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Science and Technology of Transformational Multifunctional Ultrananocrystalline Diamond (UNCD™) Coating for Industrial/High-Tech/Biomedical Applications

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Abstract
This article describes the science / technology of a transformational coating, named ultrananocrystalline diamond (UNCD™), and integration into new generations of industrial, high-tech, medical devices. UNCD films are synthesized by novel MPCVD and HFCVD processes, using patented Ar/CH_4 gas chemistry, generating unique C_2 dimers and contributing CHx (x=1, 2, 3) species, inducing nucleation/growth of UNCD films with smallest grain size today (3-5 nm), inducing unique multifunctionalities, enabling technological applications described below: UNCD coated mechanical pump seals and bearings (in worldwide market). UNCD films on AFM tips (in worldwide market), without mechanical degradation as Si / metal tips. UNCD dielectric layer in RF MEMS switches, eliminating failure of prior SiO_2 / Si_2N_3 dielectric layers. Best biocompatible UNCD coating (made of C atoms-element of life in Human DNA/cells), enabling superior medical devices/prostheses: UNCD-coated silicon - microchip (artificial retina) implantable on eye's retina, to return partial vision to people blinded by genetically induced degeneration of photoreceptors. UNCD-coated dental implants (DI), in clinical trials (35 patients implanted since 2018-present), eliminating failure, via corrosion of current metal DIs. Nitrogen-doped N-UNCD-coated commercial NG/Cu anode, enabling new generation of Li-ion batteries with orders of magnitude superior capacity energy and safer than current LIBs.

Key Word and Phrases
Ultrananocrystalline, Diamond, Coating, Multifunctionalities, Integration in Transformational Industrial, High-Tech, Medical Devices/Prostheses, Products, Improving Way/Quality of Life of People Worldwide.

1. Synthesis of UNCD Films via Microwave Plasma Chemical Vapor Deposition (MPCVD)

Ultrananocrystalline diamond (UNCD) is a transformational new paradigm material that was originally developed in film (coating) form by Auciello/Gruen/Krauss in the early 90s (see: reviews in references from early 20s [1] - [3] to 2022 [4]). The first scientific breakthrough emerged from research on investigating a new process to grow polycrystalline diamond (PCD) films without using the conventional H_2 (99%)/CH_4 (1%) gas flow in an air evacuated chamber, used in prior years, with coupled microwave power, generating a plasma (giving the name Microwave Plasma Chemical Vapor Deposition (MPCVD)), producing CHx (x=1,2 ,3) molecules, requiring H bond breaking from C atoms to produce C species, which reacting on surfaces produced microcrystalline diamond (MCD) films, subsequently turned into Nanocrystalline Diamond(NCD) films when using CH_4 (4%) [3]. The initial breakthrough process involved flowing Ar gas through an oven heated to ~ 900 ˚C, to evaporate C_{60} fullerene molecules (discovered in 1985 by Kroto/Smalley/Curl, Jr.-1996 Nobel Prize-see review in [5]). from commercial powder, carried into a MPCVD system, where microwave power induced cracking of C_{60} fullerene molecules, releasing C atoms that linked on substrates' surfaces, inducing growth of polycrystalline diamond films with ~10 nm grain size [6]. However, C_{60} fullerene molecules were extremely expensive (thousands of dollars at that time,

for few grams of C_{60} fullerene molecules), making difficult to envision bringing the UNCD coating technology to the market at low cost.

The second scientific breakthrough emerged when Auciello/Gruen/Krauss directed research using a new transformational gas flow process, replacing H_2 in the gas flow, using an Ar (99%)/ CH_4 (1%) mixture [7], inserted in a MPCVD system (Figure 1(a)), where microwave power produces a plasma, which induces the formation of a mixture of Ar^+ ions/Ar^0 neutrals, C^+ ions/C^0 neutrals, CHx^+ ions/ CHx^0 neutrals, and a key component named carbon dimers (C_2). Optical emission spectroscopy imaging of the MPCVD plasma, generated with the Ar/CH_4 chemistry, revealed that the green light emission originates from the excited C_2 dimers generated by the MPCVD process (Figure 1(b)), from methane decomposition, via reactions (1.1) and (1.2) shown below:

