A U.S. Department of Energy laboratory managed by The University of Chicago

SCIENCE AND TECHNOLOGY OF MULTIFUNCTIONAL OXIDE AND ULTRANANOCRYSTALLINE DIAMOND (UNCD™) THIN FILMS AND APPLICATIONS TO A NEW GENERATION OF MULTIFUNCTIONAL DEVICES/SYSTEMS

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Office of Science-Basic Energy Science-Materials Science
Biomedical Engineering Research
DARPA-MTO-DSO
Industry

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Industrial Funding (2003)
INTEL (memories)

Industrial Funding (2004)
Delphi (R&D Fuel Cell)
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Funding: DOE (BES, BER, OIT, CESP) DARPA

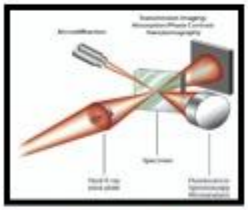
Outline

- Science and Technology of Multifunctional Oxide Thin Films and Applications:
  - Ferroelectric & Multiferroic Films, Integration and Fabrication of Nanostructures for High-Density FeRAMS and Ferroic Devices, and for Novel High Efficiency Photovoltaic Devices
  - Doped NiO Films for Novel Correlated Electron Resistive-Change Random Access Memories (CeRAMs) Based on Resistive-Conductive Mott Transition
  - Novel High-K Dielectric Super-lattice Oxide Films for Next Generation Nanoscale CMOS devices, Microchip Embedded Capacitors for implantable Biomedical Devices, and Supercapacitors for Energy Storage
  - Piezoelectric films for MEMS/NEMS Devices
- Science and Technology of a Novel Multifunctional Ultrananocrystalline Diamond (UNCD) Film and Application to a New Generation of Multifunctional Devices and Systems:
  - New Generation of Industrial Macro to Nano-Components and Devices
    - Macro Scale (UNCD coated Mechanical Pump Seals)
    - Monolithically Integrated CMOS Driver/RF MEMS Switches with UNCD Fast Charging/ Discharging Dielectric Enabling Reliable Switches for Radar an Mobile Communication Devices
    - Piezoelectrically actuated UNCD MEMS/NEMS structures for Resonators, Sensors, and Nanoswitches for new NEMS Logic System
  - Science and Technology for a New Generation of Implantable Biomedical Devices and Platform for Developmental Biology Based on UNCD
    - UNCD-Coated Microchip as Key Component of an Artificial Retina to Restore Sight to Blind People
    - UNCD-Coated Glaucoma Valve and Flexible Magnets to Treat Eye Pathologies
    - UNCD-Coated Artificial Joints, Heart Valves and Stents
    - UNCD surface as a platform for growth and Differentiation of Embryonic Stem Cells
- Start-ups as a Pathway to Commercialization
  - Advanced Diamond Technologies (ADT), Inc (2003-present)
  - Original Biomedical Implants (OBI), Inc. (2011- future)
- Vision to the Future

ANL Center for Nanoscale Materials (CNM)! …

- **Create and study novel multifunctional nanoscale materials and structures**
- **Access APS & Electron Microscopy Center**

APS



Unique 30 nm diameter synchrotron X-ray beam

CNM Scientific Themes

- **BioNanointerfaces**
- **Electronic and Magnetic Materials & Devices**
- **Nanophotonics**
- **Theory and Simulation**
- **Nanofabrication**
- **X-Ray Imaging/Nanoprobe**

Open for users from National Labs Universities and Industry from USA and International

www.nano.anl.gov

Only MPCVD for UNCD and other carbon films synthesis in a clean room

E-beam Lithography

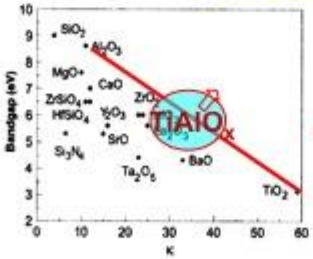
FIB/SEM

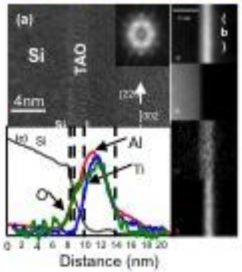
Science and Technology of Ferroelectric films for FeRAMs and Piezoelectric MEMS
and
High - K Dielectric Oxide Films for Next Generation Nanoscale CMOS Devices, Microchip Embedded Capacitors for Implantable Biomedical Devices, and Super-capacitors for Energy Storage

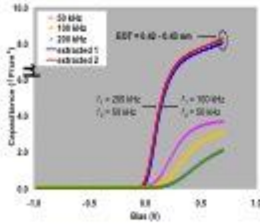
ATOMIC LAYER DEPOSITION (ALD) of $Ti_XAl_{1-X}O_Y$ For Nanoscale CMOS and High-Capacitance Capacitors for Implantable Microchips for Biomedical Devices

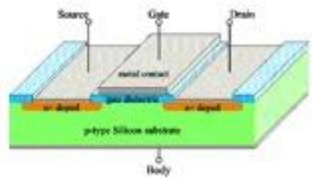
ALD System with 8" Wafer Capability

Demonstrated High Capacitance with Planar Capacitors Integrated on Si Wafer

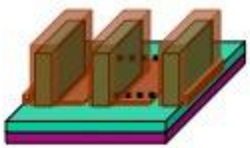








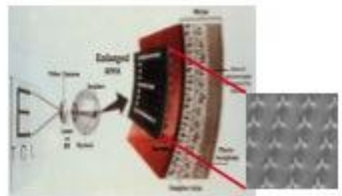
High capacitance density: (~8 μF/cm²) achieved via suppression of SiO_2 interfacial layer formation



Biocompatible TAO high- K dielectric layer enables coupling capacitor for artificial retina microchip

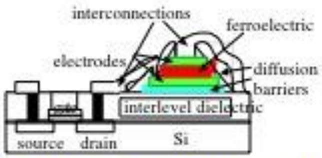
O. Auciello et al. APL 86 (2005)

O. Auciello
US patent #7,714,405, May 2010



Xiao/Auciello et al. J. Biomaterials (2006)

Ferroelectric Oxide Thin Films for Low Energy FeRAMs



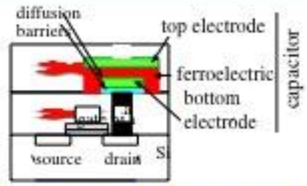
Low-density FeRAM architecture In smart cards in the market

FeRAM Smart Cards

Auciello/Scott/Ramesh (Physics Today 1998) ~ 1000 citations (2011)

Symetrix/Panasonic SBT FeRAMs

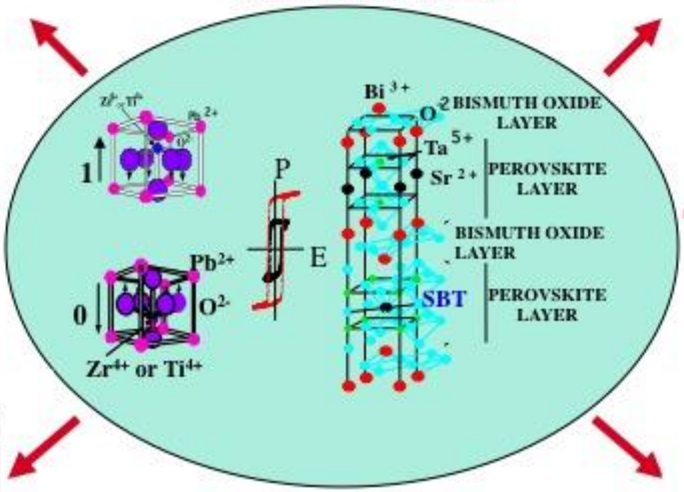
TI, Toshiba-PZT FeRAMs



High- density FeRAM architecture for Gb to Tb memories

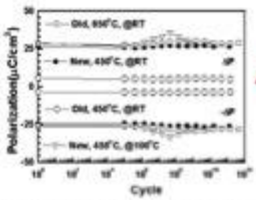
$Pb(Zr_xTi_{1-x})O_3$

Polarization fatigue, imprint, retention is controlled in PZT-based FE capacitors by using oxide electrodes



$Sr(Bi_2Ta_2)O_9$

Polarization fatigue, imprint, retention is controlled in SBT-based FE capacitors even with Pt electrodes



Polarization fatigue, imprint, retention controlled via control of oxygen vacancies at PZT/electrode interface

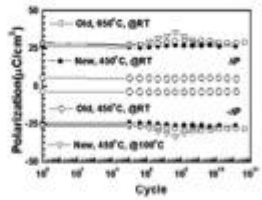


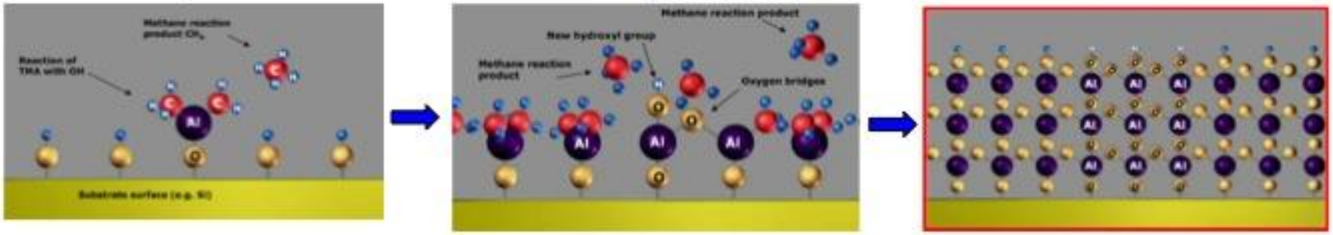
Fig.4 Liu et al

Atomic Layer Deposition (ALD)

Advance technology for thin film growth with super uniformity and atomic scale controlled thickness (conformal growth)

Self-limiting gas phase reaction

TMA pulse | **H_2O pulse** | **Al_2O_3 thin film**



Source for Al_2O_3:
H_2O and $Al(CH_3)_3$ (TMA)
1 Å/cycle @ 300 ˚C

Source for TiO_2:
H_2O and $TiCl_4$
0.3 A/cycle @ 300 ˚C

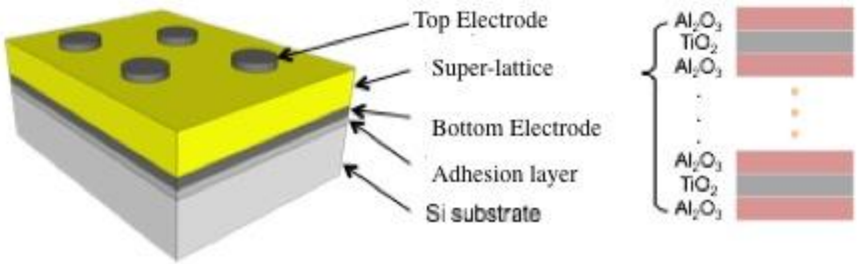
ANL-ALD Systems from Sundew Technologies provide fastest film growth due to Patented superfast valves

ALD System in ANL-MSD
200 mm wafer capability

ALD System in ANL-CNM Clean Room
200 mm wafer capability
(UPR System at CNM)
(through Katiya r /Auciello collaboration)

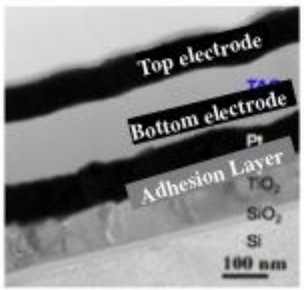
TiO_x/Al_2O_3 Superlattice Nanostructure

O. Auciello et al.
Patent Pending, 2012

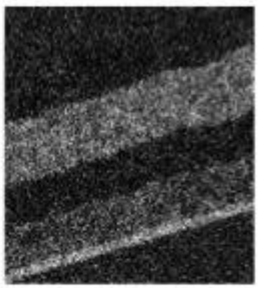


MIM capacitor

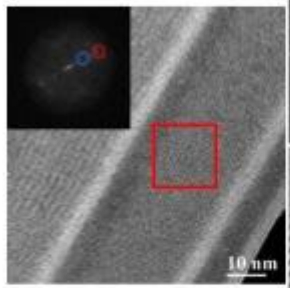
TEM

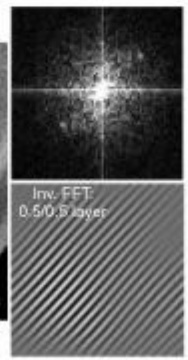


Oxygen mapping

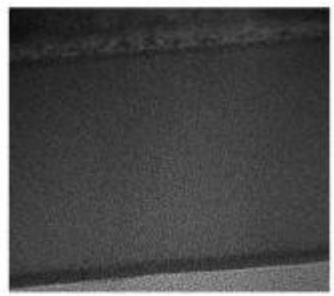


HR TEM





C.D. Phatak, J. Hiller, D. Miller

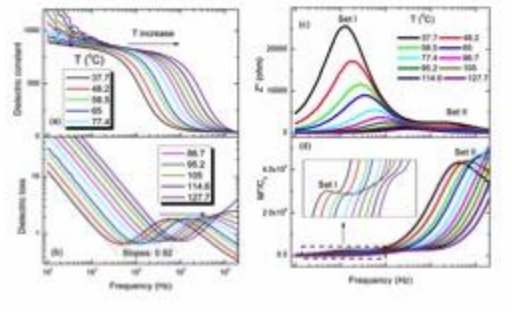


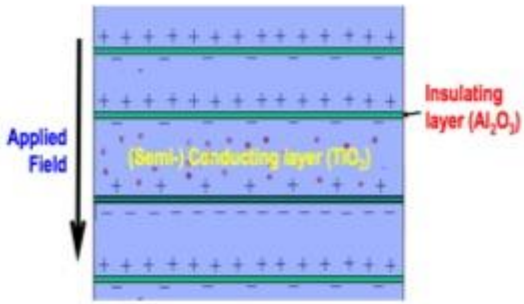
N. Zaluzec, J. Hiller, D. Miller

Maxwell-Wagner (MW) effect

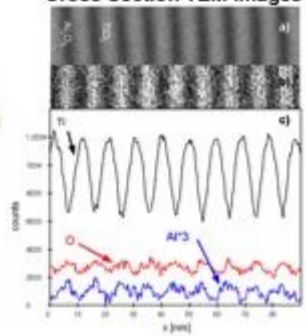
* MW effect: Charge carriers accumulation at heterogeneous semiconductor/insulator interfaces.
  Capacitance is proportional to (# of carriers) × (# of interfaces)

* Dielectric constant (k): TAO (150nm) = ~ 1000, Al_2O_3 bulk = 9 (insulating), TiO_2 bulk = 40 ~ 100 (semi-conducting)



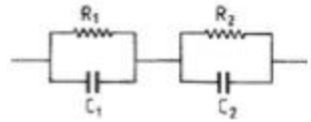


Cross Section TEM Images



EELS Analysis of Al_2O_3 / TiO_2 Nanolaminates

A typical Debye-type relaxation (dipole re-orientation): However, there are no dipoles in Al_2O_3/TiO_2 nanolaminates.



