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Mini Review

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Materials Science /Technologies Development for New Generation Biomedical Systems Based on Transformational Multifunctional / Biocompatible Ultrananocrystalline Diamond (UNCD™) Coatings

Orlando Auciello*

Distinguished Research Scientist, Texas State University, Electronic Engineering and Bioengineering, San Marcos, Texas, USA

Co-founder/CEO, Original Biomedical Implants (OBI-USA), Richardson, Texas, USA

Co-founder/CEO, Original Biomedical Implants (OBI-México), Hermosillo, Sonora, México

***Corresponding author:** Orlando Auciello, Distinguished Research Scientist, Texas State University, Electronic Engineering and Bioengineering, San Marcos, Texas, USA.

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Abstract

Diamond, the strongest best chemical corrosion resistant material from mother-Earth, has been made into a Multifunctional Ultrananocrystalline Diamond (UNCD™) coating, with a unique combination of smallest grains (2-5 nm), highest hardness (98 GPa-similar to diamond gem-100 GPa), order of magnitude lowest coefficient of friction (0.02-0.04) and highest resistance to corrosion by any fluid, including human fluids, compared to materials used in implantable medical devices and prostheses today, outstanding biocompatibility, because it is made of Carbon atoms (life's element in human DNA, cells, molecules). UNCD coatings are currently in worldwide markets in transformational new industrial mechanical pump seals/bearings and high-tech Atomic Force Microscope tips with no wear. UNCD coatings are in advanced state of development for new generation of UNCD-coated dental implants (clinical trials with implantation in 51 patients (2020-2025) demonstrated that they eliminate current 15% worldwide failure of Ti-alloys DIs in first 4-5 years, requiring replacement at extra cost and patient discomfort. In addition, transformational unique electrically conductive UNCD coating with inserted N atoms in grain boundaries (N-UNCD) provides pathways for new transformational corrosion resistant, biocompatible coating for electronic medical devices.

Introduction

Many critical properties of materials affect their performance in many key medical related systems, devices and prostheses, as described below: Dental implants, hips, knees, and other prosthesis, replacing degraded natural body parts, are currently made of metals mainly, failing earlier than desirable, due to chemical corrosion from body fluids and mechanical wear. A Si-microchip (Argus II device-artificial retina [1]), restoring partial vision to people blinded by gene-destroyed natural human retina photoreceptors, is located outside the eye (to avoid chemical corrosion of Si by eyes' fluids), connected with Pt wires, through the eye's wall, to ganglions cells, sending electrons to brain cells to restore partial vision to blind people.

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Current Li-ion batteries, with graphite/copper anodes, are extensively used in cell phone/portable electronics/implantable powered medical devices (defibrillator/pacemaker), exhibiting undesirable capacity energy degradation via Li ions degradation of the graphite layer [2].

Fast purification/disinfection of surgical instruments, protection masks against viruses and other pathogens' processes, developing on surfaces of systems, can be done fast via passing electrical current through water, between conductive metal electrodes, creating Ozone (O3) molecules, which kill all viruses/bacteria/pathogens on surfaces, when exposed to a beam of Ozonated water. The problem with metal electrodes is water-induced corrosion, which requires early than desirable electrode changes. Current metal-based seals / bearings / gears in mechanical pumps, used for mixing chemicals to produce pharmaceutical drugs, exhibit high friction and induce biofouling produced by metal particles inserting in the chemical fluid being mixed. Related to the above information, this article provides a brief review of the fundamental and applied materials science performed during several years, which resulted in the development of the Transformational UNCD coating, made of 2-5 nm/10-9meter grains, and N-UNCD (10 nm grains) coatings which exhibits unique combination of transformational physical, mechanical, lowest friction, chemical, electronic, thermal, and biological properties, similarly to those of diamond gems. The UNCDTM and N-UNCDTM coatings enable new generations of biomedical systems to improve way and quality of life of humans.

Materials Science of Transformational Ultrananocrystalline Diamond (UNCDTM) and Nitrogen-Inserted Grain Boundaries N-UNCD™) Films (Coatings)

Growth of UNCD and Unique Electrically Conductive Nitrogen-Grain Boundary Inserted N-UNCD Films via Microwave Plasma Chemical Vapor Deposition (MPCVD)