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \qquad (1.1) \quad ; \quad C_2H_2 \rightarrow C_2 + H_2 \qquad (1.2)$$

The C_2 dimers, with contribution of CHx species, as indicated by computer simulations [8], induce the growth of film defined as ultrananocrystalline diamond (UNCD), since High Resolution Transmission Electron Microscopy showed gran sizes in the range 3-5 nm (smallest gran size for any PCD film known today – see: Figures 1(c) and 1(d)). Another breakthrough related to the patented [9] UNCD coating technology is that the industrial MPCVD system, shown in Figure 1 (a), produces extremely uniform UNCD films on 200 mm diameter substrates (Figure 1 (e), providing the basis for technological applications of UNCD films. Other groups worldwide are growing and investigating UNCD films (see reviews in [1] – [4]).

Another key outcome of the transformational MPCVD process growing UNCD films, was the demonstration that UNCD films can be grown at much lower temperatures (350-400 ˚C) (see: reviews in references [3] and [4]) than any other PCD films, enabling encapsulation of Si microchips for a transformational new technology to return partial vision to blind people (see: Figure 3).

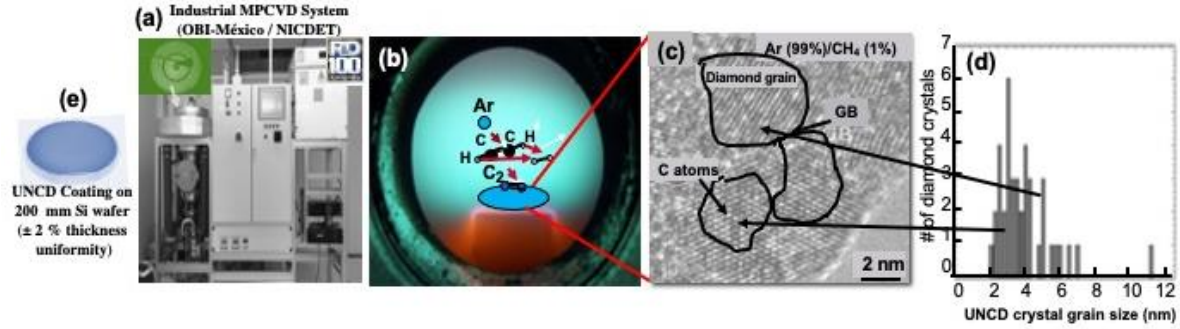

Fig. 1(a) Picture of industrial MPCVD system (IPLAS-GMBH-German), currently operational in the company OBI-México growing UNCD coatings on large array of metal based dental implants vertically distributed around 200 mm diameter holder; **(b)** Picture of green plasma growing UNCD film on a Si substrate; **(c)** HRTEM image of a UNCD film showing the diamond grains with 3-5 nm dimensions, confirmed by quantitative statistical measurements shown in **(d)**; **(e)** Uniform UNCD film grown on 200 mm diameter Si wafer.

Another transformational materials science/technological development, related to UNCD films, was the development of a process to grow electrically conductive UNCD films [3], [4], [10] via the MPCVD process, using an $Ar/CH_4/N_2$ gas mixture, which induced the formation of a plasma containing Ar, C, CHx and N ions and neutral atoms, such that N atoms are inserted in the grain boundaries of the named N-UNCD films, linking to open C atoms' bonds and providing electrons ejected from atoms' orbitals, with electrons moving through grain boundaries, enabling the unique electrically conductive N-UNCD coating [10]. Independent groups worldwide reproduced the growth of N-UNCD films [11], which are formed by grains of 10-15 nanometers and grain boundaries of 1-2 nanometers [10], [11].

The initial process to grow UNCD films, using the MPCVD technique described above, was based on doing a conventional seeding of the substrates' surface inserting the substrate in a

container with nano-diamond particle/methanol solution in a sonicator system, where ultrasonic waves sake the diamond particles immersing then on the substrate surface, where they act as seeds inducing the growth of the UNCD films, or any other PCD films (see detailed description of this process in reviews [1] – [4]. Subsequently, a process was developed named Bias Enhanced Nucleation-Bias Enhanced Growth (BEN-BEG), whereby electrically conductive and semiconductive substrates are biased with a negative voltage, attracting C^+ and CHx^+ ionic species, which get implanted in the surface/sub-surface region of the substrate nucleating carbide layers that induce the UNCD film growth [3], [4]. The BEN-BEG process also was implemented by groups worldwide growing other PCD films (see: reviews in references [3], [4]).

