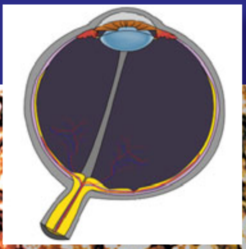

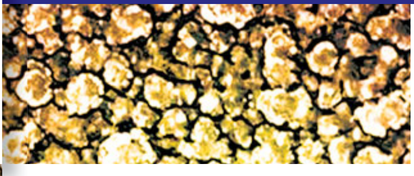

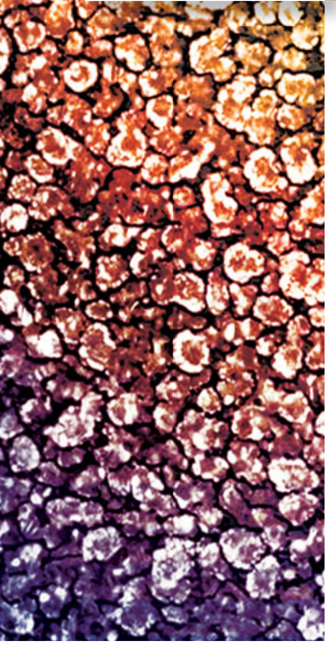

Biocompatible ultrananocrystalline diamond coatings for implantable medical devices

Orlando Auciello, Pablo Gurman, Maria B. Guglielmotti,
Daniel G. Olmedo, Alejandro Berra, and Mario J. Saravia

A novel multifunctional and biocompatible ultrananocrystalline diamond (UNCD) film technology developed recently represents a new material with a unique combination of functionalities, including biocompatibility, to enable a new generation of implantable medical devices and scaffolds for tissue engineering. Following a description of the synthesis and properties of UNCD films and a comparison with other diamond film technologies, this article focuses on descriptions of key UNCD-based medical devices to treat specific medical conditions requiring effective therapies: (1) A UNCD-coated microchip (artificial retina) implantable inside the eye on the retina to restore partial vision to people blinded by retinitis pigmentosa and macular degeneration produced by genetically induced degeneration of the retina photoreceptors. (2) A UNCD-coated intraocular device for treatment of glaucoma in the eye. (3) UNCD-coated metal dental implants with potential order of magnitude longer life and superior performance than current implants.

Synthesis and structure of ultrananocrystalline diamond films

Diamond thin films are of great interest and are being investigated because of many current (e.g., diamond coated mechanical pump seals and bearings) and potential (e.g., microelectromechanical/nanoelectromechanical systems [MEMS/NEMS]) applications to enable a new generation of multifunctional devices.[1] Several types of diamond thin films have been synthesized and systematically studied, exhibiting different microstructures, surface morphologies, and properties. Diamond films have been grown on the surfaces of insulators, semiconductors, and metals. Following surface pretreatment, or "seeding" (embedding micro- or nanodiamond particles on the substrate surface), diamond films are grown on the seeds mainly using microwave plasma-enhanced chemical vapor deposition (MPCVD) or hot filament chemical vapor deposition (HFCVD).[1,2] For the MPCVD method, a mixture of gases is inserted into an air evacuated chamber, and microwave power is coupled to the gas to produce a plasma involving ionized and neutral atoms and molecules containing C, H, and other components such as Ar. In the HFCVD process, an array of hot filaments heated up to 2200°C induces cracking of the CH_4 molecules, producing radicals that induce the growth of diamond films.[1,2] The use of a hydrogen-rich chemistry (H_2 [balance]/CH_4 [0.1 to 4%])[1,2] results in microcrystalline diamond (MCD) (1–5 µm grains and columnar microstructure) (for ~1% CH_4) and nanocrystalline diamond (NCD) (10–100 nm grains) (for up to ~4% CH_4) films. MCD and NCD films grown on surfaces of insulators (oxides), semiconductors, and metals seeded with diamond micro-/nanoparticles without particle surface functionalization exhibit low initial nucleation densities ($<10^{10}/cm^2$) due to agglomeration of the particles on the substrate surface. MCD surfaces are rough (root mean square [rms] ~10% of film thickness).[1,2] On the other hand, high diamond film nucleation densities are achieved ($>10^{12}/cm^2$) using a seeding process involving functionalized diamond particles to avoid agglomeration,[3] which is also used to grow relatively smooth, high-quality NCD films at 600–800°C.[1,2]

The H_2/CH_4 chemistry-based growth process is driven by CH_x ($x = 2–3$) radicals interacting with the substrate surface.

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This involves the hydrogen abstraction process, ultimately resulting in carbon atoms bonding into positions corresponding to the diamond lattice. The atomic hydrogen in the plasma preferentially etches a graphitic phase that codeposits with the diamond phase. However, atomic hydrogen also etches the diamond phase, although at a ~50 times lower rate than for graphite, resulting in the formation of intergranular voids and columnar morphology with large grains (≥1 μm). The MCD films exhibit high residual compressive stress, poor intergranular adhesion, very rough surfaces, and high coefficient of friction (≥0.5).[1,2] Consequently, MCD films are not well suited for medical devices requiring very low coefficient of friction and low wear, such as orthopedic implants. The grain size can be reduced to 10–100 nm, characteristic of NCD films, by increasing the CH_4/H_2 ratio in the plasma. This results in relatively smooth NCD films,[1,2] but with increased non-diamond components at the grain boundaries.[2] NCD films grown with high sp^3 content,[2] using a CH_4 (0.3%)/H_2 (99.7%) gas mixture, exhibit the NCD structure for thickness ≤ few hundred nm, but above that, grain coarsening dominates due to a lack of re-nucleation, and the film develops columns, increased grain size, and roughness.