In the early 90s, Auciello/Gruen/Krauss developed a new MPCVD process to produce UNCD films with the smallest grain dimensions (2-5 nm) [3] demonstrated today, enabling transformational technological applications, as shown further on in this minireview. The new MPCVD process growing UNCD films involves flowing an Ar (99%-less expensive gas))/CH4 (1%) gas mixture [3,4], into an air evacuated chamber. Microwave power, applied to the gas mixture, produces a green plasma (Figure 1(a)), which contain Ar+ ions interacting with broken CH4 molecules in the gas phase, generating two C atoms linked to each other (C=C), forming C2 dimers, emitting green light (see C=C in Figure 1(a)), and CHx (x=1, 2, 3) molecules. Since C2 dimers do not have H atoms attached in the open bonds, like in processes growing Microcrystalline Diamond (MCD-≥ 1micron grains) and Nanocrystalline Diamond (NCD-20-100s nm grains) films (see reviews [4-7], C2 dimers / CHx react quickly on substrates' surfaces, inducing nucleation / growth of UNCD films (Figures 1(b) and 1(c)), providing the bases for the patented [3] film named UNCD (Figure 1).

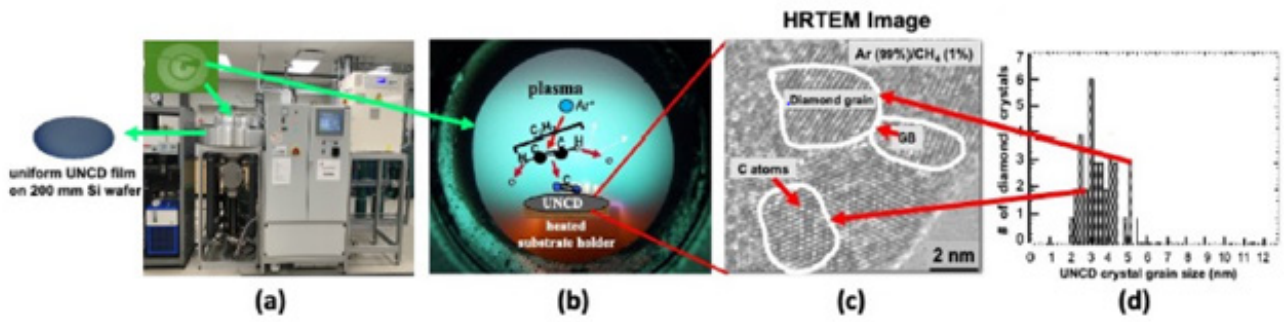

Figure 1: (a) Picture of microwave plasma created via excitation of Ar (99%)/CH4 (1%) gas mixture (the schematic shows Ar ions producing the key C2 dimers that initiate the UNCD films' nucleation and subsequent growth, jointly with CHx (x= 1, 2, 3) molecules created in the plasma, all reacting on the substrate's surface); (b) High Resolution Transmission Electron Microscopy (HRTEM) image of a UNCD film grown on a silicon substrate (the white dots are C atoms in diamond crystal lattice positions in the grain); (c) UNCD grain dimensions measured via HRTEM.

A key outcome of the R&D on UNCD films is that they can be grown at the lowest temperature (350-400˚C) than any other Poly-Crystalline Diamond (PCD) films [4], enabling encapsulation of Si microchips for a transformational new artificial retina to return partial vision to people blind by retinitis pigmentosa (see Figure 3). The initial R&D involved growing UNCD films, using conventional chemical seeding of substrate surface with UNCD particles/methanol solution in an ultrasonic wave generator, shacking UNCD particles and inserting them on the substrate's surface, to induce nucleation/growth of UNCD films. However, marketing of UNCD coating technology, requires reduced cost. In this sense, Auciello et al. developed a Bias-Enhanced-Nucleation/Bias-Enhanced Growth (BEN-BEG) process, accelerating C2+ and CHx+ ions from the plasma, implanting them in the subsurface area of negatively biased substrates, inducing nucleation and growth of UNCD films, thus, eliminating extra cost of the chemical seeding process (BEN-BEG process grows UNCD films with grain sizes identical as as shown in (Figure 1 (b)).

Another key outcome of the R&D was the development of a process to grow electrically conductive UNCD films (first demonstrated electrically conductive diamond film) via MPCVD, using Ar/CH4/N2 gas mixture, resulting in formation of a plasma containing Ar, C, CHx and N ions / neutral atoms. Extensive materials characterization, including measurements of electrical conductivity, demonstrated that N atoms are inserted in the grain boundaries of N-UNCD films, reacting chemically with open bonds of C atoms and providing electrons ejected from atoms, and acquiring enough energy to move through the grain boundaries, enabling unique electrically conductive/patented [5] N-UNCD coating. Independent groups worldwide reproduced N-UNCD films [6,7]. Comprehensive descriptions of the materials science related to UNCD and N-UNCD films, via the MPCVDs process, are published in recent reviews [4,6,7,8], including references to work by worldwide groups. 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 (HRTEM), providing complementary chemical, physical, structural, and atomic scale information on the UNCD and N-UNCD films.