MW relaxation: When current passes through the multilayer structures, charged carriers (mainly Oxygen vacancies) can accumulate at the interface and cause the Maxwell-Wagner relaxation, also called Interfacial relaxation.

$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \frac{1}{i\omega C_0 Z^*} = \varepsilon'_\infty + \frac{\varepsilon'_s - \varepsilon'_\infty}{1 + i\omega\tau} - i\frac{\sigma'}{\omega}$$

$$f = f_0 \exp(-\frac{U}{k_B T})$$

Activation energy from Arrhenius plot:
~0.4 eV, oxygen vacancy

$$\varepsilon'_\infty = \frac{1}{C_0}\frac{1}{\frac{1}{C_1} + \frac{1}{C_2}}, \quad \varepsilon'_s = \frac{R_1^2 C_1 + R_2^2 C_2}{C_0 (R_1 + R_2)^2}, \quad \sigma' = \frac{1}{C_0 (R_1 + R_2)}, \quad and \quad \tau = \frac{R_1 R_2 (C_1 + C_2)}{(R_1 + R_2)}$$

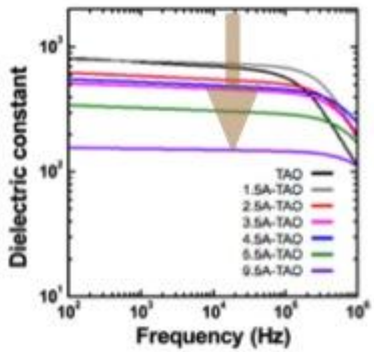
Minimize Leakage Approach (Patent Pending)

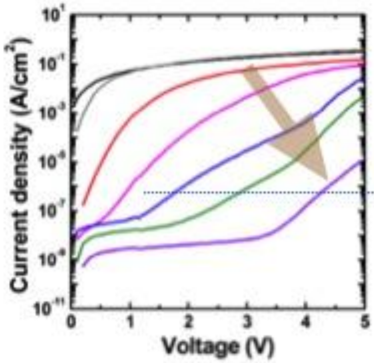
Approaches

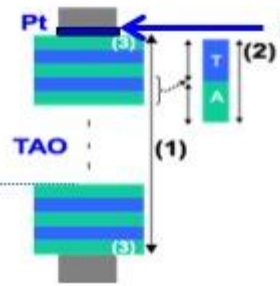
(1) Increase k and resistance

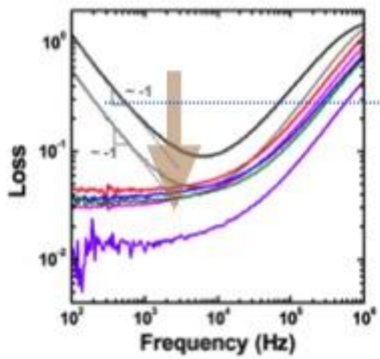
(2) Oxygen vacancy control

(3) Stop leakage path with oxide interface layer









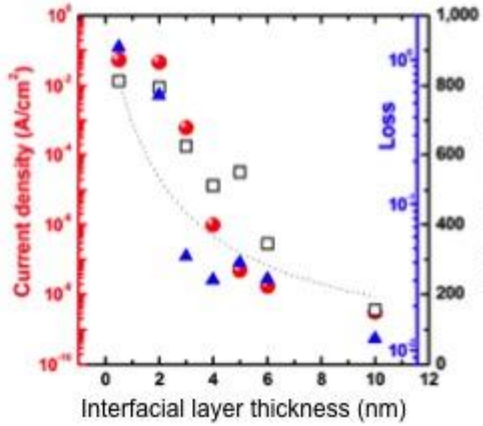
Stop Leakage Approach

k (dielectric constant) ↘

D (loss) ↘↘↘

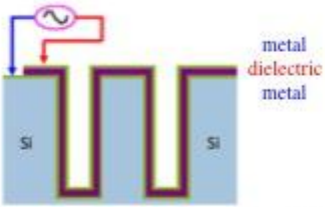
J (leakage current density) ↘↘↘

Y.Q. Wu et. al, Appl. Phys. Lett. 90, 072105 (2007)



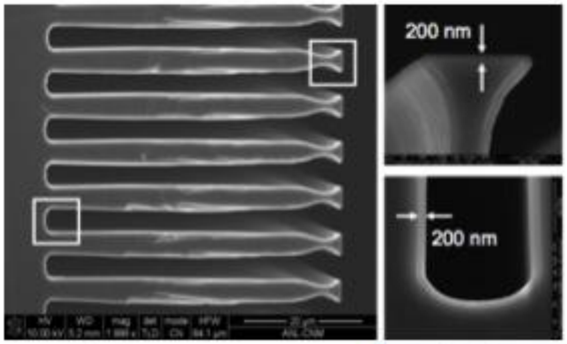
TAO Applications to High Capacitance Capacitors and Next Generation Nanoscale CMOS Devices

3-D High capacitance capacitor



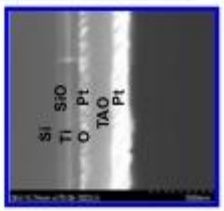
$$C = \frac{\kappa \varepsilon_0 A}{t}$$

Capacitance increase by area and k



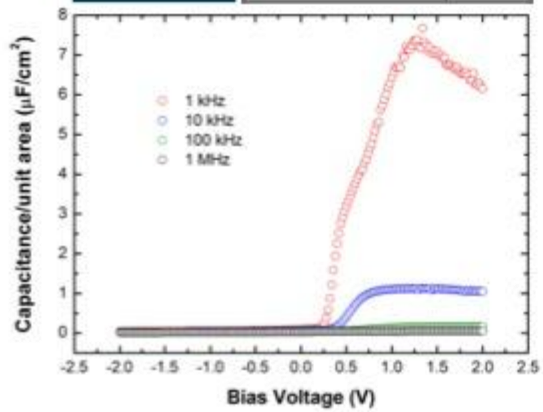
- Al_2O_3 / TiO_2 grown by ALD
- Film shows conformal growth along with the morphology of 3D structure

- 8 $\mu F/cm^2$ @ Si array trench



High-k gate oxide

TAO thickness (nm)	
Capacitance ($\mu F/cm^2$) @ 1 kHz and 2 V	~ 10
k	210
EOT (nm)	0.56

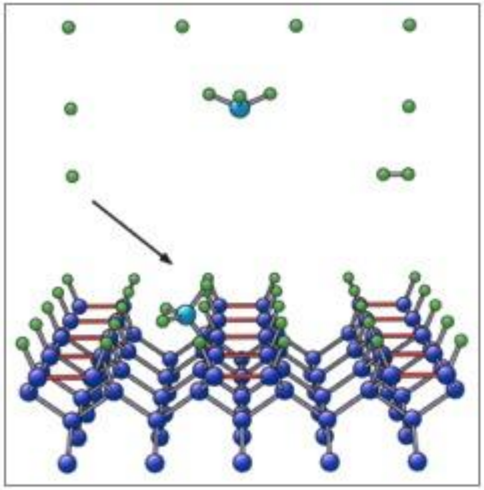


UNIQUE MULTIFUNCTIONAL ULTRANANOCRYSTALLINE DIAMOND (UNCD) FILM TECHNOLOGY

Fundamentals of UNCD Films

CH_4/H_2 Chemistry for MCD Growth

1960's to present: Unsuccessful for Large Scale Commercialization

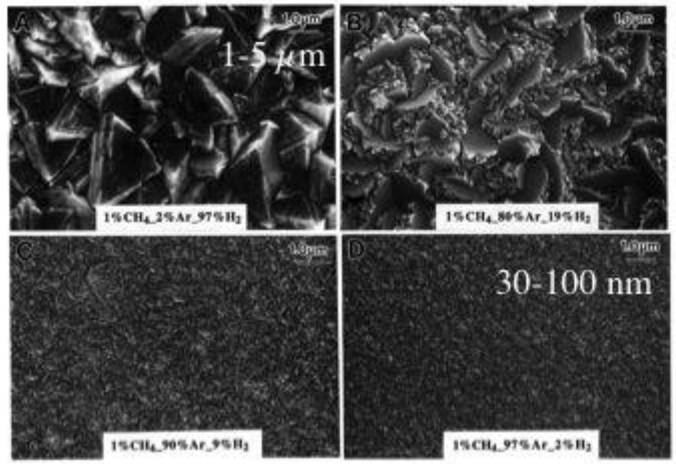


Growth Conditions
*** 1% CH_4, 99% H_2 @ 100 Torr**
*** 600-800 °C substrate temperature**

H abstraction from Diamond surface to insert methyl group results in high activation energy:

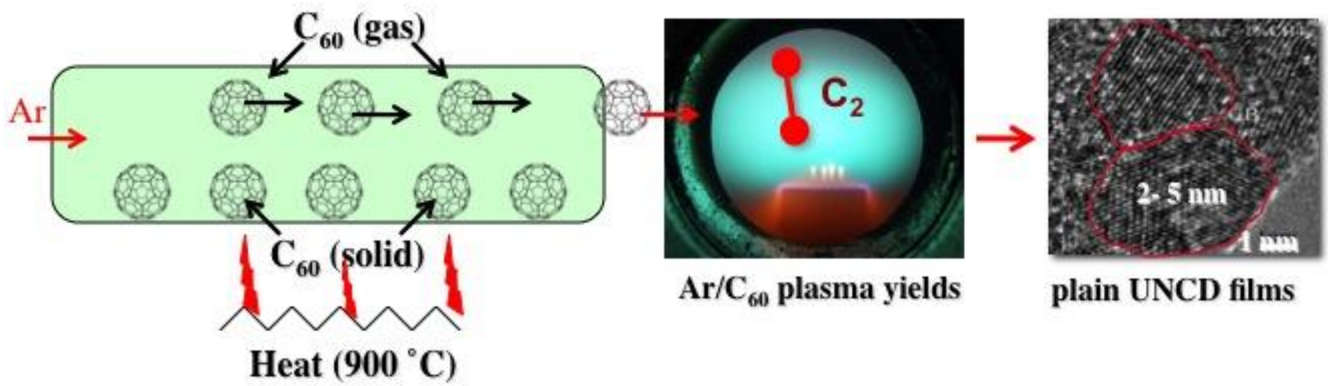
ΔG=-20-30 kcal/mole

- **Low nucleation density: (10^4-10^8 /cm^2)**
- **Columnar growth**
- **Large grain size(1-5 μm)**
- **High surface roughness: (≤ 1 μm)**



ARGONNE'S UNCD Growth Process Using C_{60} Molecules Carried into MPCVD Chamber: Scientific Success, But !!!!!

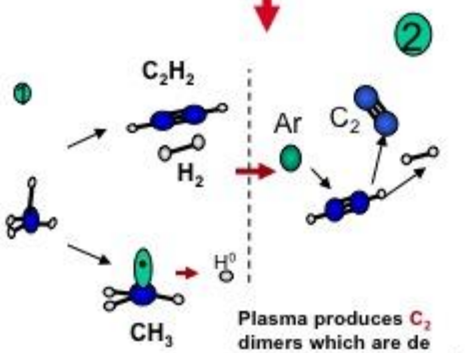
- Expensive
- Complicated
- Dirty oven connected to clean MPCVD chamber
- Difficult to scale up to cover large area substrates



ARGONNE's UNCD Film Synthesis Approach

- UNCD films are grown using a plasma containing Ar (99%) /CH_4 (1%) → ($Ar/C_2H_2/H_2$)

Substrate is seeded with nanocrystalline diamond



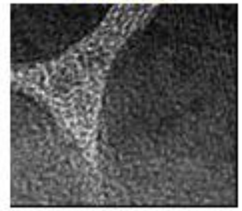
Plasma produces C_2 dimers which are de precursors that nucleate and contribute to UNCD growth

The C_2 dimers form sp^3 chemical bonds on the substrate surface:

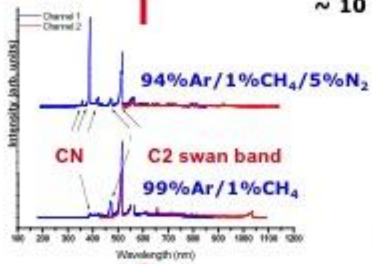
- Low activation energy (6 Kcal/mol)
- High re-nucleation density (10^{10} /cm ^{2})

$Ar/CH_4/N_2$ plasma yield N-UNCD films

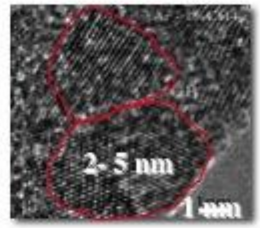
HRTEM



Nitrogen-doped UNCD films have ~ 10 nm grains and 1-2 nm GB



Ar/CH_4 plasma yield plain UNCD films



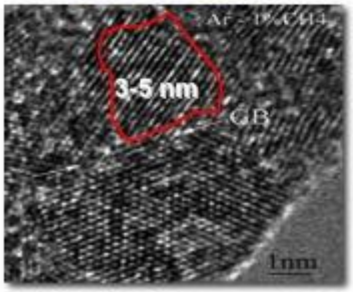
Plain view TEM of UNCD film
3 - 5 nm grains/0.4 nm GB