In contrast to MCD and NCD film growth, ultrananocrystalline diamond (UNCD) films are produced by MPCVD using a novel (patented[4]) argon-rich chemistry [Ar (99%)/CH_4(1%)][1] with no hydrogen added.[1,4] This produces carbon dimers (C_2) and CH_x radicals in the plasma, from methane decomposition, via reactions (1) and (2) described below:

$$2CH_4 \rightarrow C_2H_2 + 3H_2 \tag{1}$$

$$C_2H_2 \rightarrow C_2 + H_2. \tag{2}$$

Initial work indicated that C_2 dimers play a critical role in UNCD film nucleation and growth.[1,5] Calculations predicted that the C_2 dimers have low activation energy (~6 kcal/mol) for insertion into the substrate surface, thus establishing the nucleation characteristics of UNCD films. Recent modeling indicates that while the C_2 population in the plasma is high, the population near the surface may be low, and other hydrocarbon radicals (e.g., CH_3, C_2H_2) are also substantial or the main contributors to the UNCD film growth.[6] This model, however, could not fully explain the low temperature growth (≤400°C) of UNCD films. 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, arising mainly from thermal decomposition of methane to acetylene in the plasma.[1]

The uniqueness of UNCD films is that they exhibit a nanostructure with the smallest grain size obtainable today for diamond films (see **Figure 1**a). Important also is that insertion of nitrogen in the gas mixture (e.g., Ar [79 sccm]/CH_4 [1 sccm]/N_2 [20 sccm]) results in UNCD films, named N-UNCD, with ~10 nm grain size and ~2 nm wide grain boundaries (Figure 1b).[7] N-UNCD films are semi-metallic, with nitrogen incorporated into grain boundaries, thereby satisfying dangling C bonds and providing electrons for electrical conduction.

A critical outcome of the UNCD nucleation and growth process is that these diamond films are produced at the lowest temperatures (350–400°C) possible today, as measured by thermocouples in contact with the substrate during growth and most importantly by the demonstrated growth of UNCD films to encapsulate complementary metal oxide semiconductor (CMOS) devices, which exhibit similar performance before and after growing UNCD films on them. The CMOS device would be destroyed if diamond films were grown on them at temperatures much higher than 400°C; thus, integrating UNCD coatings with CMOS devices is an alternative to the thermocouple method (described previously) in cross-checking the low-temperature growth of UNCD films.[1] To the best of the authors' knowledge, a similar demonstration of low-temperature NCD film integration with CMOS devices has not been published in the open literature yet. Low-temperature UNCD film growth on CMOS devices forms the basis for monolithically integrated UNCD-MEMS/NEMS/CMOS devices[1,8] and for UNCD-coated CMOS microchips implantable inside the human body.[1,9]

Bias-enhanced nucleation and bias-enhanced growth (BEN/BEG) is the latest development in the synthesis of UNCD films. The process involves biasing the substrate with a negative voltage (~ –150 to –300 V) to attract C^+ and CH_x^+ ions from

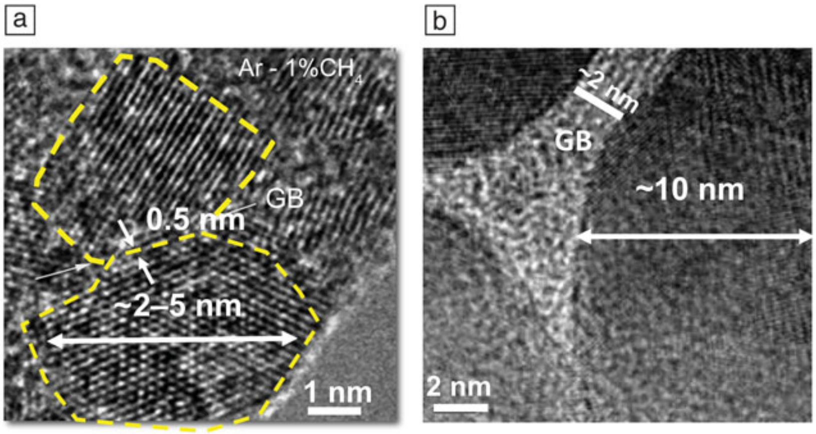

Figure 1. High-resolution transmission electron microscopy micrographs of (a) plain ultrananocrystalline diamond (UNCD) films (~2–5 nm grain size and 0.5 nm grain boundary width) and (b) N-UNCD (with nitrogen atoms inserted in grain boundaries) films (~10 nm grain size and ~2 nm grain boundary width) produced by microwave plasma-enhanced chemical vapor deposition. Reprinted with permission from Reference 43. © 2001 American Institute of Physics. Note: GB, grain boundary.

the plasma, sub-planting several Angstroms into the material (from the surface), and producing a carbide nucleation layer to grow UNCD films. BEN/BEG provides several advantages over conventional UNCD growth, namely, (1) comparable or better seeding efficiency, (2) stronger adhesion to substrates, and (3) an integrated fully dry nucleation/growth process only using plasmas. BEN/BEG processes, using H_2/CH_4 chemistry, produced NCD (30–100 nm grains) films exhibiting diamond cluster formation, relatively high surface roughness, high compressive stress, film delamination, and high non-diamond phase content.[10] UNCD films were produced using BEN with H_2/CH_4 plasma chemistry for the BEN step, but growing the UNCD films without bias, did not yield optimum nanostructure and properties.[11] More recently, a low pressure BEN/BEG process was developed using Ar/CH_4 chemistry, which yielded UNCD films with an identical nanostructure to that shown in Figure 1a: low stress (~80–100 MPa), smooth surfaces (rms ~4–6 nm), and higher growth rates (~1 μm/hr)[12] than for UNCD films grown without bias (~0.2–0.3 μm/h).[1] BEN/BEG UNCD films may be the most appropriate approach for coating of dental and other prostheses.