Growth of UNCD and N-UNCD Films via Hot Filament Chemical Vapor Deposition (HFCVD)

Another key scientific/technological endeavor focused on developing processes to grow UNCD and N-UNCD films via the HFCVD technique, which involves using arrays of parallel tungsten (W) filaments (see Figure 2 (a)), heated to ~ 2,300˚C, via electric current. The high temperature sees (Figure 2 (b)) transfer energy to CH4, H2, and N2 molecules, flowing through the filaments, breaking them into C atoms, CHx (x =1, 2, or 3) molecules, H and N atoms, similarly to the MPCVD process, enabling growth of UNCD [8] and N-UNCD films [8]. More recently, R&D focused on developing a process to grow UNCD films, via the HFCVD process, on HfO2 [9], as key oxide template layer on Si, since HfO2 is the main gate oxide layer in all Si-based micro/nano-electronic devices worldwide. Systematic tailoring of gases flow demonstrated the feasibility of growing UNCD (Figure 2 (c)), NCD (Figure 2 (d)) and MCD (Figure 2 (e)) films, which showed that UNCD films exhibit the densest / smoother surface topography, and can be grown with extremely uniform film thickness and nanostructure on 100 mm diameter Si wafer (Figure 2 (f)) [9], 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)) [10], showing the pathway for future growth of uniform micro/nanostructured UNCD films on up to 300 mm diameter Si wafers for new electronic technologies. The HFCVD/BEN-BEG process has also been demonstrated by independent groups [11] (Figure 2).

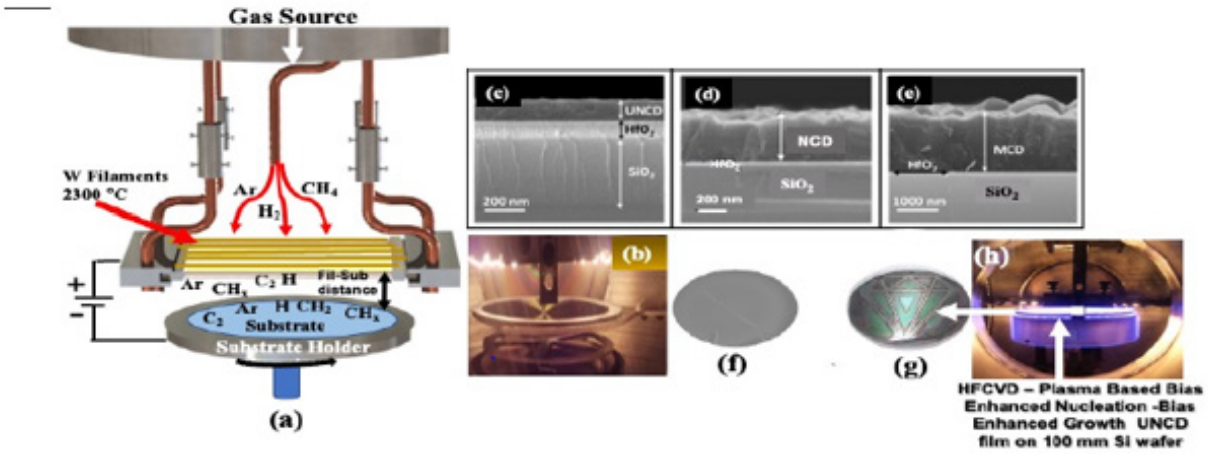

Figure 2: (a) Schematic of HFCVD array of W filaments on top of a 100 mm diameter substrate and gas flow to grow UNCD / N-UNCD films; (b) Picture of HFCVD system during growth of UNCD film on a 100 mm diameter Si wafer; Cross-section SEM images of UNCD film (c), NCD film (d) and MCD film (g) grown on HfO2/SiO2 /Si wafers; (f) uniform UNCD film grown on 100 mm diameter Si wafer with HfO2 layer; (g) UNCD film grow on micro-patterned W layer on a Si wader, via BEN-BEG process on the W layers. (h) Picture of HFCVD process with plasma created on the surface of W patterned on Si wafer (g).