Auciello et al.
APL 79 (2001)1441

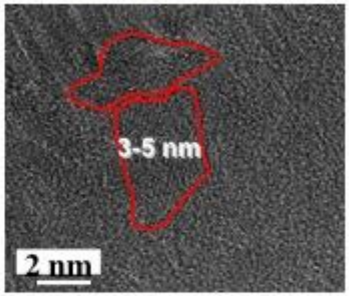
Auciello et al.
Diamond & Related Mater. vol. 10 (2001) 1952

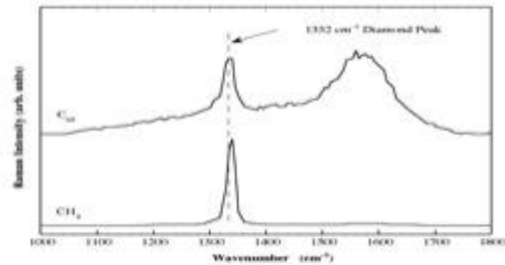
Nanostructural and Chemical Bonding Characterization of UNCD Films

800 ˚C UNCD

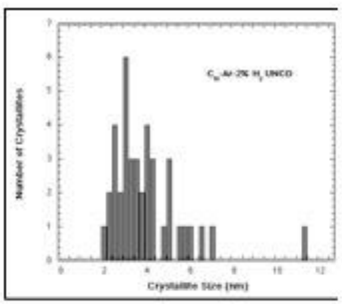


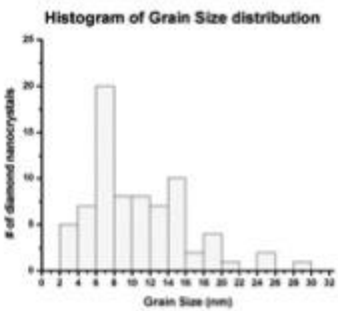
400 ˚C UNCD

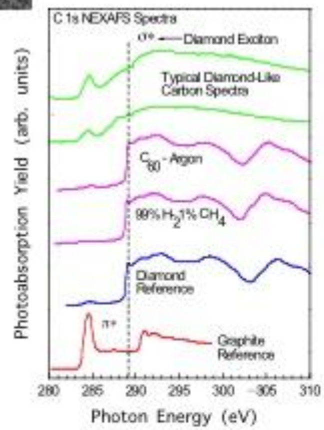


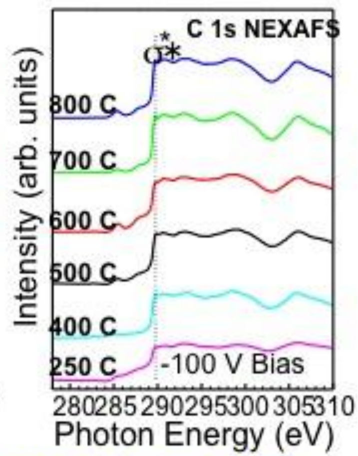


UV Raman spectra of UNC and MCD films grown at 800 ˚C



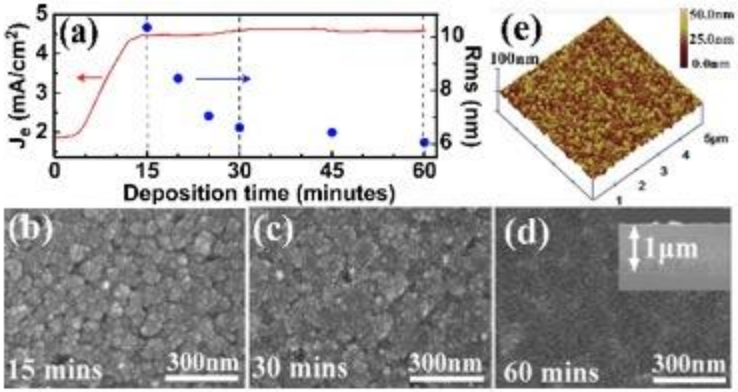




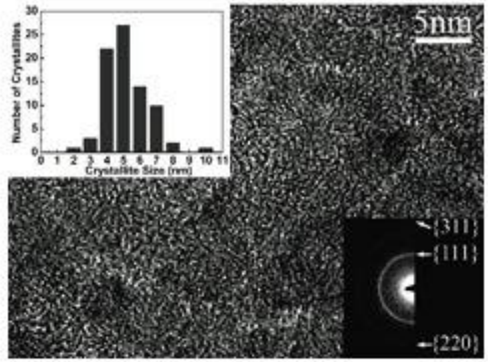


(NEXAF) spectra of UNCD and other carbon-based films
(Terminelo/ Carlisle/Gruen/Krauss/Auciello (1996-present)

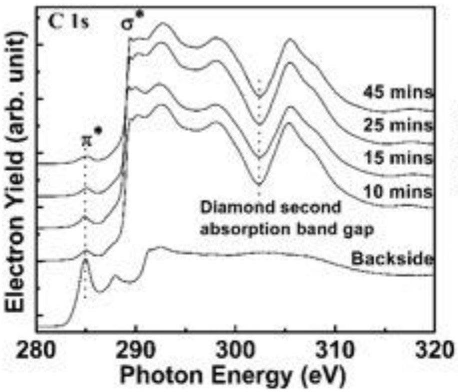
BEN-BEG of UNCD Films: Current vs Deposition Time and Correlation to Surface Morphology, HRTEM and NEXAFS Studies



Current and rms roughness vs deposition time



HRTEM studies show UNCD nanostructure plus grain size statistics of UNCD

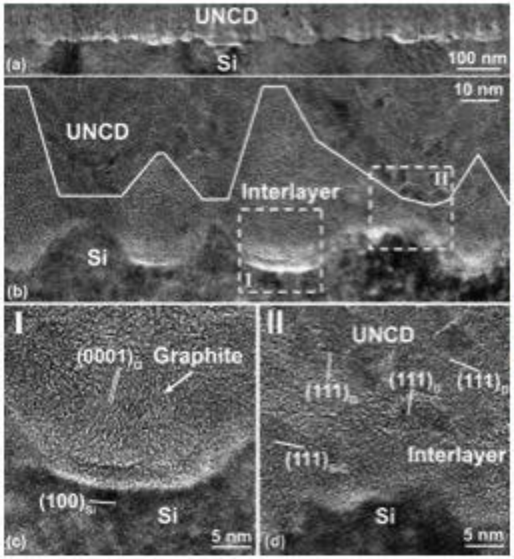


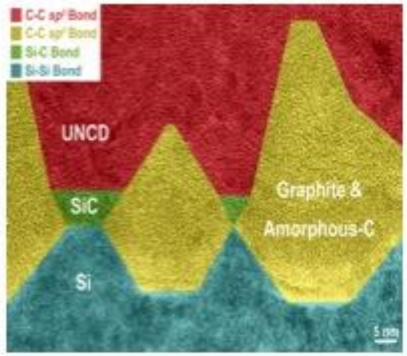
NEXAFS shows diamond/UNCD signature

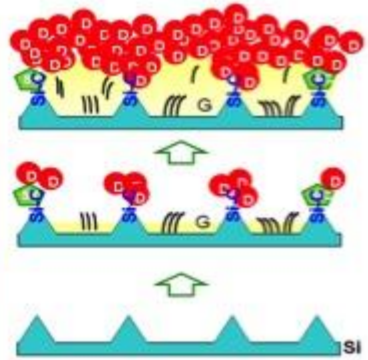
4 " Si wafer coated with uniform UNCD film (needs R&D to grow uniform UNCD films on 6" and 8" wafers)

Chen/Auciello et al.
Appl. Phys. Lett. **92** (2008)

HRTEM Studies of Nucleation Layer and UNCD Film on Si Surface Pretreated with H-Plasma With Bias + BEN-BEG



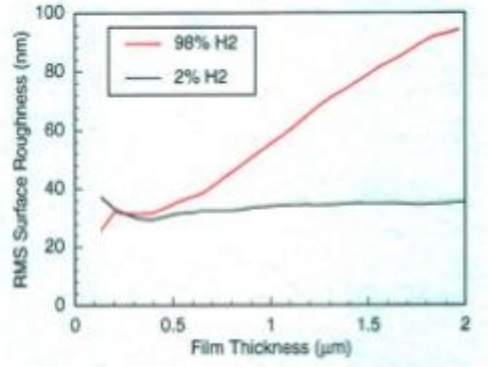


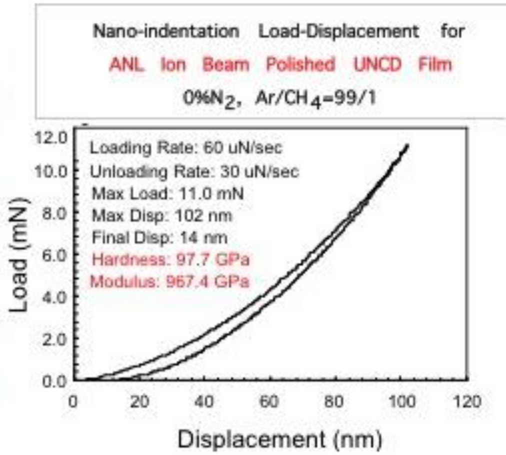


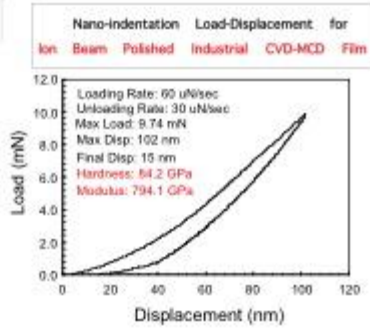
- SiC phases are formed at the peaks of the Si surface triangular profile due to the active unsaturated Si bond and the enhanced local electrical field.

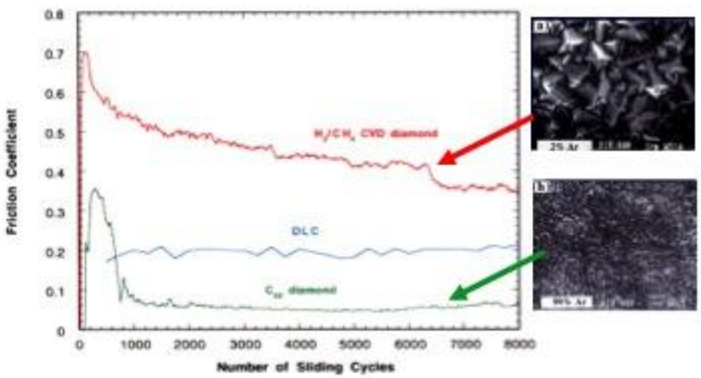
- The UNCD grains preferentially grow at the peaks of the triangular substrate surface profile and rapidly cover the a-C and oriented graphite phases formed in the valley of the surface profile.

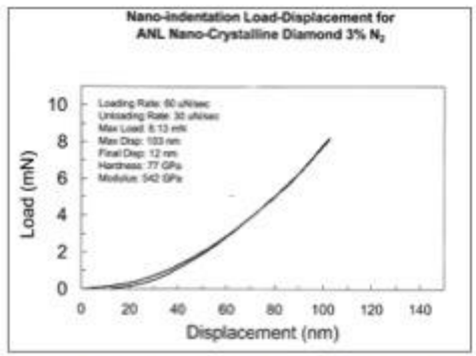
Properties of UNCD











Hardness of nitrogen-doped UNCD films

Summary of Multifunctional Properties of UNCD Films

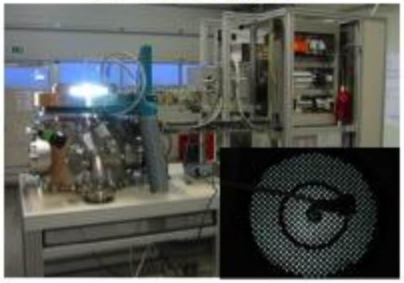
- **Electrical Conductivity**
  N-type UNCD (N in grain boundaries) (~260 $\Omega \cdot cm^{-1}$ at RT!) tunable
  B-doped UNCD (B-substitutional in diamond lattice (metallic)
- **Mechanical**
  Hardness (98 GPa), Young modulus (998 GPa) fracture strength (~ 5 GPa)
  X-diamond (100 Gpa), X-diamond (1100 Gpa)
- **Tribological**
  Low friction (~0.02-0.04 *in air*), High wear/corrosion resistance
  Low *Stiction*, Smooth, Conformal Coating
  RMS roughness (~ 4-20 nm as deposited)
- **Low-Temperature Deposition**
  ~0.2-0.4 um/hr at 350-400 °C
- **Surface Micromachining**
  UNCD-MEMS/NEMS
- **Field Emission**
  Low threshold (~2 V/μm), stable
- **Electrochemical**
  Wide working potential (4 eV) biocompatible
- **Surface Chemistry**
  Express DNA, Proteins on UNCD surface

Selected Properties of Si, SiC, and Diamond

Property	Silicon	Silicon Carbide	Diamond
Lattice Constant (Å)	5.43	4.35	**3.57**
Cohesive Energy (eV)	4.64	6.34	**7.36**
Young's Modulus (GPa)	130	450	**1200**
Shear Modulus (GPa)	80	149	**577**
Hardness (kg/mm^2)	1,000	3,500	**10,000**
Fracture Toughness	1.0	5.2	**5.3**
Flexural Strength (MPa)	127.6	670	**2944**
Friction Coefficient	0.4-0.6	0.2-0.5	**0.01-0.04**
Relative Wear Life	1.0		**10,000**

Tools for Growth of UNCD Films For Military and Commercial Applications

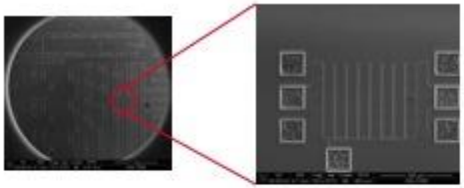
11" IPLAS System



New Lambda MPCVD System at ANL-CNM

Only MPCVD for UNCD and carbon films synthesis in a clean room

ADT Commercializes Large Area UNCD Films via HFCVD



UNCD (400 ˚C) Coating on 150 mm Si wafer (± 5% thickness uniformity)

300 mm Si Wafer coated with UNCD Film (± 3% film thickness uniformity)