Properties of UNCD films

The properties of UNCD films most relevant to the development of medical implants and devices include (1) hardness (98 GPa) and Young's modulus (980 GPa)[1] close to corresponding values for single crystal diamond (100 GPa and 1200 GPa, respectively); (2) one of the lowest coefficients of friction (0.02–0.04)[1] of any coating developed today; (3) high fracture strength (~5.3 GPa);[1] (4) relatively high electrical conductivity via incorporation of N atoms in the grain boundaries (N-UNCD)[1] (Garret et al. recently demonstrated excellent performance of N-UNCD-coated metallic electrodes for neural stimulation.[13]) or B atoms substitution for C atoms in the diamond lattice (B-UNCD)[1] to provide electrons into the conduction band, yielding electrical conductivity;[14] (5) extreme resistance to chemical attack by body fluids, as demonstrated by an UNCD-coated Si microchip implanted inside rabbit eyes as the main component of an artificial retina with the aim to restore partial sight to people blinded by genetically induced degeneration of photoreceptors;[9] and (6) the use of UNCD films as scaffolds for efficient stem cell growth and differentiation for tissue engineering[15] (this characteristic may enable enhanced grafting of UNCD-coated dental and other implants via bone cell growth onto the UNCD surface of the implant).

Applications of UNCD coatings in implants and medical devices

Coatings for encapsulation of silicon-based microchips

Research has been conducted over the last two decades to develop implantable prostheses and hybrid bionic systems to restore lost human motor and sensory functions. First-generation neural prostheses are being used to restore hearing and sight via cochlear implants[16] and artificial vision devices, respectively.[17]

Human vision is produced by photons from the images penetrating the eye and exciting the retina photoreceptors. The photonic excitation is transformed into electrical pulses, which excite the bipolar cells connected to the photoreceptors. The bipolar cells amplify the electrical pulses and inject them into the ganglion cells (cells that send electrical pulses to the brain) (see Figure 3a), from where the pulses are transmitted through the axons (wire-like electrical pulse carriers connected to the ganglion cells), which bundle altogether to form the optical nerve that carries the electrical signals to the brain where the images are finally formed. Several approaches have been investigated to restore sight to people born with natural sight, who become blind by genetically induced degeneration of retina photoreceptors, which results in retinitis pigmentosa (**Figure 2**a) affecting young people (~15–30 years old), and macular degeneration (Figure 2b) affecting older people (≥50 years old).

Vision restoration technologies

Vision restoration technologies being explored include (1) a flexible digital viewing device, including tools to manipulate information from images and to provide the means for the patient to navigate (move) following visual input;[18] (2) microsystem-based visual prosthesis, involving a spiral electrode around the optic nerve, connected to an implanted stimulator, which receives images from an external camera and translates them into electrical signals that stimulate the optic nerve;[18] (3) a miniature telescope implanted in the eye's posterior chamber, which works by increasing (~3 times) the size of the image projected onto the retina to overcome a central blind spot;[19] (4) a microchip located behind the retina connected to the MPDA (the Tübingen micro-photodiode array [MPDA] project), collecting incident light and transforming it into electrical current stimulating the retina ganglion cells;[20]

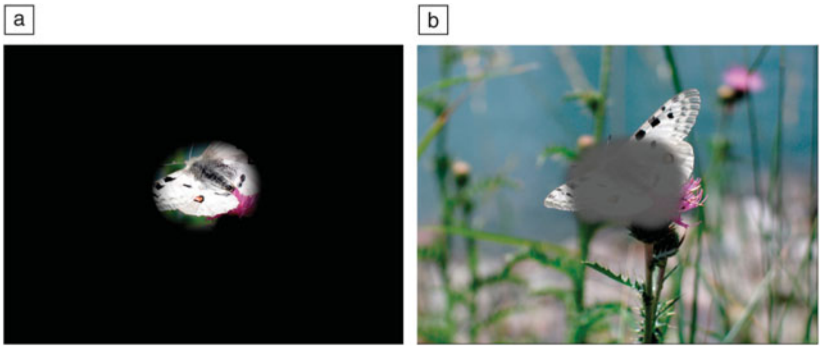

Figure 2. (a) Tubular vision, characteristic of people with retinitis pigmentosa, until they become totally blind, upon losing the last photoreceptors. (b) Peripheral vision characteristic of people with macular degeneration. Reprinted with permission from Reference 33. © 2013 Woodhead Publishing Limited.