Properties of UNCD, N-UNCD, B-UNCD Films

These coatings exhibit unique combination of mechanical (compared with the diamond gem-strongest material on Earth), tribological, and electrical properties, when doped with appropriate atoms, as described below (Table 1)

Table: 1

Material	Dopant	Property	Value	(Units)
Diamond Gem		Hardness	100	Giga Pascal •
UNCD Film		Hardness	98	Giga Pascal
Diamond Gem		Young Modulus	1,200	Giga Pascal
UNCD Film		Young Modulus	998	Giga Pascal
UNCD Film		Friction Coefficient	0.02-0.04	No units
UNCD Film		Wear of Surface	~ 0.0	microns
N-UNCD Film		Electrical Conduction	~ 200	Ohms.cm
			(near metallic)	
B-UNCD Film	N atoms (in GB)	Electrical Conduction compare	~0.078	
	B atoms replace c atoms in diamond lattice		Cu=0.0034	Ohms.cm

Conclusions

The UNCD films' properties provide unique multifunctionalities, enabling new generations of industrial, electronic, high-tech, and implantable medical devices / prostheses, promoting improvement in the way and quality of life of people worldwide, (Figure 3) shows a summary of UNCD-coated high-tech and medical devices/prostheses in the world market and in advanced state of development for near insertion in worldwide markets, as described in a book edited by O. Auciello [12] (Figure 3).

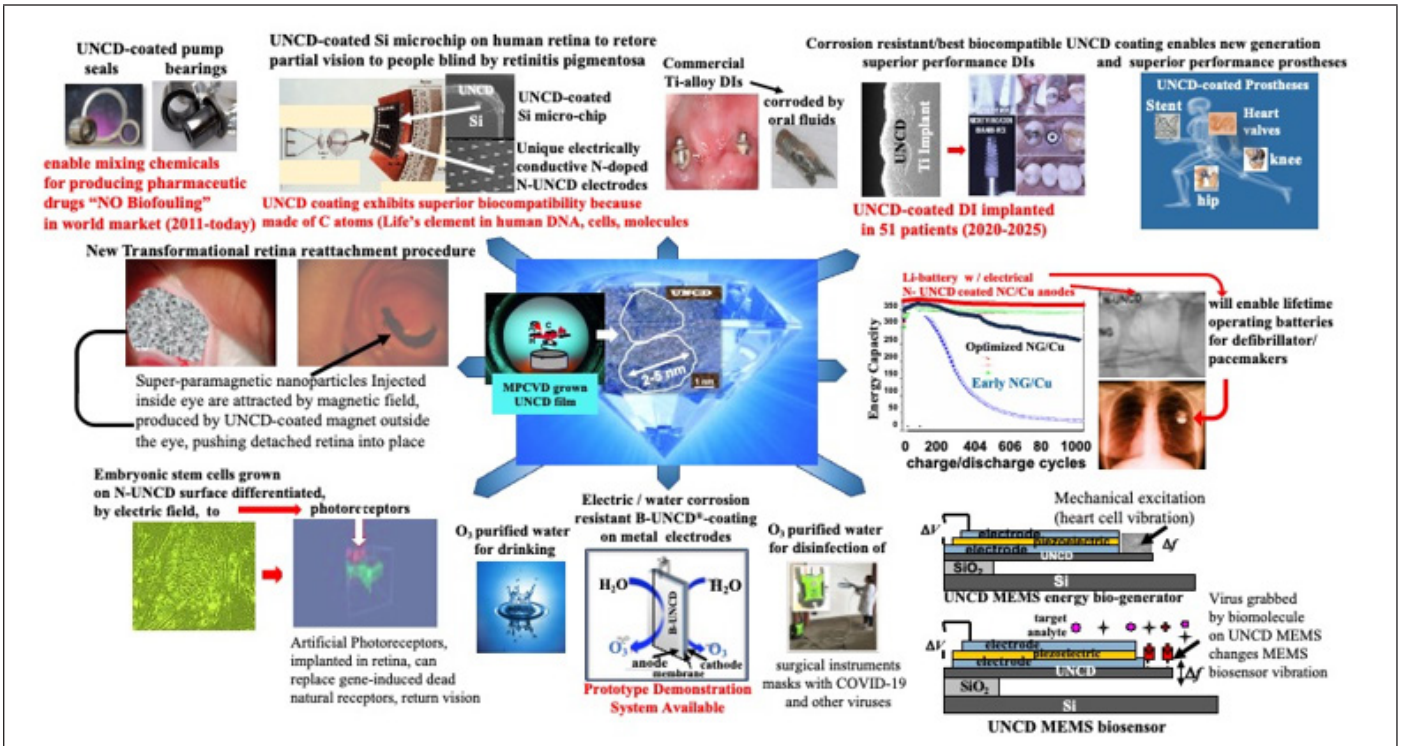

Figure 3: Summary view of transformational high-tech / medical devices / prostheses based on the UNCD coating.

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Conflict of Interest

None.

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