2. Synthesis of UNCD and N-UNCD Films via Hot Filament Chemical Vapor Deposition (HFCVD)

Another key scientific/technological development focused on growing UNCD and N-UNCD films via the HFCVD technique, which involves using arrays of parallel tungsten (W) filaments (see: Figure 2(a)) heated to about 2,300˚C, glowing bright (Figure 2(b)), via electric current, transferring energy to CH_4, H_2, and N_2 molecules flowing through the filament array, breaking them into C atoms, CHx (x =1, 2, or 3) molecules, H and N atoms, as it happens in the MPCVD process, enabling growth of PCD films. R&D demonstrated a process to grow PCD films, via the HFCVD process, on HfO_2 [12], as key oxide template layer on Si, since HfO_2 is the main gate oxide layer in all Si-based micro/nano-electronic devices today. Systematic tailoring of gases flow induced growth of UNCD (Figure 2 (c)), NCD (Figure 2 (d)) and MCD (Figure 2 (e)) films, which showed that UNCD films exhibit the densest structure and smoother surface topography. In addition, related R&D demonstrated the feasibility of growing extremely uniform films in thickness and nanostructure on 100 mm diameter Si wafer, via normal HFCVD process (Figure 2 (f)) [13], and on micro-structured W layers on a 100 mm diameter Si wafer, using a HFCVD BEN-BEG growth process focused on the W layers (Figure 2 (g)) [13], showing the pathway for future growth of uniform micro/nanostructured UNCD films on up to 300 mm diameter Si wafers for new electronic technologies. Other groups worldwide have shown HFCVD /BEN-BEG of other PCD films (see review in CH1 of reference [4]).

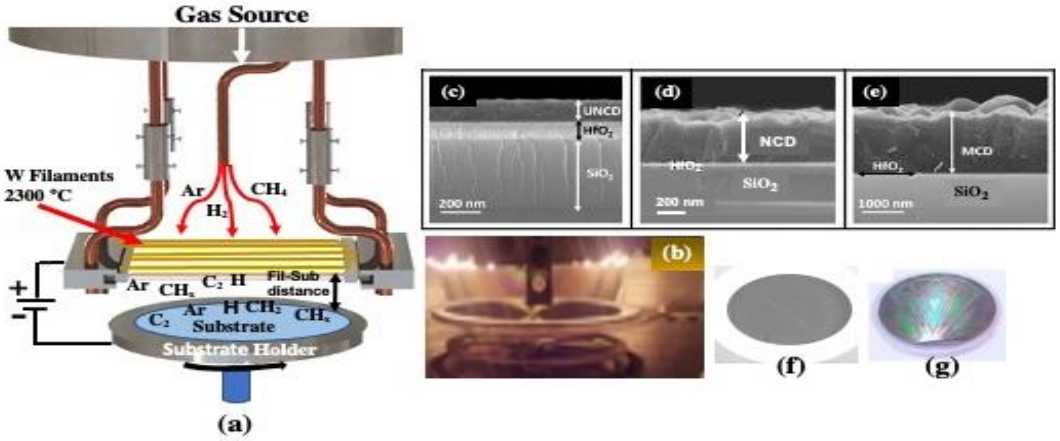

Fig. 2 (a) Schematic sowing a HFCVD array of W filaments on top of a 100 mm diameter substrate and the gas flow to grow UNCD / N-UNCD films; **(b)** Picture of HFCVD system during growth of UNCD film on a 100 mm diameter Si wafer; Cross-section SEM images of UNCD **(c)**, NCD **(d)** and MCD **(g)** films, respectively, grown on HfO_2/SiO_2 layers on Si wafers; **(f)** uniform UNCD film grown on a 100m diameter Si wafer with HfO_2 template layer; **(g)** micro-structured UNCD film grow on a micro-patterned W layer on a Si wader, using the BEN-BEG process.