(5) an artificial silicon retina, involving a microchip containing photodiodes that detect light and convert it into electrical pulses stimulating ganglion cells (project was discontinued); (6) a photovoltaic retinal prosthesis, with a subretinal photodiode array and an infrared image projection system mounted on video goggles that transmits information from a video camera, processes it in a mobile computer, and displays it on pulsed near-infrared (850–915 nm) video goggles, thus projecting images onto the retina via eye optics to activate photodiodes in the subretinal implant to convert light into pulsed bi-phasic electric current in each pixel;[21] (7) the Dobelle eye, involving a camera mounted on glasses that transmits images to a stimulator chip implanted in the brain's primary visual cortex and injects electrical pulses directly to the brain cells;[22] (8) an intracortical visual prosthesis with intra-cortical electrode arrays, similar to the Dobelle system, but with increased spatial resolution based on more electrodes per unit area;[23] (9) a microchip with 98 stimulating electrodes projected for implantation in the supra-choroidal space (a device with 1024 electrodes is under development), being developed by Bionic Vision Australia (national consortium of researchers from the Bionics Institute, the Centre for Eye Research Australia, and several universities);[24] (10) the Harvard/MIT retinal implant, involving a subretinal stimulator chip with an electrode array beneath the retina that receives images beamed from a camera mounted on glasses, decodes them, and stimulates ganglion cells with electrical pulses;[25] and (11) the Argus II retinal prosthesis, involving a chip that in the final rendition would be implanted inside the eye on the ganglion cell layer, located in the retina (**Figure 3**a), receive an image from a charge-coupled device camera on a pair of glasses, and inject processed electrical pulses, with image inscription, to the ganglion cells through a large electrode array, such that pulses are finally transmitted to the brain, via the ganglion cell axon bundle (optical nerve), for image formation on the brain cortical region.[26]

The Argus II device was developed by a team of researchers from universities, national laboratories, and Second Sight (a company currently commercializing the device) during a 10-year US Department of Energy-funded project. The Argus II device (named one of the top 25 inventions for 2013 by *TIME* magazine) is currently among the most advanced artificial retina devices[26] and is the only one currently available commercially in the United States and Europe to restore partial sight to people blind by retinitis pigmentosa.

Coatings technologies for encapsulation of implantable microchips

Artificial vision prostheses involving silicon (Si)-based microchips, in the ultimate rendition, implanted inside the eye, should be encapsulated with a hermetic/biocompatible coating to inhibit a chemical destructive attack of Si by the eye's saline humour (fluid). Hermetic coatings for encapsulation of medical implants should have a double functionality of protecting the implantable device as well as the surrounding tissues to enable long service times free of electronic failure. Two types of packaging technologies are being developed: (1) hard shell (used in the current commercial Argus II device), and (2) encapsulating coatings. For implantable microchips, encapsulating coatings provide a better platform for miniaturization to enable implantation inside the eye, since the hard shell is too big for insertion into the eye. The coatings should be hermetic and biocompatible, because the Si CMOS device performance can be affected by the eye's saline solution, resulting in the microchip destruction.[27]

Coating materials currently being evaluated for encapsulating implantable Si microchips include SiO_2,[28] SiC,[29] polytetrafluoroethylene and polyimide,[30] and parylene.[30] SiO_2 coatings exhibited dissolution and decay when implanted in animals up to six months.[27] Polyimide and other polymers are inexpensive and flexible, but absorb significant quantities of water, resulting in electrical leakage, and are not hermetic, enabling chemical attack and eventual destruction of the encapsulated chip.

In contrast, UNCD coatings exhibit a unique combination of properties previously described; and for the encapsulation of an artificial retina Si microchip, UNCD coatings are the only

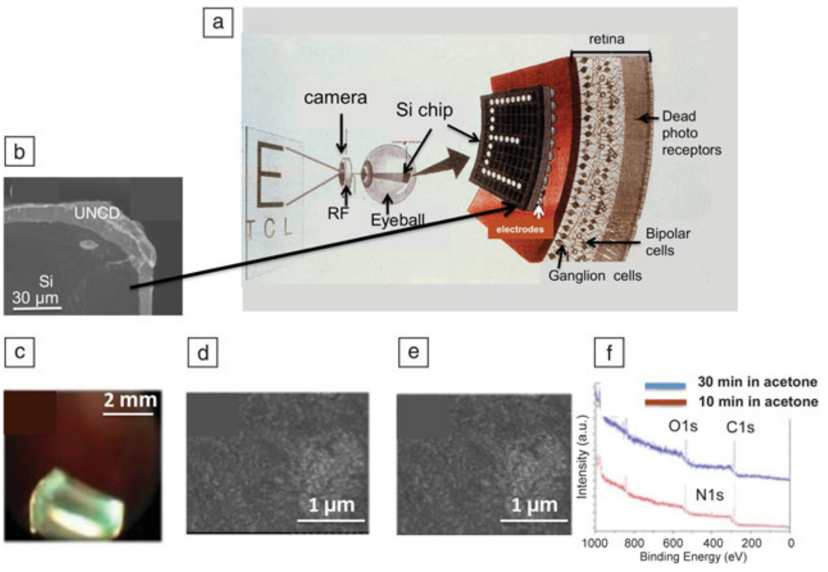

Figure 3. (a) Schematic of artificial retina concept (Argus II device in its final future rendition); (b) cross-sectional scanning electron microscopy (SEM) micrograph of an ultrananocrystalline diamond (UNCD)-coated Si chip showing the UNCD dense hermetic characteristic; (c) picture of UNCD-coated Si chip implanted in a rabbit eye for about one year; SEM micrograph of UNCD coating (d) before implantation and (e) after implantation, showing no degradation; and (f) x-ray photoelectron spectroscopy analysis of UNCD coating after implantation, showing no surface chemical modification after being exposed to the eye's saline humour (O1s, N1s, and C1s correspond to the atomic levels of the elements with electron occupancy). Reprinted with permission from Reference 33. © 2013 Woodhead Publishing Limited. Note: RF, radio frequency.

diamond-based coatings that can be grown at ~400°C (maximum sustainable temperature) on CMOS devices without destruction[1] and with excellent performance when implanted in animals' eyes for long periods of time.[9] Extensive *in vivo* animal studies involving implantation of UNCD-coated Si chips in rabbit eyes (Figure 3b–c), followed by scanning electron microscopy studies (Figure d–e) and x-ray photoelectron spectroscopy (Figure 3f) measurements for surface chemical analysis, showed that the UNCD coating provides encapsulation that may enable long-term (measured in years) implantation of a Si chip inside the eye without any degradation.[9]

Details of the development of UNCD films as biocompatible coatings for encapsulation of the artificial retina microchip can be found in Reference 9, while details on the Argus II device development are found in References 26 and 31.