2003 R&D 100 Award ANL/UNCD-IPLAS technologies

2008 R&D Award UNCD Seals

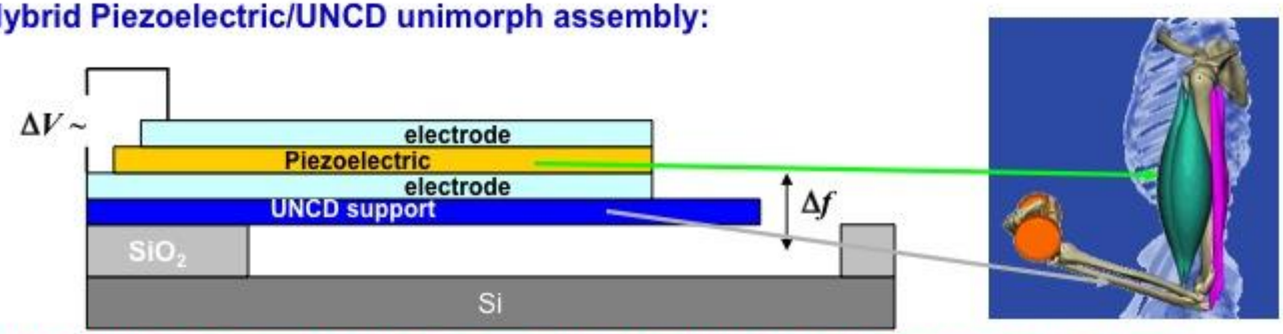
2006 FLC Award to O. Auciello / J. Carlisle for Technology UNCD transfer to the Market

ADVANCED DIAMOND TECHNOLOGIES

O. Auciello/J.A. Carlisle (Founders-2003)
J. Yerger (CEO)

Hybrid PZT/UNCD MEMS/NEMS Integration

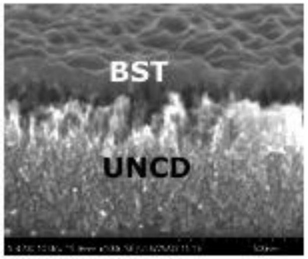
Hybrid Piezoelectric/UNCD unimorph assembly:



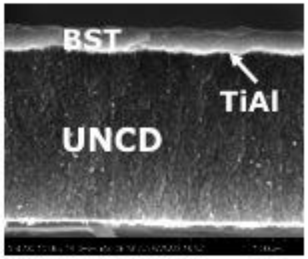
PZT/UNCD integration has several potential piezoelectric applications,
however, there are scientific and technological barriers to MEMS applications:

- **UNCD growth need to be optimized for uniform thickness (achieved 5% uniformity on 150 mm wafer)**
- **Interface delamination between metal electrode-UNCD (under control)**
- **Integration of piezoelectric (e.g., PZT) and UNCD: oxidation of diamond (Oxygen diffusion barrier developed)**
- **Micro and nano fabrication for PZT-UNCD structures (demonstrated)**
- **Piezoelectric actuation of hybrid PZT/UNCD micro/nano cantilevers (demonstrated)**

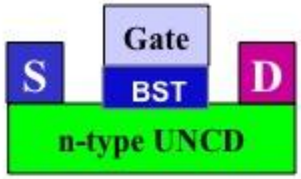
Oxide/UNCD Integration FOR MEMS/NEMS/Electronics Multifunctional Devices



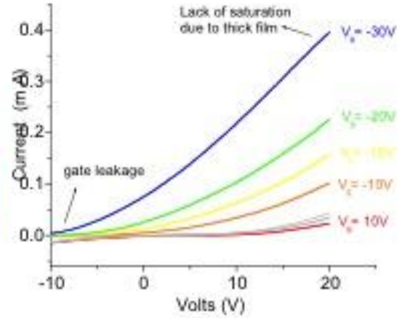
$Ba_xSr_{1-x}TiO_3$/UNCD results in diamond etching

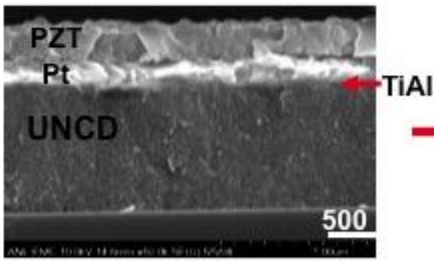


BST/TiAl/UNCD: TiAl layer enables oxide/ diamond integration

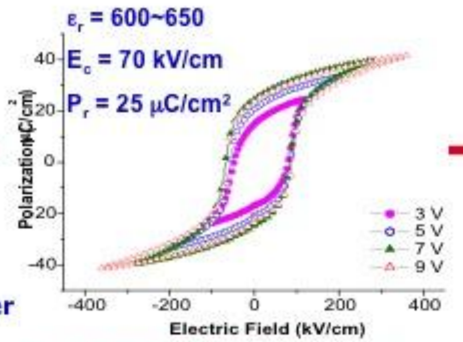


First BST/UNCD hybrid MISFET

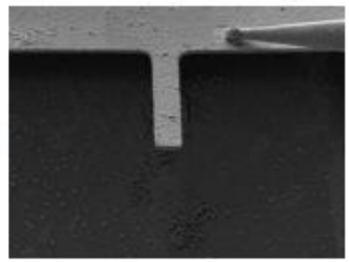




$PbZr_xTi_{1-x}O_3$/Pt/TiAl/UNCD: TiAl layer enables Piezo/ diamond integration



First Pt/PZT/Pt/TiAl/UNCD capacitor with excellent properties demonstrated



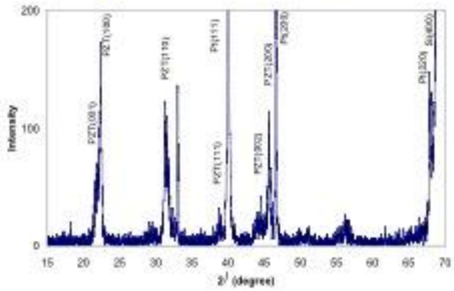
First PZT/UNCD hybrid resonator

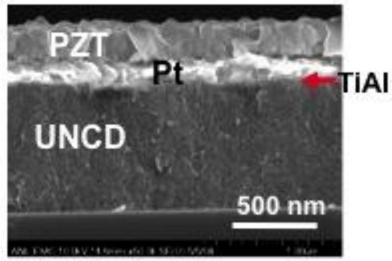
1 BILLION CYCLE DEMONSTRATED

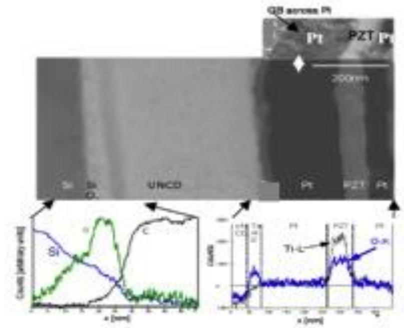
$Pb(Zr_{0.47}Ti_{0.53})O_3$ (PZT) Film Synthesis and PZT/UNCD Integration Strategies for Piezoactuated MEMS/NEMS

Materials and Device Performance Characterization

- **Synthesis and Properties of PZT films**

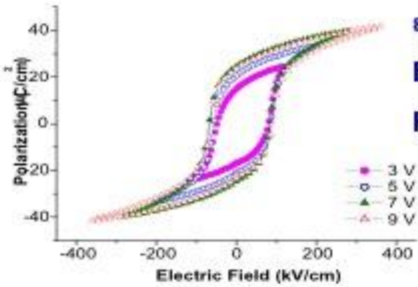






$PbZr_xTi_{1-x}O_3$/Pt/TiAl/UNCD enables robust oxide Piezoelectric/ diamond integration

First Pt/PZT/Pt/TiAl/UNCD capacitor with excellent properties demonstrated



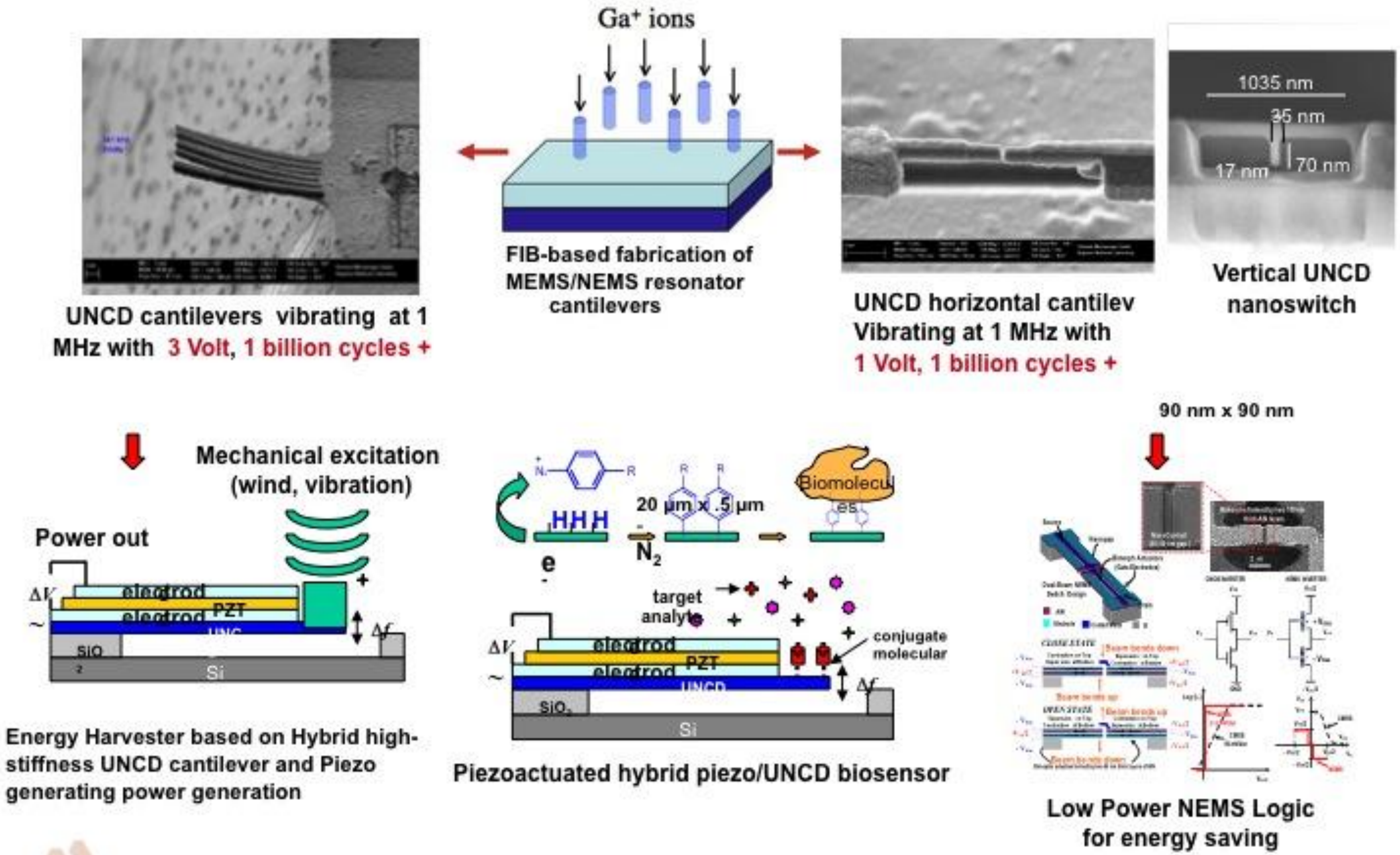
ε_r = 600~650

E_c = 70 kV/cm

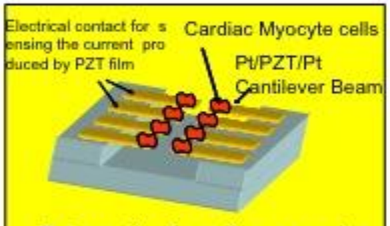
P_r = 25 $\mu C/cm^2$

Auciello et al APL (2007)

Hybrid PZT/UNCD Resonant Cantilevers for Piezoactuated MEMS Energy Harvesters / NEMS Logic System

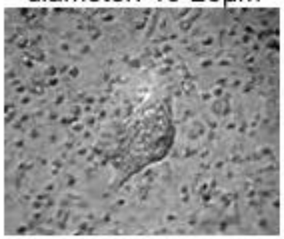


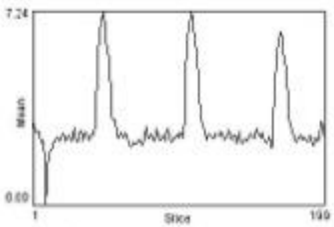
Cardiac Cells Mediated Actuation of Piezoelectric Micro/Nanocantilevers for Biopower Generation



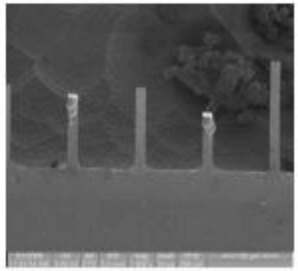
Schematic of cardiac myocytes on PZT cantilevers.

Cardio myocyte
length: 50 -100μm
diameter: 10-25μm





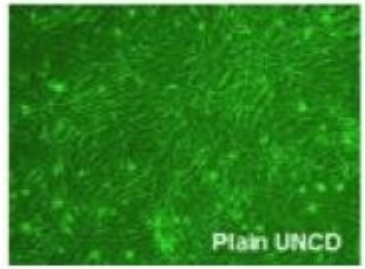
Intensity graph of the beating of cardiac myocyte



Cell suspension dropped onto protein coated UNCD cantilever array chip integrated with Pt/PZT/Pt, resulting in randomly attached cells to cantilever, and cultured.