Comprehensive descriptions of the materials science related to UNCD / N-UNCD films, via the MPCVD and HFCVD processes, are published in recent reviews [1]-[4], including references to work by worldwide groups on UNCD/N-UNCD films. The reviews include descriptions of characterization of films via Raman and Infra-Red Spectroscopies, X-ray Photoelectron Spectroscopy (XPS), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and High-

Resolution Transmission Electron Microscopy (HRTEM0, providing complementary chemical, physical, structural, and atomic scale information on the films.

The UNCD films exhibit a unique combination of superior physical, mechanical, tribological, chemical, thermal, electronic, and biocompatible properties, providing unique combination of multifunctionalities, enabling new generations of industrial, high-tech, and implantable medical devices / prostheses, promoting improvement in the way and quality of life of people worldwide, as shown in the next section.

3. Transformational UNCD-Coated Products in Worldwide Market and Under Development

Transformational UNCD coating-based industrial, high-tech, medical device/prostheses products are described below (Figure 3).

UNCD-coated Industrial Products in Worldwide Market: UNCD-coated mechanical pumps seals and bearing have been marketed by Advanced Diamond Technologies [14] since 2010. The UNCD-coated pump seals enable 20% saving in energy cost of running pumps, due to extremely low coefficient of friction of UNCD. In addition, UNCD-coated mechanical pump seals / bearing last years without replacement (mid-left image-Figure 3).

UNCD-coated High-Tech Products:

Atomic Force Microscope tips in World Market *(*top-left image-Figure 3), made of UNCD, provide superior performance for nanoscale imaging of surfaces without mechanical degradation, as for Si or metal tips.

B-UNCD-coated Electrodes for Water Purification Systems Under Development: Metallic electrodes coated with electrically conductive / water corrosion resistant Boron-doped B-UNCD coating [1], [4], 14], are in advanced state of development, for water purification, via electrical current passed through water, creating Ozone (O_3) molecules, which kill viruses, bacteria, and any other pathogens. (top- center image - Figure 3).

N-UNCD Coating for Transformational Li-Ion Batterie' Anodes Under Development*:* N-UNCD-coating on commercial Natural Graphite (NG)/Copper (Cu) anode of Li-ion batteries (LIBs) eliminates Li-ions-induced chemical degradation of the NG layer, enabling LIBs with stable capacity energy vs charge discharge cycles (red curve on top-right image-Figure 3). The N-UNCD-coated NG/Cu anodes enable a new generation of LIBs with orders of magnitude longer life without charging and safer than current LIBs.

RF MEMS Switches with UNCD Dielectric Layers for RF Communication and Radar Devices: R&D demonstrated that UNCD dielectric layer provides, for the first time, the capability for RF MEMS switches without failure as it occurred in prior switches involving SiO_2 or Si_2N_3 dielectric layers failing due to sticking of the movable switch membrane to the dielectric layer on top of bottom electrode (mid-right side - Figure 3).

UNCD-Coated External and Implantable Medical Devices / Prostheses:

UNCD-coated Silicon Microchip (Artificial Retina) to Return Partial Vision to Blind People**:** UNCD-encapsulated Si chip, with large integrated electrodes' array (left-bottom image -Figure 3), can be implanted on the ganglion cells' layer, receiving images from a CCD camera on glasses, processing the image and injecting electrons on the ganglion cells, transferring charges to the brain through their axons, to return partial vision to people blind by gene-induced death of natural photoreceptors. The Argus II device, developed in a 10-year R&D project (2000-2010), is currently implanted commercially by Second Sight in the USA and Europe, returning partial vision to people blind by retinitis pigmentosa.

UNCD-coated Metal Dental Implants (DI): Current commercial DI made mainly of Ti-alloys are chemically corroded by oral fluids (bottom-image-left Figure 3) (16 % Ti-alloys DI fail worldwide in the first 4-5 years due to chemical corrosion). UNCD coating eliminates corrosion and provides stronger bone attachment, via superior bone's cell growth on the UNCD surface than on Ti-alloy. Clinical trials (2018-present) done by Drs. López and Auciello, implanting 35 patients (bottom image-right-Figure 3), demonstrated that UNCD-coated Ti-alloy provide a transformational prosthesis.