UNCD coatings for treatment of glaucoma

Glaucoma is a medical condition characterized by increased intraocular pressure (IOP) either through increased production or decreased outflow of the eye's saline humour in the eye's anterior chamber (**Figure 4**a). Normally, the aqueous humour flows out of the eye through a mesh-like channel called the trabecular mesh. If the channels become blocked, fluid builds up in the inner part of the eye, resulting in glaucoma.

Less common causes of glaucoma include a blunt or chemical injury to the eye, severe eye infection, blockage of blood vessels or eye inflammation, and eye surgery to correct another condition. Glaucoma usually occurs in both eyes, although each eye is differently affected. The increased IOP may result in optic nerve damage (Figure 4b), thus causing damaged vision or blindness.

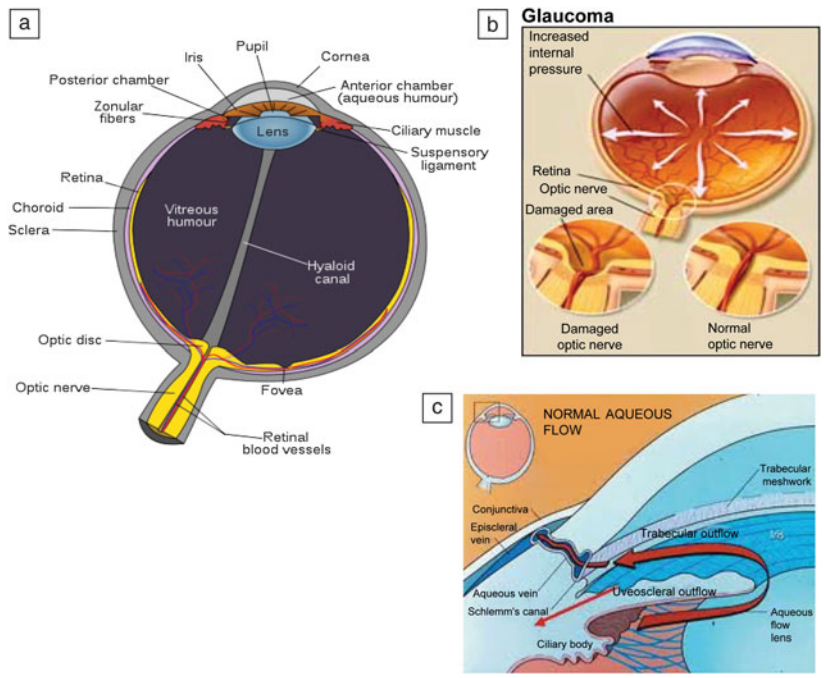

Figure 4. (a) Schematic of a human eye showing key components; (b) schematic of a glaucoma condition showing optic nerve damage; and (c) schematic showing humour eye drainage flow. Reprinted with permission from Reference 33. © 2013 Woodhead Publishing Limited.

There may be open- or closed-angle glaucoma. Closed-angle glaucoma can appear suddenly and painfully, with rapid visual loss. Open-angle, chronic glaucoma progression is slower, and lost vision is not noticed until the disease has progressed significantly. Once lost, the damaged visual field cannot be recovered. Glaucoma is the second leading cause of blindness after cataracts. Glaucoma affects one in 40 adults over 40 years of age. It is estimated that by 2020, 80 million people worldwide will suffer from glaucoma.[32] Early detection of glaucoma served to arrest or slow the progression via pharmacological, surgical means, or, as a last resort, glaucoma drainage devices. Further details about glaucoma can be found in Reference 32.

UNCD coatings for long-life glaucoma drainage devices

When pharmacotherapies and surgery have failed, glaucoma drainage devices represent an option (**Figure 5**a). An important unsolved problem with current glaucoma drainage devices is the host reaction against the polymer surface of the implant, occurring immediately after implantation (seconds to minutes and extending for several hours after implantation[34]). This occurs via protein layer adhesion to the hydrophilic (water absorbent) polymer-based surface of the device, resulting in an inflammatory response developing within the first eight hours. Macrophages are recruited, by chemical signals, to the implant site where they secrete growth factors that stimulate fibroblast cells responsible for collagen production, producing a fibrous capsule around the implant. After a few weeks, a complete fibrotic reaction occurs, isolating the implant from the rest of the body. This fibrous capsule produces deleterious effects on glaucoma drainage devices, leading to filtration failure.[35]

The rest of this subsection focuses on describing the work done in joint collaboration between researchers at The University of Texas-Dallas, the University of Buenos Aires, and the Hospital Austral in Buenos Aires, Argentina, aimed to demonstrate the effectiveness of a UNCD coating in avoiding fibrotic capsule development around a glaucoma silicone-based drainage device that impairs the drainage of the eye's saline humour. All experiments were conducted following the US National Institutes of Health (NIH) and the Administración Nacional de Medicamentos, Alimentos y Tecnología Médica (ANMAT) guidelines (Argentina's FDA equivalent) for animal care. The experiments involved two rabbits, each receiving one uncoated drainage device (Figure 5b) in one eye, and one coated