Preliminary power = 1-3 μW

(In collaboration with R. Bashir, Purdue Univ)



Mouse Embryonic Fibroblast grown on UNCD surface

ANL Work on Development of UNCD as Dielectric layer for RF MEMS Switches

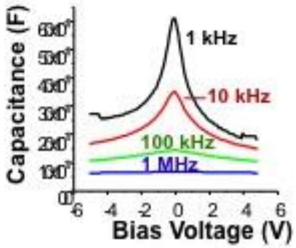
Development of low temperature UNCD films as RF MEMS switch dielectrics

Task

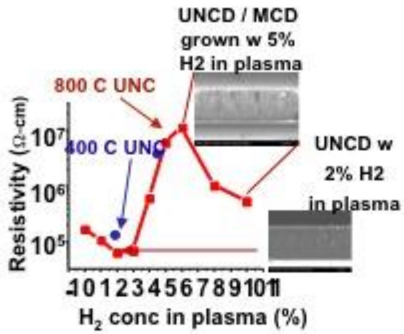
Development of processes to tailor dielectric properties of UNCD films and measurement of UNCD dielectric properties for optimization as dielectric layer in RF MEMS Switches →

Measurements

For UNCD films grown With 5% H_2 in plasma



Tunable UNCD capacitance



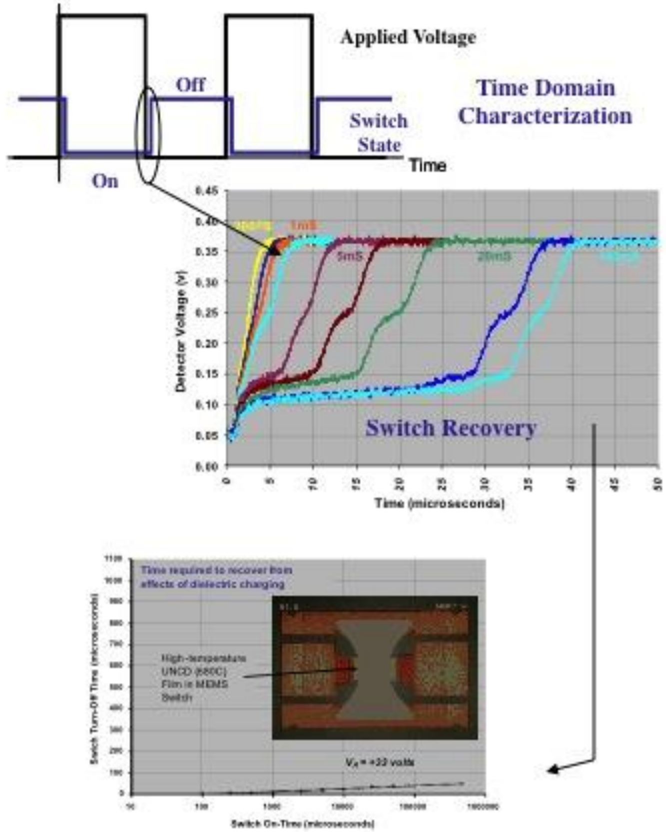
Tailored UNCD resistivity via hydrogen incorporation

Milestones (April 2008)

Development of optimized LR and negligible stiction LT UNCD dielectric for application as dielectric layer with controlled leakage for RF MEMS switches

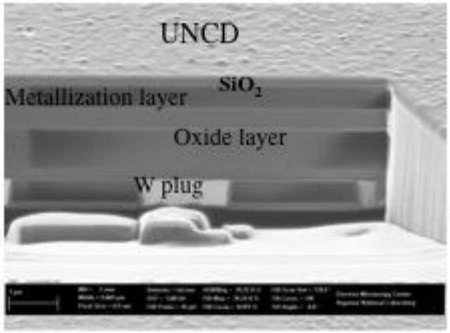
UNCD Charging Characteristics

- Physics of dielectric charging in UNCD is fundamentally different from conventional MEMS dielectrics (SiO_2 or Si_3N_4)
- Charging in UNCD occurs extremely quickly
  - Time constant on the order of 100 μs (compared to 10-100 s for silicon dioxide)
  - Device fails very quickly
- However, discharging process is also very fast
  - Device recovers very rapidly
- In most radar applications, required on-time of switch is less than 10-100msec
  - This enables the switch to fully recover within the allotted switching time of the MEMS switch (typically < 50 μs)
- Completely new paradigm in device operation
  - Fails quickly, but recovers very quickly
  - Patent pending
- Concept has been demonstrated/ measured in MEMS switches fabricated with 400°C UNCD devices.

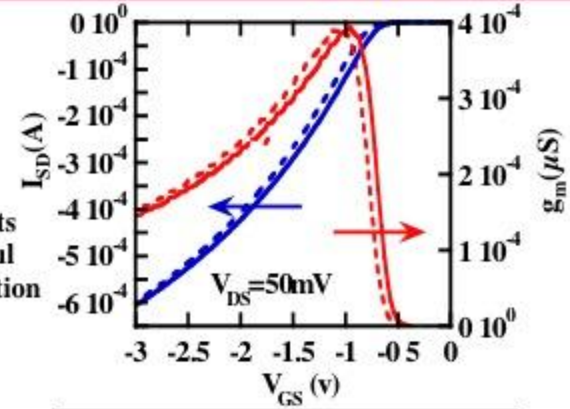


UNCD CMOS Integration (DARPA-HERMIT Program)

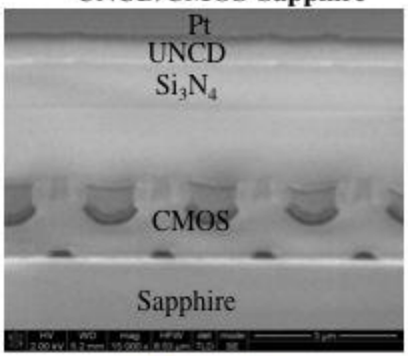
FIB cross-section image of UNCD/CMOS-Si



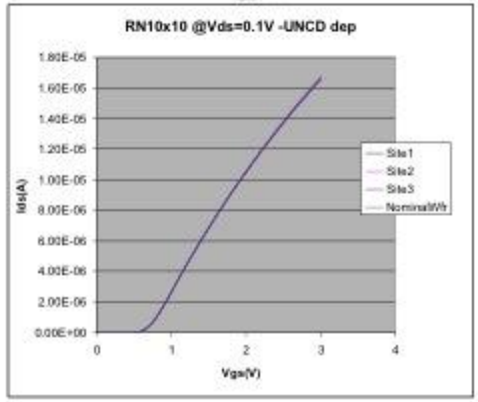
Electrical measurements demonstrated successful UNCD/Si-CMOS integration



FIB cross-section image of UNCD/CMOS-Sapphire



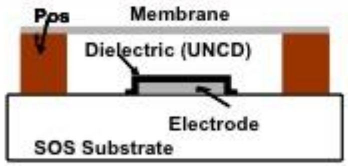
Electrical measurements demonstrated successful UNCD/SiOSapphire CMOS-integration

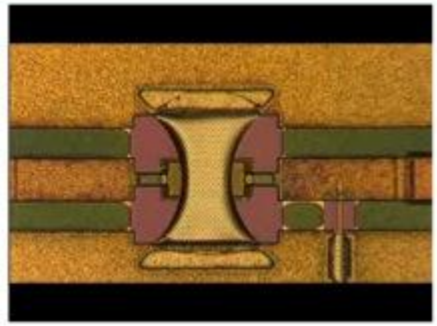


Argonne NATIONAL LABORATORY · ADVANCED DIAMOND TECHNOLOGIES, INC. · imt · MEMtronics · PeregrineSemiconductor

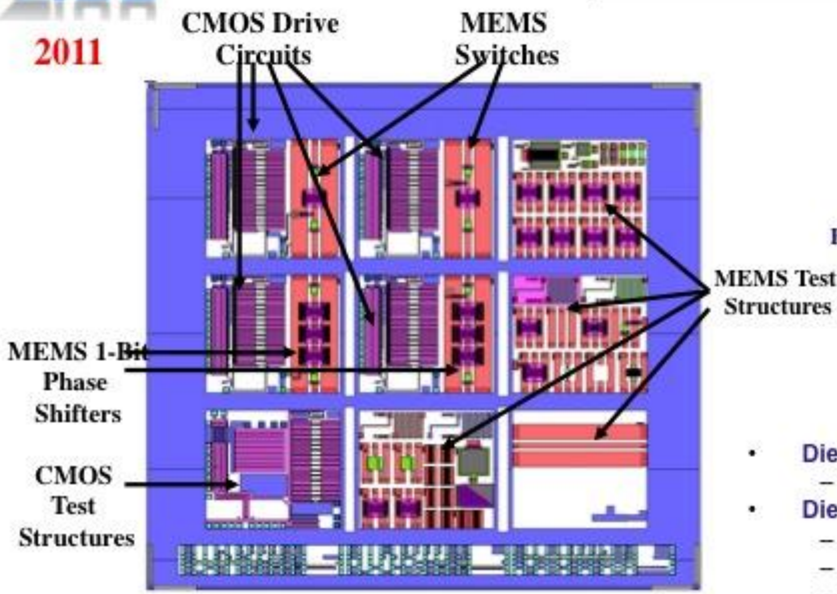
RF UNCD-MEMS Switches/SOS-CMOS Integration

2011

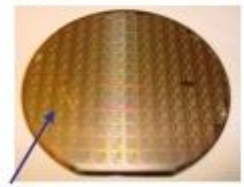




50 Billion Cycles Demonstrated



Peregrine SOS CMOS Wafer



- Die size
  - 10.1 mm x 10.1 mm
- Die includes
  - CMOS driver circuits
  - CMOS test structures
  - MEMS switches and 1-bit phase shifters
  - MEMS test structures
- 150mm wafer contains 130 dies

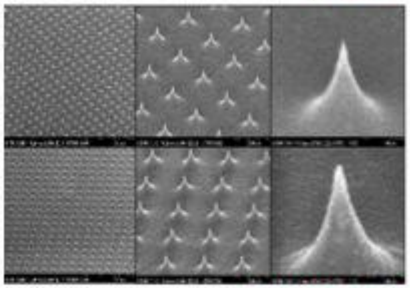
DARPA-HERMIT Program (2005-2011)
Product in Prototype Stage
Needs funding to bring to market

Application of UNCD Films to Field Emission Devices

Current contract with Goddard Space Center to develop UNCD field emission cathodes for mass spectrometers for deep space exploration

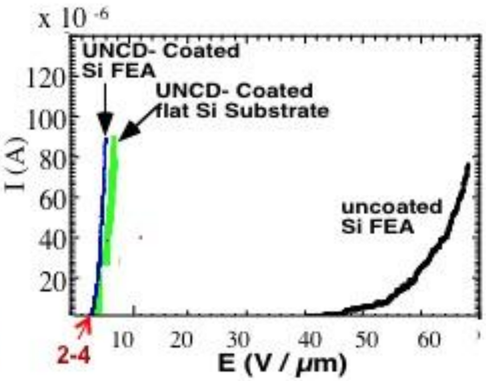
1000 "REAL" hrs stable emission demonstrated

Uncoated Si tips

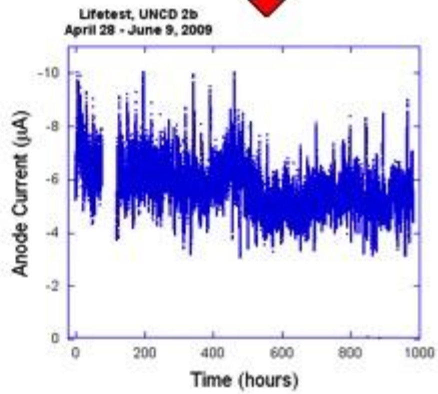


UNCD-coated Si tips

Large Si tip array coated with UNCD film for field emission, using bias-enhanced growth



UNCD surfaces exhibit << threshold voltage for field emission (2-4 V/μm) than Si (40-50 V/μm) or metal surfaces and UNCD flat surfaces exhibit as low FE field as UNCD on tips

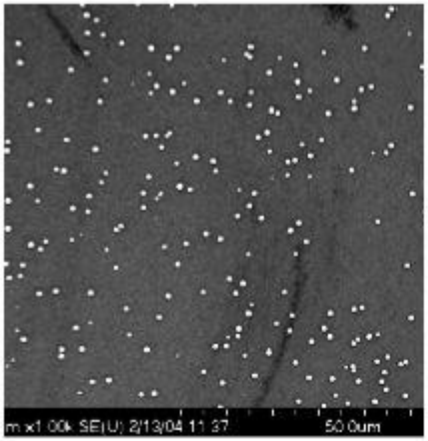


UNCD-coated Si tip array exhibited stable emission for ~1000 hrs in ~ 10-6 Torr

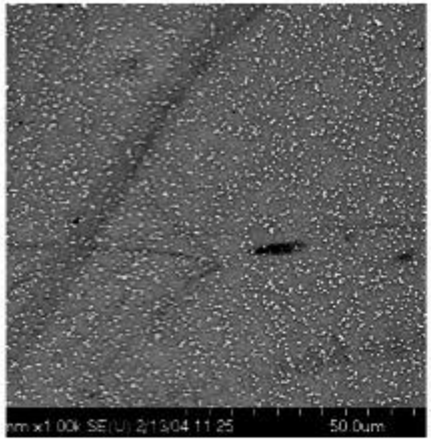
Auciello/Carlisle et al. APL 94 (2003) 4079
Krauss/Auciello et al., JAP 89 (2001) 2958

Auciello/Sumant/Getty (Goddard Space Center- Work in progress (2010)

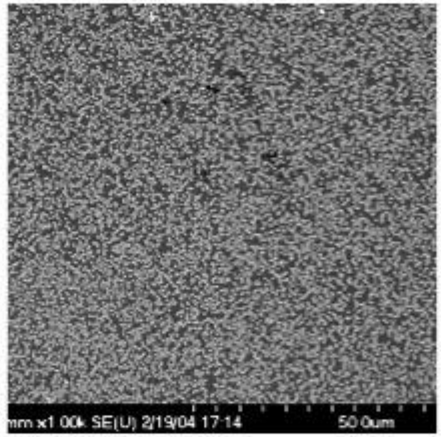
Fuel Cell Electrodes Based on Pt Nanoparticles Embedded on Electrically Conductive NUNCD or BUNCD Film Surfaces



100 s



400 s



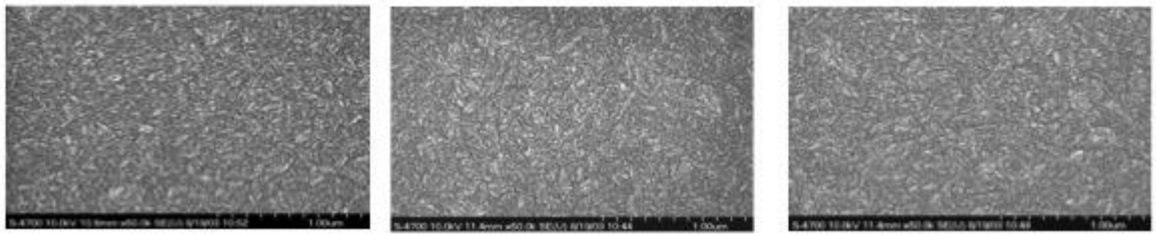
600 s

Galvanostatic electrodeposition of Pt was performed in 1 mM K_2PtCl_6 + 0.1 M $HClO_4$ using a current density of 0.4 mA/cm^2. We are able to control the particle size and distribution density by adjusting the deposition time and current density. Using pulse deposition we are able to deposit Pt particles with size less than 20 nm.

