptor biomolecule on the surface of a UNCD micro-cantilever, using the photochemically induced attachment of an amine-terminated alkene, followed by the attachment of a heterobifunctional linker molecule and the receptor (*e.g.* synthetic DNA strands, biotinylated amino acids or proteins, etc.).[17] This approach has been shown to result in very stable functionalization, and is also very highly
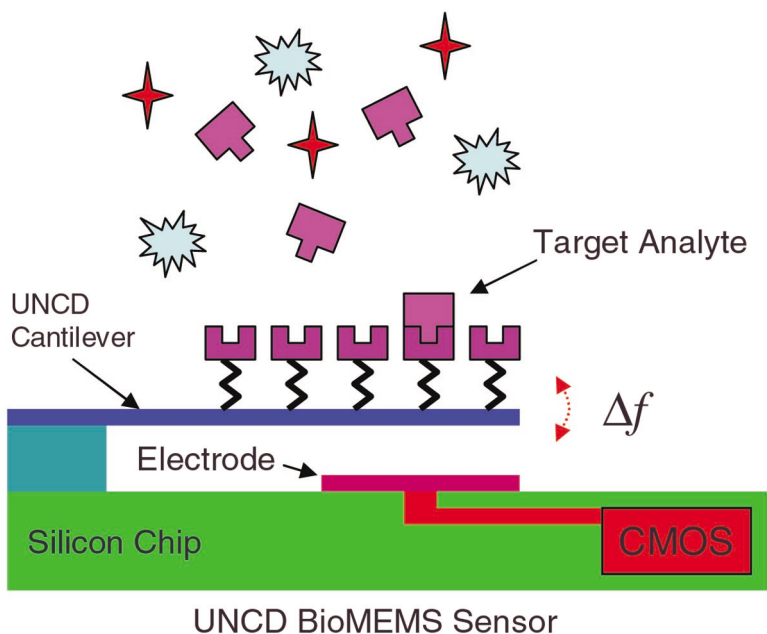
FIG. 4. Schematic of a UNCD-based bioMEMS sensor (see text for discussion).

resistant to non-selective absorption of non-targeted pathogens. The detection of biomolecules can be made through the measurement of changes in the vibration frequency of the cantilever resulting from the added mass of biomolecules. An array of UNCD microcantilevers recently fabricated by us is shown in Fig. 5.[10] Since UNCD films can be grown at low temperatures (≤ 400°C), a UNCD-based MEMS cantilever biosensor can be integrated with CMOS electronics, thus enabling the production of a fully integrated bioMEMS/CMOS device.

To summarize, UNCD films are synthesized using inert-gas-rich plasmas and have a unique nanoscale structure that clearly distinguishes them from natural diamond and other diamond films. UNCD also has many exceptional materials properties and many potential applications, particularly in MEMS and as a platform material for biomedical devices. ■
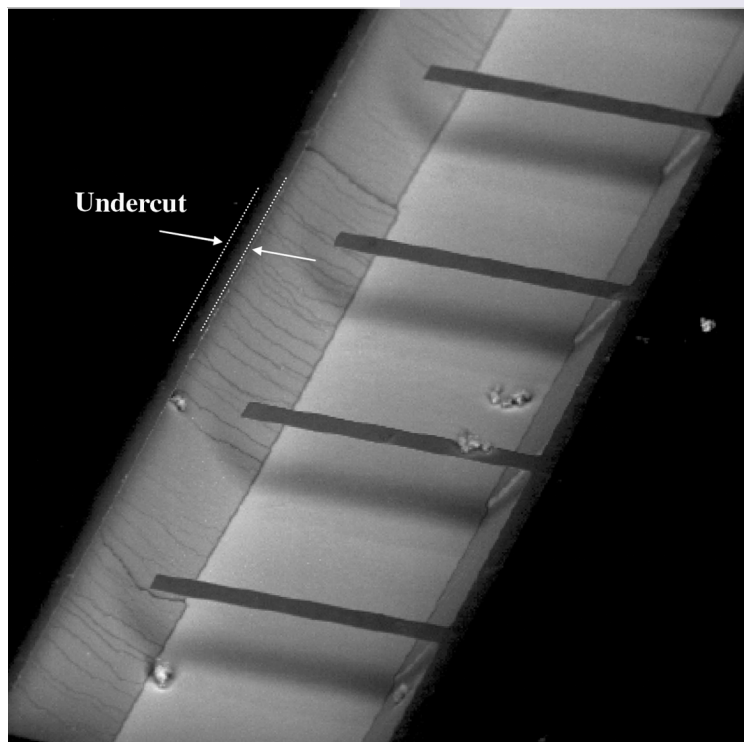
FIG. 5. UNCD microcantilevers fabricated using microelectronic-compatible fabrication processes. These cantilevers can be used as the basis for vibration sensitive biosensors as described in the text.

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