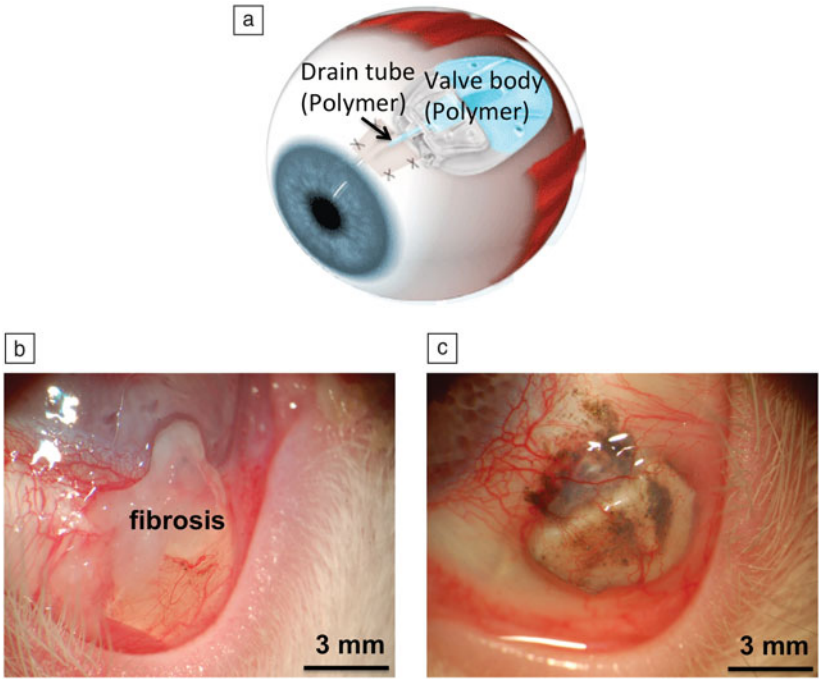

Figure 5. (a) Schematic of a human eye showing implantation of a glaucoma drainage device. Note the need for two incisions: one for inserting the large (~17 × 12 mm) body of the valve, and one for insertion of the drain tube; (b) optical image of an uncoated glaucoma valve 24 hours after implantation into a rabbit's eye, showing fibrosis over the implant surface; (c) ultrananocrystalline diamond-coated glaucoma valve about four months after implantation in the second eye of the same rabbit for which the uncoated valve was implanted (showing no fibrosis).[33]

with a low temperature (~400°C) UNCD film (Figure 5c) in the other eye. The experimental approach was conducted in order to reduce the number of animals involved and avoid inter-individual variability from using different animals in one experiment. In the 24 hours after implantation, the uncoated device was covered with fibrosis due to protein adhesion in the eye, while the UNCD-coated device remained clear even after several months of implantation.[33] This was a demonstration of the effectiveness of UNCD films as bio-inert/biocompatible encapsulating coatings to improve, by orders of magnitude, the lifetime of the implanted devices.

The lack of protein adhesion on the surface of the UNCD-coated drainage device is attributed to the fact that the surface of UNCD films is extremely hydrophobic due to the hydrogen termination of the surface of the as-deposited UNCD films.[1]

UNCD-coated grid as new glaucoma treatment implant

As mentioned earlier, current glaucoma drainage devices are relatively large and require two surgical incisions, as indicated in Figure 5a. The USA-Argentina collaboration group is developing an alternative approach, involving implanting a small grid (~3 mm in diameter), featuring hundreds to thousands of small holes formed by the boundaries of a grid of thin wires in the clogged trabecular meshwork region (**Figure 6**a).[33]

Preclinical trials were conducted in an animal facility at the University of Buenos Aires, Argentina, following protocols approved by NIH and ANMAT for animal care. It was expected that the large number of holes in the grid would provide very efficient drainage of the eye's humour. The grid was coated with a UNCD film. Initial experiments were performed using copper (Cu) grids to demonstrate the power of the UNCD film as a bioinert/biocompatible coating. It is well known that Cu elicits unacceptable toxicity in the eye, and if the UNCD coating were not hermetic, the eye humour would permeate though it, and the eye would recognize the presence of Cu underneath the UNCD film and eject the grid. Figure 6b shows a Cu grid, implanted in the trabecular region of one rabbit eye, being biologically rejected and expulsed outside the eye in about 24 hours after implantation.[33] In contrast, a UNCD-coated grid implanted in the other eye (Figure 6c), remained totally inert inside the eye for several months.[33]

This initial work shows a promising drainage device technology and much less invasive surgical procedure for treating glaucoma, due both to the much smaller device and simpler surgical procedure. Titanium (Ti) will be used as a grid material in future work, since UNCD films grow very well on Ti[1] and will protect Ti from chemical attack by the eye's saline humour.