UNCD-coated Stents), Hips, Knees: Initial R&D performed by Auciello's group since 2019 is demonstrating that UNCD coating may produce transformational stents, his, knees and other prostheses (bottom-right corner-Figure 3).

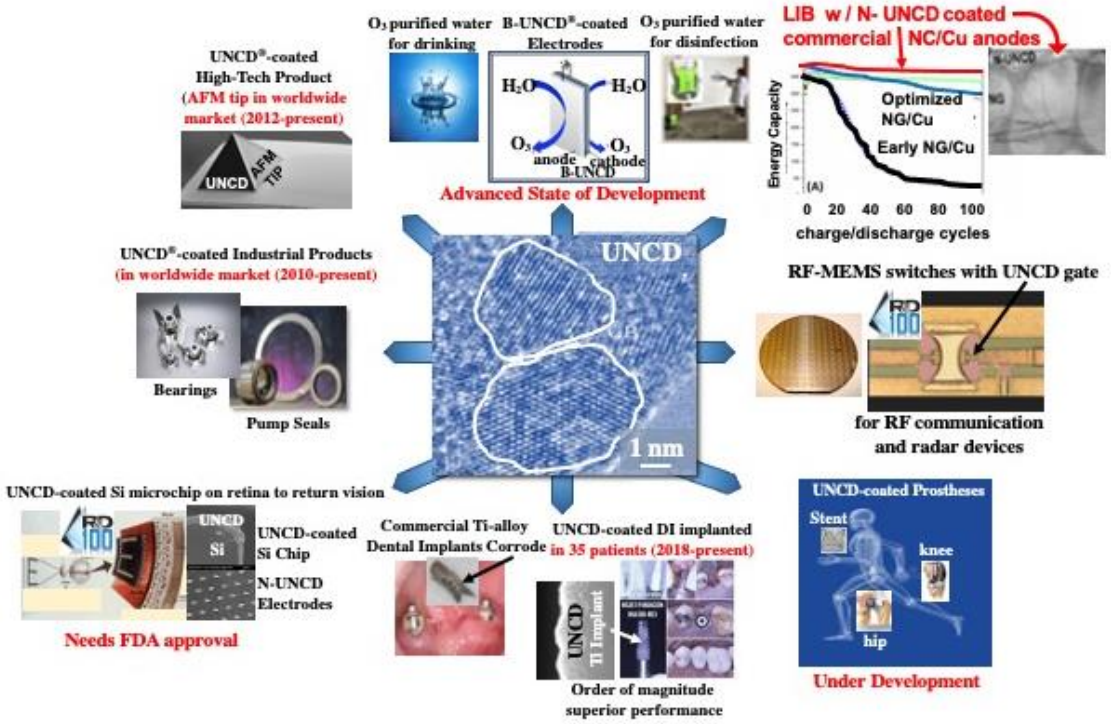

Fig. 5 Transformational UNCD-coated Industrial products in the world market, and high-tech and external and implantable medical devices / prostheses under development for insertion in worldwide market.

UNCD coating exhibits unique combination of complementary mechanical, physical, chemical, biocompatible and biological properties to produce new generations of transformational external and implantable medical devices / prostheses. A comprehensive review of materials science, technological development and applications of UNCD-coated high-tech and external and implantable medical devices / prostheses is presented in 10 Chapters of a book in press [4].

4. Conclusions

Fundamental and applied science on the transformational UNCD coating and numerous technological applications demonstrated until now and those upcoming, have proven that UNCD represents a new paradigm material in film (coating) form, which exhibits a broad range of functionalities applicable to a large range of multifunctional industrial, high-tech and medical devices/prostheses. Many groups worldwide are now doing R&D on UNCD films.

What is another key future technological application for UNCD coatings? Recent R&D performed by Auciello's group, demonstrated growth of UNCD coatings on HfO_2 layers (Figure 3 (c)) and integration with high-k dielectric films, providing the bases for potential application of UNCD coating to produce new diamond-based micro/nano-electronic devices. State tuned for future articles in this field.

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