Electrochemical Stability of UNCD vs Classy Carbon

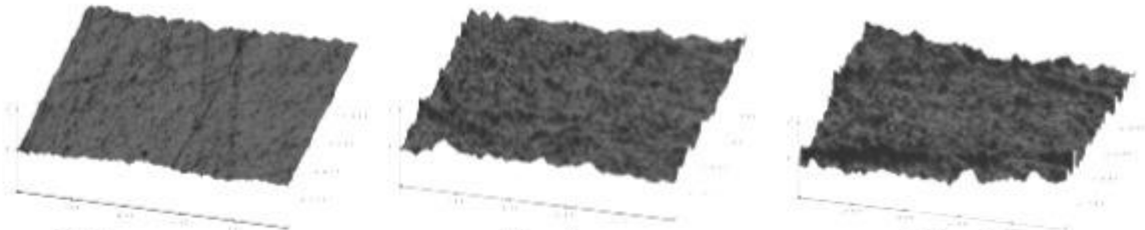
Electrode Potential: 2.5 V vs. Ag/AgCl in 0.1 M $HClO_4$.

UNCD



Before 10 min. 30 min.

Glassy Carbon

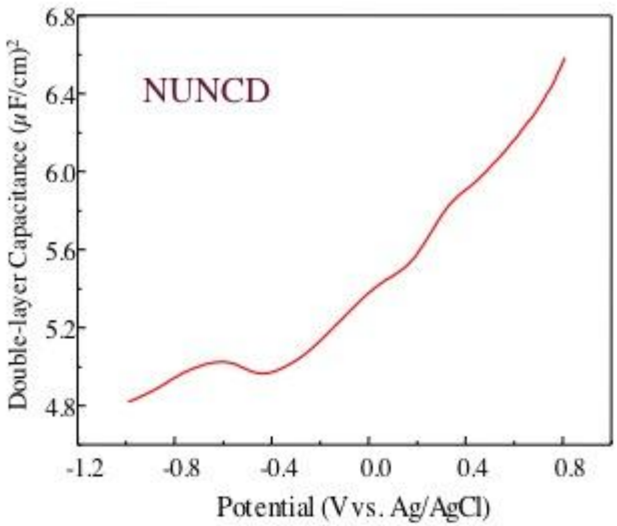


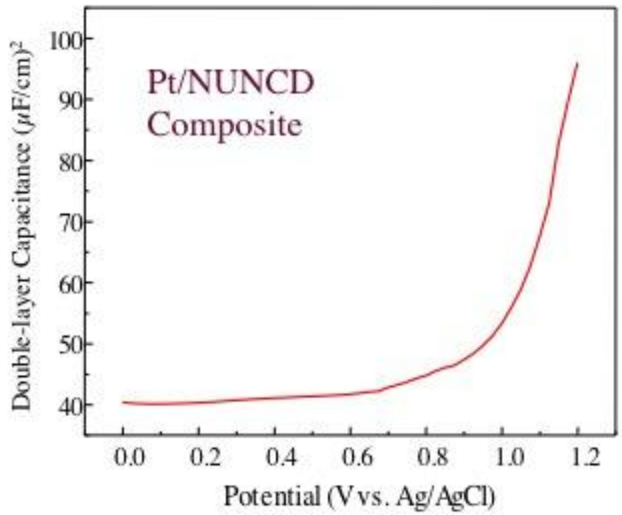
Before 10 min. 15 min.

Question: Is the difference between the chemical and electrochemical stabilities of UNCD vs. glassy and other carbons due to the directionality of sp^2 vs. sp^3 bonding and/or bond strength?

- Carbon black: particle size: < 5 nm to > 300 nm
- UNCD: grain size: 3-5

UNCD vs Pt Nanoparticle-UNCD Electrode Double Layer Capacitances

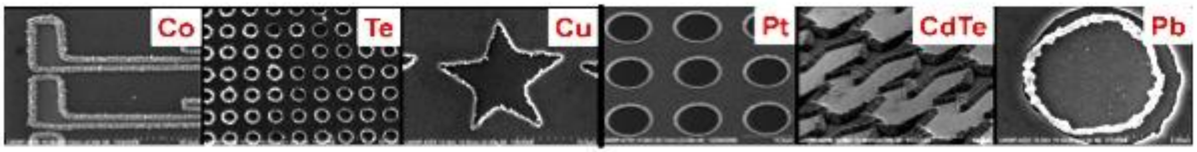


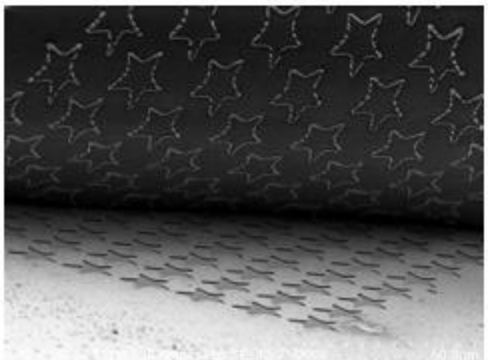


The double layer capacitance of the Pt/UNCD composite electrode is one order of magnitude higher than that of plain UNCD.

Auciello / Sumant, Diamond and Related Materials (Invited Review)19 (2010) 699

Development of UNCD/N-UNCD Multilayers as Reusable Template for Electrochemical Growth of Nanowires





D.A. Dissing, E. A. Terrell, D. B. Seley, M. P. Zach

Dept. of Chemistry, University of Wisconsin – Stevens Point

A. V. Sumant,[1] R. Divan, [1] S. Miller,[1] O. Auciello,[1,2]

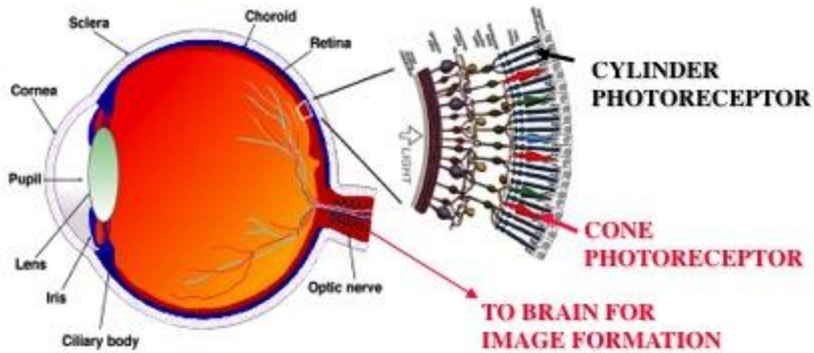
[1]Center for Nanoscale Materials, [2]Materials Science Division
Argonne National Laboratory

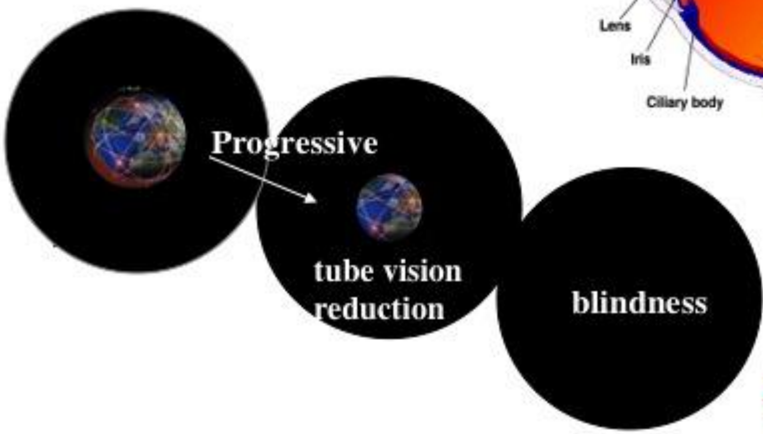
Advanced Materials (2011)

Biomedical Applications of UNCD Films

Towards an Artificial Retina for the Blind!….

RETINA DEGENERATION:
A GLOBAL PROBLEM!……
About 25 million people worldwide





Genetically-induced death of Photoreceptors leads to

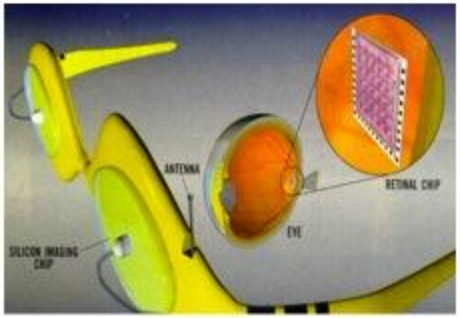
2009 R&D 100 Award
2009 R&D 100 Top Editor's Choice Award

Department of Energy
Office of Biological and Environmental Research
Medical Sciences Division

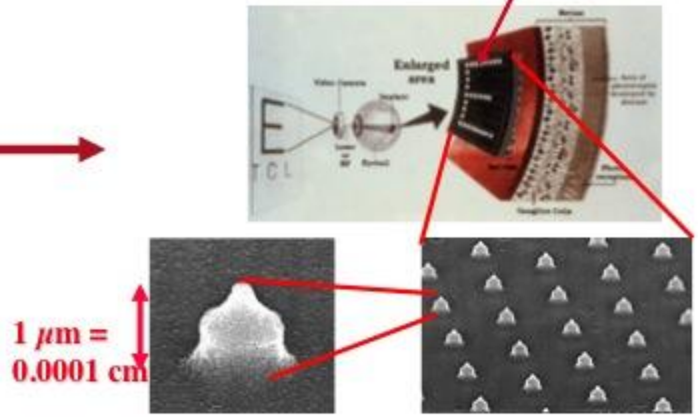
University of Southern California(Doheny Eye Institute)
North Carolina State University, Univ.California-Santa Cruz, CALTECH
Argonne, Lawrence Livermore, ORNL, Los Alamos, Sandia National Labs.
Second Sight (Industrial Partner)

Artificial Retina Based on Implantable Microchip

ANL's UNCD hermetic, bio-inert coating technology enables implantation of Si-based microchip onto the human retina via protection of Si from chemical attach by the eye's saline solution.



CCD camera on glasses capture image and transmits it via RF to microchip implanted on retina. Microchip sends electrical pulses to retina and from there to brain via optical nerve to restore vision



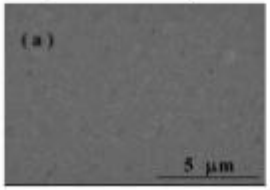
High-conductivity N-Doped UNCD microtips could be used for corrosion resistant electrode array

MEMS retina adaptable electrodes

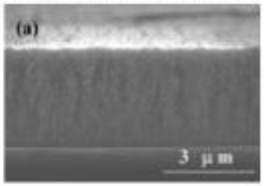
Xiao/Auciello et al.
J. Biomedical Materials 77B (2) (2006) 273

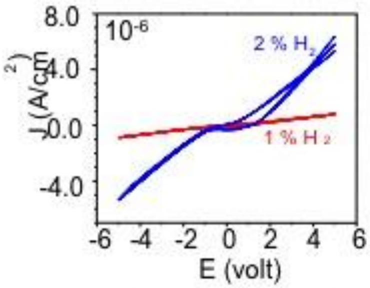
Research on Hermetic UNCD Coatings :
Optimization of Insulating Properties

Hydrogen incorporation into grain boundaries satisfy dangling bonds resulting in reduction of leakage current, but need to keep hydrogen incorporation low to yield UNCD structure

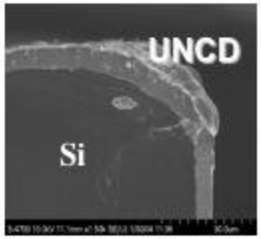


Plain UNCD and 1% H

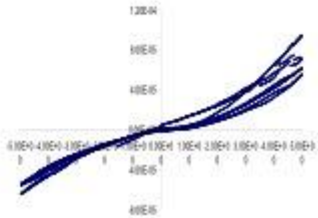




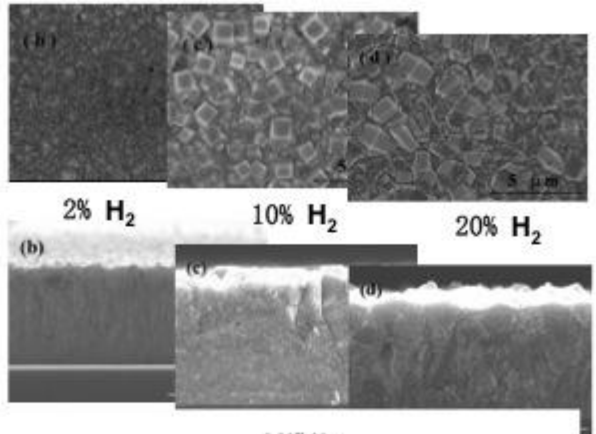
Low leakage in saline for flat UNCD films

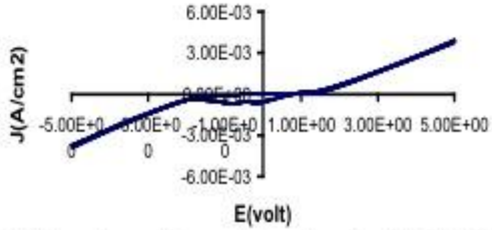


Encapsulating UNCD film grown on "swizzle"-like Si substrate with 1% H in Ar/CH_4 plasma