UNCD coatings for new dental implants

Pure Ti and Ti alloys are widely used in dental and orthopedic implants. The use of Ti-based prostheses was motivated by past work showing that Ti-based implants exhibit appropriate mechanical properties and biocompatibility.[36] However, recent literature on the performance of Ti implants in patients indicates that they exhibit failures, specifically due to loss of osseointegration (a direct structural and functional connection between ordered living bone and the surface of a load-carrying implant) and corrosion.[37]

Current Ti-based dental implants, used to replace missing teeth, fail due to body fluids-induced Ti corrosion,[38] which releases metallic particles from the Ti surface into local tissue from where it could reach the systemic circulation,[39] with a potential increase in metal levels in the plasma. These elevated levels could result in systemic toxicity, as observed for other metallic implants.[40] On exposure to air or liquid, titanium develops a passivating titanium dioxide (TiO_2) layer that makes it nonreactive. It is well known that the TiO_2 layer prevents corrosion. However, when it is in contact with body tissue and fluids, electrochemical processes take place, rendering it prone to breakage, which releases ions/particles into

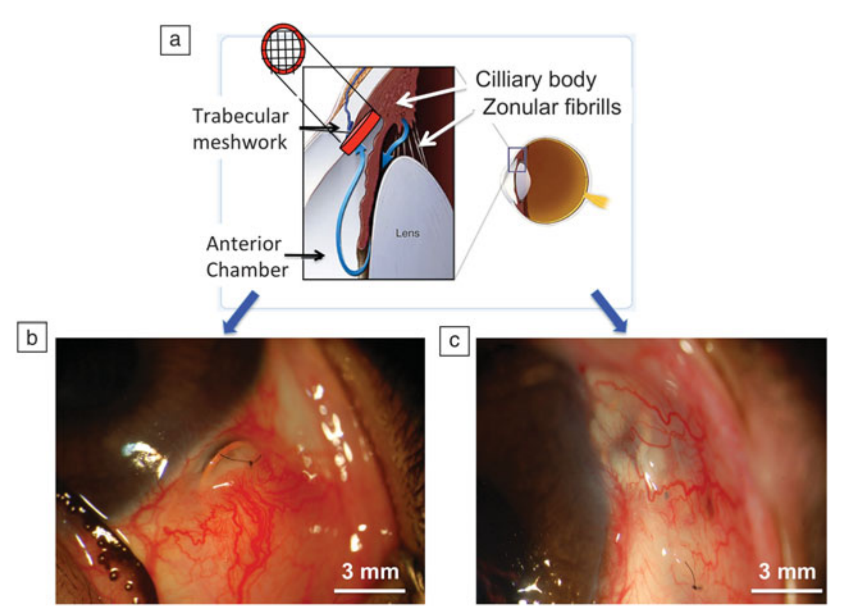

Figure 6. (a) Schematic of a new smaller glaucoma drain device based on an ultrananocrystalline diamond (UNCD)-coated grid with hundreds to thousands of holes, implanted in the trabecular meshwork. Optical pictures of grids implanted in the trabecular meshwork region of separate rabbit's eyes in the same animal: (b) Uncoated Cu grid showing rejection in about 24 hours, and (c) UNCD-coated Cu grid after several months implantation, showing no rejection. Reprinted with permission from Reference 33. © 2013 Woodhead Publishing Limited.

the milieu. Once the passivating oxide layer is eliminated, the Ti implant acts as an *in vivo* electrode that produces electrochemical reactions in the tissue.

UNCD-coated metallic implants exhibit extreme resistance to chemical attack by body fluids.[1,9] In addition, roughening of the Ti implant surface by micromachining followed by coating with UNCD films produces a chemically resistant micro-roughened surface that can enhance osseointegration, as demonstrated previously for roughened Ti implant surfaces.[41] In addition, recent work demonstrated that NCD coatings exhibit increased resistance to bacterial adhesion as compared to stainless steel and Ti.[42]

In one study, Ti laminar implants were used as samples for *in vivo* tests. The samples used were (1) uncoated Ti, (2) UNCD-coated Ti (**Figure** 7a), and (3) UNCD/W-coated Ti, wherein a W layer was grown on the surface of the Ti implant using magnetron sputter-deposition to enhance the density of UNCD coatings, which was demonstrated by the formation of a dense tungsten carbide (WC) template interface on the surface of the W layer.[1] The UNCD coatings were grown on all samples using the MPCVD method.[1] Male Wistar rats were used to study the interaction of uncoated Ti and UNCD-coated Ti implants with bone. NIH guidelines as well as the Ethics Principles of the Faculty of Dentistry, University of Buenos Aires, for surgical procedures and care of laboratory animals, were followed.

The histological analysis of the samples from the control and experimental groups revealed areas of lamellar bone in close contact with the surface (osseointegration) (Figure 7b) and areas of bone marrow in contact with the implant surface (myelointegration). These studies showed that UNCD has good biocompatibility as a coating material for dental implants. Among other factors, the clinical success of implants depends on osseointegration of the implant and, if coated, on the coating/substrate reliability. Histological studies indicated that the UNCD-coated Ti implants in this study achieved excellent osseointegration, without exhibiting any inflammatory reactions (Figure 7b).

The unique mechanical, tribological, chemical, and biological properties of UNCD films demonstrated in the work reviewed in this article indicate that UNCD coatings may enable the manufacturing of a new generation of dental implants with anticorrosion properties, which can provide more superior performance than current uncoated metal-based implants.