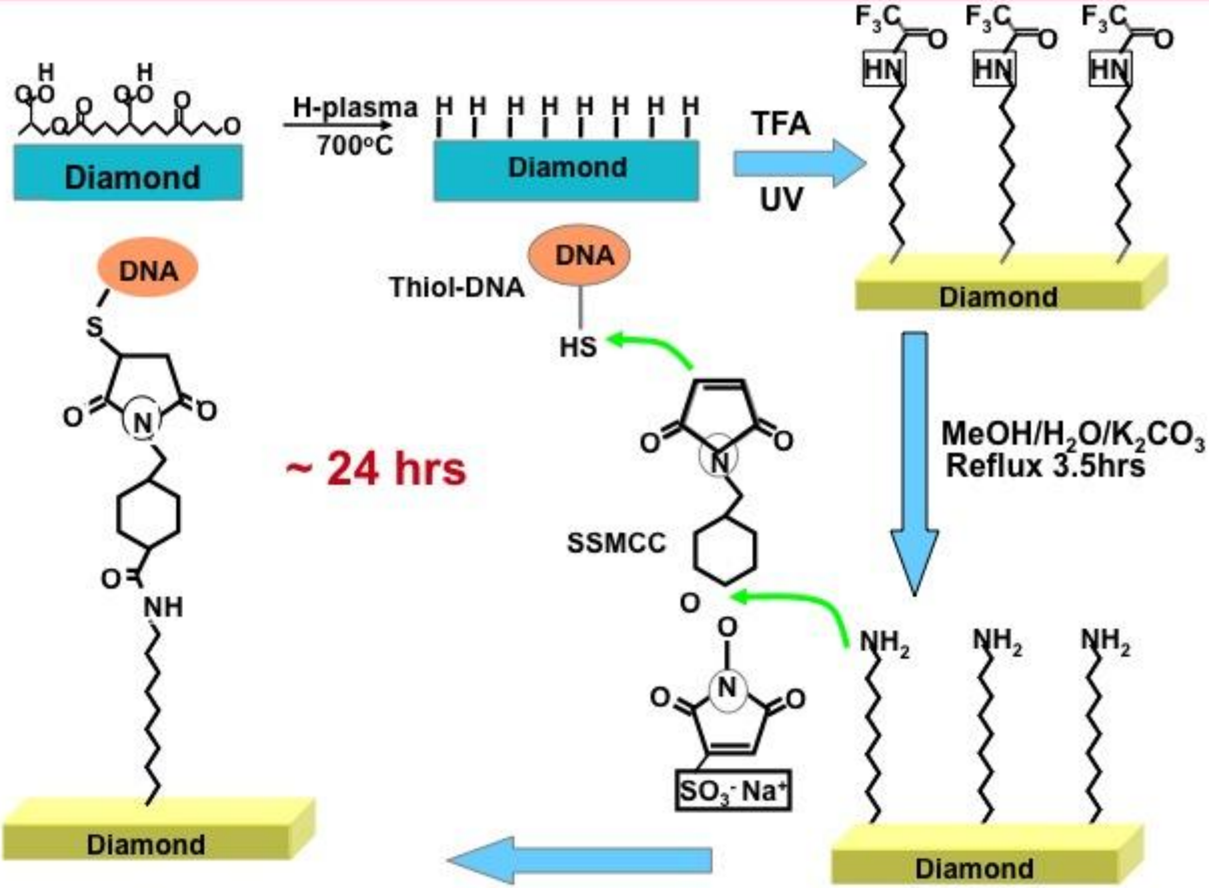
Intermediate leakage in saline for encapsulating UNCD films on "swizzle"-like Si substrates





High leakage in saline for flat UNCD films with relatively high H_2 in plasma

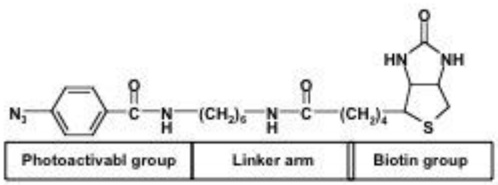
Chemical Conditioning Covalent Linking of DNA to Diamond Surface

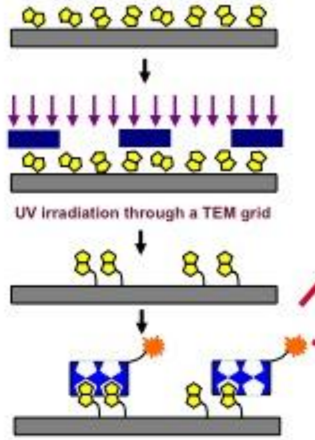


PROTEIN PATTERNING ON UNCD VIA PHOTOBIOTIN ACTIVATION

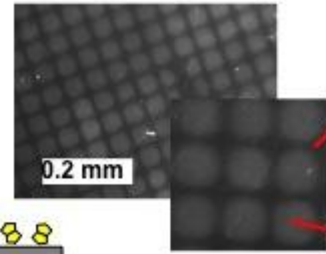
Selective covalent immobilization of biotin

Needs Funding
To develop Biosensors



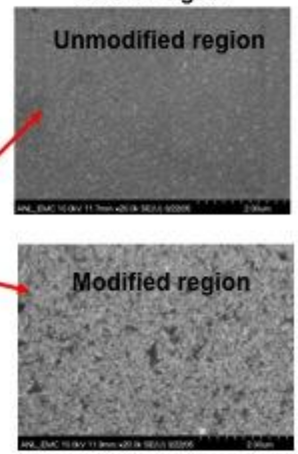


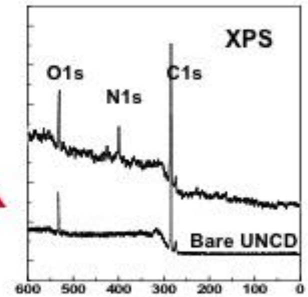
Fluorescence Microscopy



100 by 100 μm
25 μm spacing

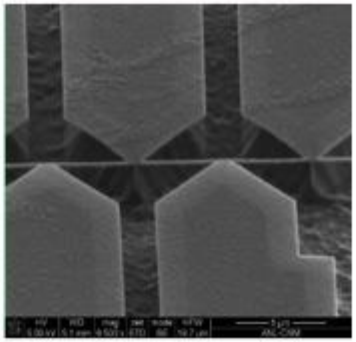
SEM images

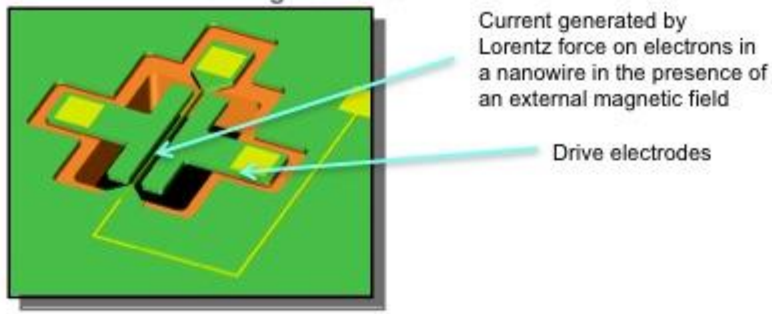


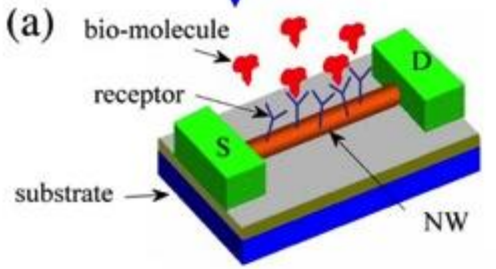


Future… Nanoscale patterning

UNCD nanowires: Possible Applications







Studies of interaction of bio-molecules with diamond nanowire and development of sensors with increased sensitivity and new functionality

Nonlinear NEMS magnetometer

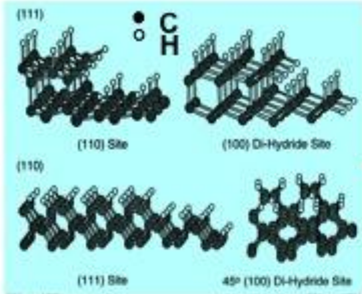
- Does not require integration with magnetic materials or micro-magnets
- Compatible with CMOS
- Can be combined into a compact three-axis device to measure gradients
- Consume little power during operation
- Reduction in size should allow us to achieve good spatial resolution.

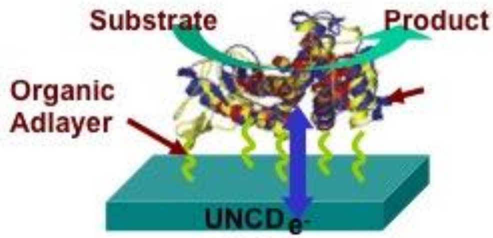
A.V. Sumant[1], L. Ocola[1], D. Wang[2], D. Lopez[1], O. Auciello[1,3] and D. Mancini[1]

[1]Center for Nanoscale Materials, [3] Materials Science Division
Argonne National Laboratory
[2] Department of Physics, University of Puerto Rico

UNCD Films as Platform for Developmental Biology: A New Frontier

- H-terminated diamond surface
  - Inherently low reactivity of C-H bonds
  - Radical reactions —- the general approach
    - *Plasma (O_2, NH_3) treatment*
    - *Photochemical reaction*
    - *Thermochemical reaction*
- UNCD plays a dual role
  - Robust support for biomolecules
  - Electrochemical signal transducer

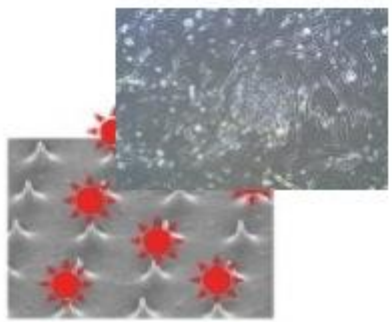




Stem Cell Growth on UNCD Surface: New Platform for Stem Cell Research

Science

- Understand growth mechanism
- Understand stem cell/UNCD interface
- Explore possible stem cell differentiation
- into specific cells on UNCD surfaces
- Investigate cell/UNCD interface for electrical, chemical, bio communicatic with live cells in biological systems



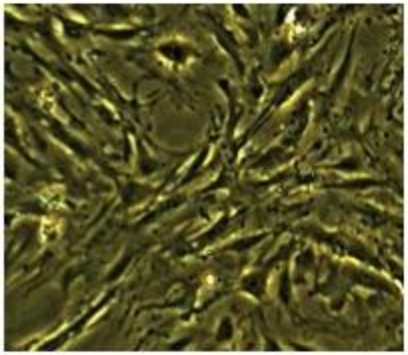
Impact

- Grow retina photoreceptor cells for artificial retina
- Grow brain cells on UNCD electrodes for bio-inspired electrodes for brain cell stimulation
- Grow generic nerve cells on UNCD for nerve stimulation (e.g., spinal cord cells)

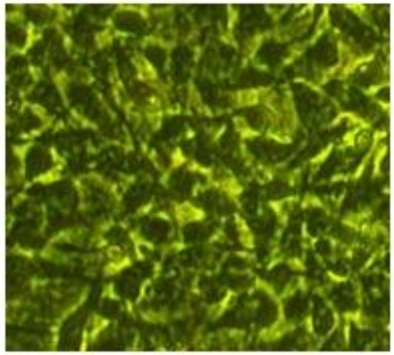
H9 cells grown on UNCD-coated quartz dish

Use of UNCD Surfaces for Developmental Biology

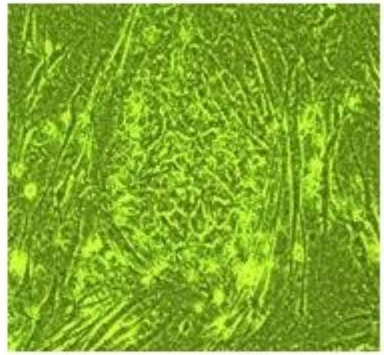
Optical pictures of different cell growth on UNCD



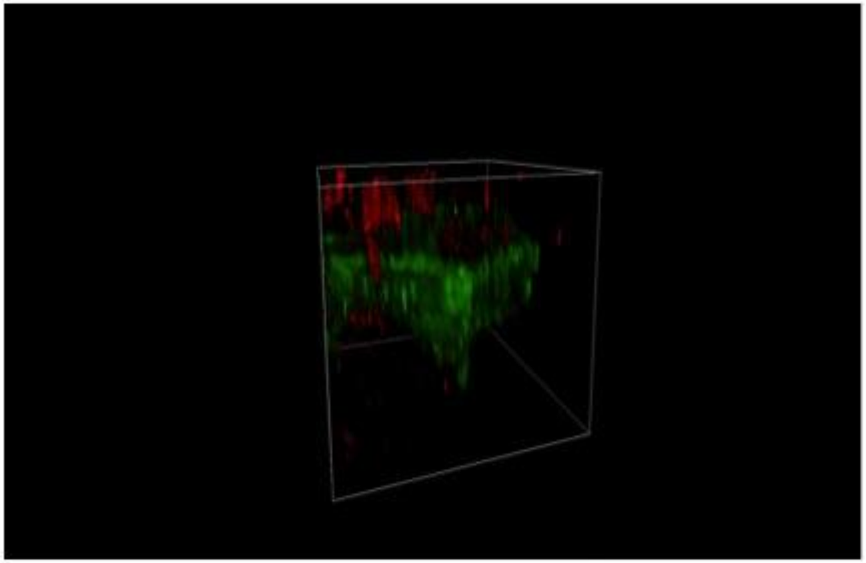
fibroblasts

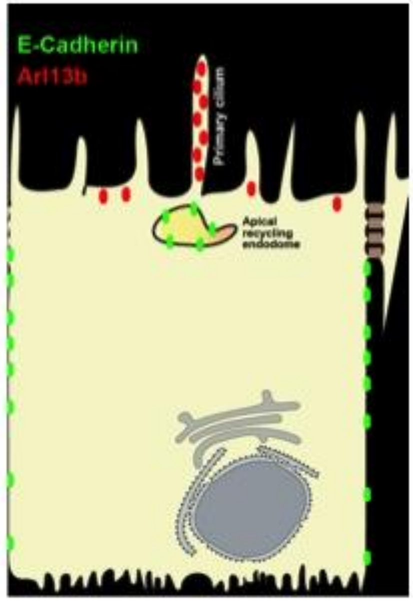


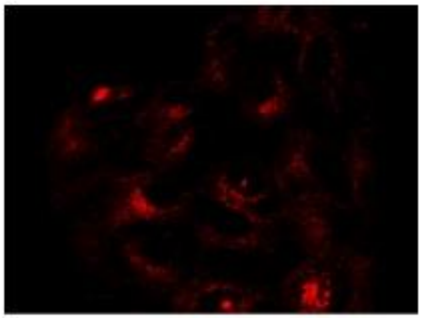
neurons



stem cells




E-Cadherin
Arl13b
Primary cilium
Apical
recycling
endodome



Commercialization of UNCD Films

ADVANCED DIAMOND TECHNOLOGIES, INC.