Summary

The discussion of the fundamental and applied materials science as well as implant and device development and testing for representative key medical implants and devices based on UNCD coatings shows that this material provides a unique combination of mechanical, tribological, chemical, and biological properties,

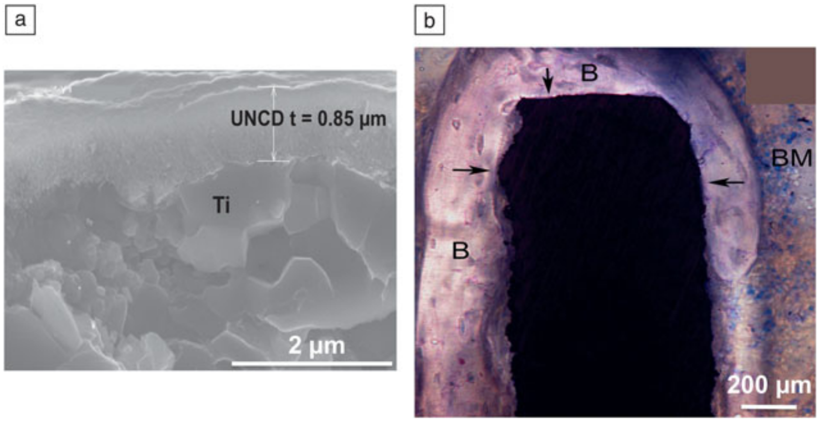

Figure 7. (a) Cross-sectional scanning electron microscopy micrograph of an ultrananocrystalline diamond (UNCD) film grown on a Ti implant, showing high density and smoothness of the UNCD film surface. (b) Micrograph of the implant-tissue interface (UNCD-coated Ti). Lamellar bone tissue (B) in close contact with the surface of the implant (in black), showing good osseointegration. BM (bone marrow), Mag. x400. Note: *t*, thickness.[33]

which will help develop new medical implants and devices with superior performance compared to those currently based on other materials. In this respect, UNCD coatings will enable a new generation of chemically robust (resistant to chemical attack by body fluids) UNCD-coated prostheses (e.g., artificial hips knees, elbows, dental implants), UNCD-coated catheters, and electrically conductive N-UNCD-coated electrodes for neural stimulation. In addition, it has been demonstrated that UNCD surfaces can provide new scaffolds for stem cell growth[15] and differentiation, opening new opportunities in the field of tissue engineering.

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Natalia Tapia, Chapter President
Centro de Investigación y de Estudios Avanzados
del Instituto Politécnico Nacional (Cinvestav-IPN)
Mexico City, MEXICO

Interdisciplinary Collaboration

The MRS Student Chapter at WSU was organized by students who recognized the need to bring together a diverse group of students who were working in materials science. The campus is spread out geographically and students pursuing PhD degrees in MSE can be advised by chemistry or physics professors who are located far from the MSE department located in the engineering buildings. There is no distinction made between students whose advisors are in different departments or colleges, and the MRS Student Chapter has been a great vehicle to promote unity within the disciplines here.

David Field, Chapter Faculty Advisor
Washington State University
Pullman, Washington, USA

The MRS University Chapter Experience

The MRS University Chapter Program provides invaluable experiences and benefits for student members, but don't take our word for it. **Our Chapter Members Say It Best!**

Leadership Development

The Materials Research Society, along with our local Binghamton University Chapter, has positively influenced my commitment to materials science and technology. We were inspired by our advisor, Professor M. Stanley Whittingham, to start this Chapter … and motivated by his enthusiasm and our faith to bring science to the general public, we continue to hold numerous events taken from MRS, i.e. MAKING STUFF and NanoDays. As our organization grows, we keep growing our events, and have found a solid and welcoming place in our community. Apart from the target audience, our events also benefit the volunteers, who gained valuable experience both from preparation, interaction, and activities. We feel proud and grateful to be part of an MRS University Chapter.

Tianchan Jiang, Chapter President
Binghamton University
Binghamton, New York, USA

Education Outreach

Our Chapter has enabled us to establish collaborations among the scientists on campus through informal social events, in addition to providing opportunities to participate in outreach. Integrating the science outreach efforts of Vanderbilt's community into our local community is one of our primary goals. As a University Chapter, we received a grant through the Materials Research Society Foundation to bring emerging materials science and hands-on activities to disadvantaged students and teachers in rural Tennessee. Without these seed funds, our Vanderbilt program, Materials Outreach for Rural Education (MORE), would not have been possible.

Amy Ng, Chapter President
Vanderbilt/Fisk Universities
Nashville, Tennessee, USA

Professional Growth

Starting and advising an MRS University Chapter is truly a rewarding experience. One can see professional growth of students, who start feeling like members of the worldwide materials research community. I come to MRS meetings with a "team," not just a couple of my students. Exciting initiatives and project ideas generated by students are amazing. Not surprisingly, some of the most prominent materials scientists, such as Millie Dresselhaus (MIT) or Stan Whittingham (SUNY Binghamton), have been acting as Faculty Advisors for many years.

Yury Gogotsi, Chapter Faculty Advisor
Drexel University
Philadelphia, Pennsylvania, USA

Building Chapters of the Future

I had the chance to present at the 2012 MRS Fall Meeting's Sustainability Forum, while being over 9000 km away from the meeting venue. I felt as if I was actually in Boston, being able to take questions, address them and getting into discussions with the committee. Thanks to the Materials Research Society and our local MRS-KAUST University Chapter for making this possible.

Ahmed E. Mansour, Chapter Vice President
King Abdullah University of Science and Technology (KAUST)
Thuwal, SAUDI ARABIA

Chapter Support

As a graduate student, it is key to broaden your spectrum of what is taking place in the research world in real time. MRS opens up many avenues, especially when working from a University Chapter. Direct contact with MRS associates helps keep everyone abreast of conferences, Chapter opportunities and activities that otherwise may not have been as easily accessible. MRS also rewards student memberships with rebates and travel expenditures, helping promote student involvement as well as Chapter building. We were able to host a multitude of meetings and seminars as well as send students to attend MRS conferences to promote their research.

Chinedu Okoro, Chapter President
Tuskegee University
Tuskegee, Alabama, USA

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