Founded (2003): Spun-off from ANL as 1st company from National Lab with founders / Lab holding equity

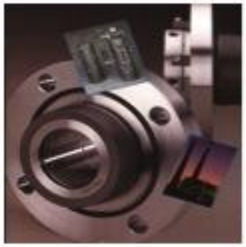
Founders: O. Auciello (currently: consultant), J.A. Carlisle (CTO)

J. Yerger (CEO)

- Manufacturer of products with superior attributes due to the exceptional properties of UNCD
- **Exclusive licensee to portfolio of UNCD patents from Argonne National Laboratory-DOE**
- Platform technology with ability to create significant businesses across multiple industries and end-use applications
- Revenue generating with strong customer base (IBM, 3M, John Crane, Flowserve, NASA, Merck-Millipore)
- Privately held, investor-backed company located in Romeoville, Illinois
- 5,000 sq feet
- **16 employees (+5 TBH) as of 2011**
- **$15 million+ in R&D funding, $6 million private investment**
- **CLOSED INVESTMENT FOR $5.2 MILLIONS WITH FOREIGN INVESTORS AND SERIES D ($3 MILLIONS), JULY 8, 2011)**

U. S. Secretary of Energy Samuel Bodman and HR Judy Biggert at ADT ribbon cutting, April 2007

UNCD-Coated Mechanical Pump Seals as Energy Saving Components



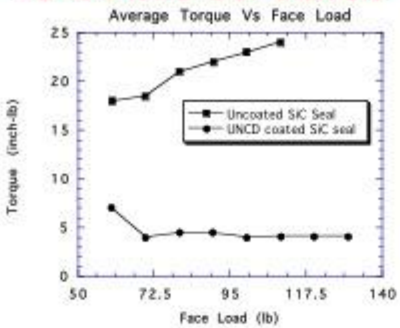
PUMP SEALS

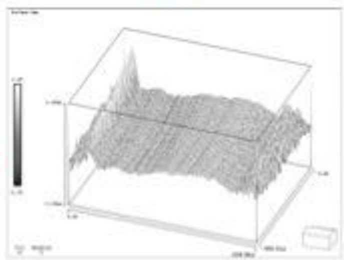
Uncoated SiC Seal

UNCD-coated SiC Seal

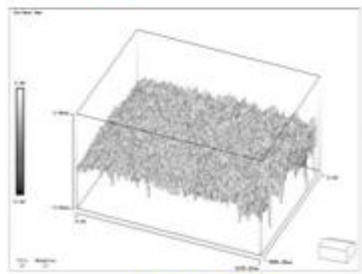
Test Conditions: Chamber Pressure: 100 psi Pump Speed: 3600 RPM

UNCD-Coated SiC Seals exhibit
~ 5-10 X lower COF than SIC





~0.8 um wear on SiC



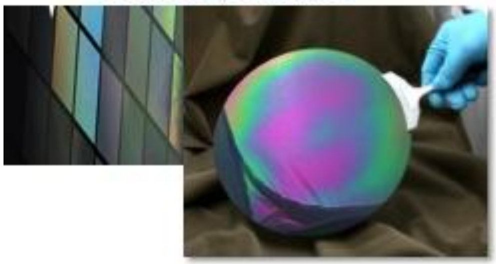
No wear

1st Product Launched by ADT now in the market (2008)

Sumant/Auciello/Erdemir et al. Tribology Trans. 48 (2005) 24

Shipping Products Exploiting Superior Mechanical and Tribological Properties of UNCD

UNCD® Wafers
For Fab of MEMS,
Including Energy Harvesting
Market: $1 billion



2010

UNCD®-coated Mech Pump Seals
For 20% Energy Savings in
Operation of Mechanical Pumps
Market: $500 million

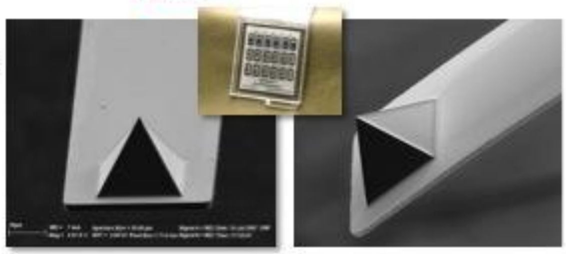
2009

UNCD®-coated Gears
For Merck-Millipore Mixers
for Production of
Pharmaceutical Drugs
Market: $1.5 billion

2011

UNCD NaDia AFM Probes®
Market: $150 million

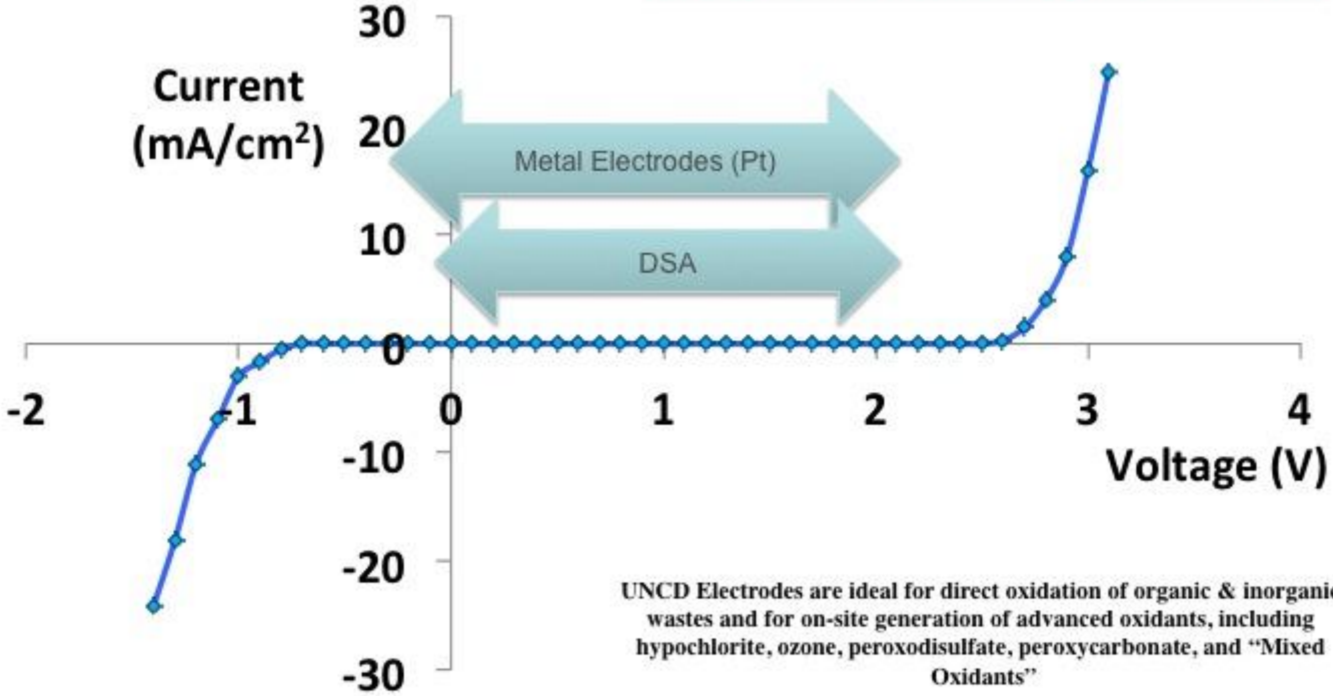
2009



UNCD ELECTRODES FOR WATER PURIFICATION

Cyclic Voltammogram of UNCD Electrode in 1M $NaClO_4$

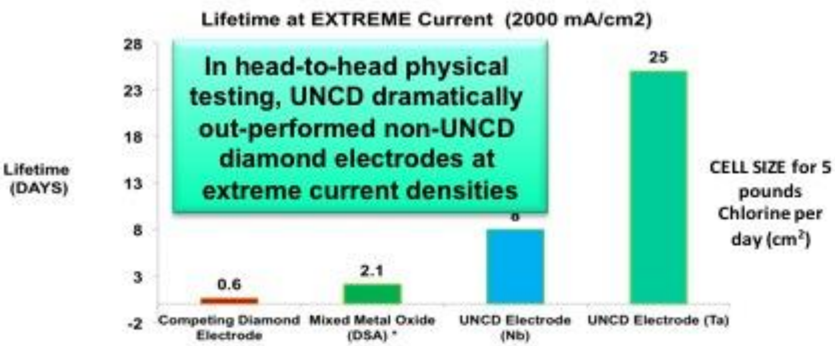
UNCD Electrodes have a larger operating voltage window than any other material.

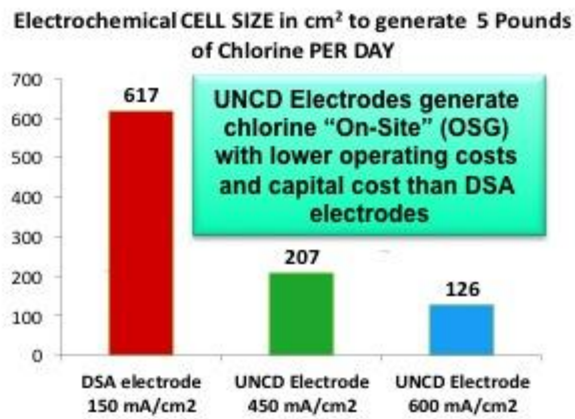


UNCD Electrodes are ideal for direct oxidation of organic & inorganic wastes and for on-site generation of advanced oxidants, including hypochlorite, ozone, peroxodisulfate, peroxycarbonate, and "Mixed Oxidants"

UNCD® Electrodes (Launched to Market, May 2011)

Bringing the Power of Diamond to Electrochemical Water Treatment Technologies





UNCD Electrodes are >10x most durable than OTHER diamond electrodes currently on the market

UNCD FILMS FOR NEXT GENERATION ELECTRODES FOR FUEL CELL AND LITION-SULFUR BATTERIES CAPABLE OF ENABLING A 500 MILES CAR

TWO PATENTS PENDING

OBI

OBI

Original Biomedical Implants, Inc.

Founders

Technologist

O. Auciello (UNCD and Oxide Film and Device Expert),
P. Gurman (MD, Bio-device manufacturing),
A. Berra (Biochemist and Animal Clinical Trials Expert)

Angel Investors

R. Geras (Owner/Director, La Salle Investments)
C. Davis (CIO, La Salle Investments)

OBI was Incorporated in Delaware on July 29, 2011

Product in Advanced State of Development: Eye Liquid Drain Valves for Treatment of Glaucoma (with U of Buenos Aires and Hospital Austral-Argentina)

(Pre-clinical Trials in Animals Close to Completion)

Dimensions:

~ 1.7 x 1 cm

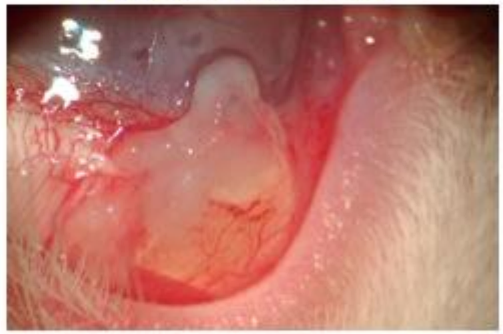
Baerveldt®
Pars Plana BG 102-350
Glaucoma Implant
(Abbott)

UNCD-Coated Commercial Ahmed Valve Implanted in rabbit eye

Patent Pending (2012)

Ahmed valve
(coated with UNCD)
(NO Bio-fouling) (NO fibrosis)
in rabbit eye)

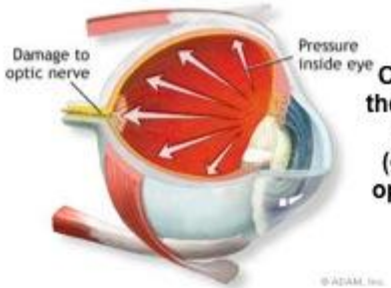
Uncoated Commercial Ahmed Valve Implanted in rabbit eye



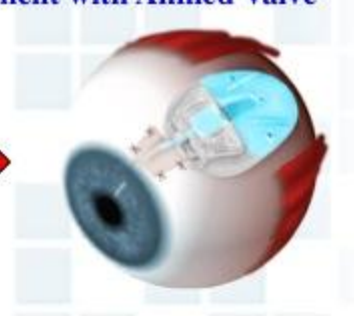
Ahmed valve
(silicone without coating)
(Bio-fouling (fibrosis) in rabbit eye)

Comparison of Ahmed Valve vs New UNCD-Coated Grid Draining Device for Treatment of Glaucoma (with U of Buenos Aires and Hospital Austral-Argentina)

Current Glaucoma Treatment with Ahmed Valve

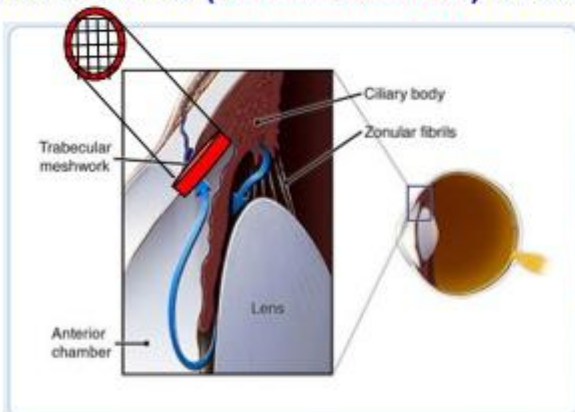


Overpressure inside the eye due to clogged trabecular region (glaucoma) leads to optical nerve damage and blindness

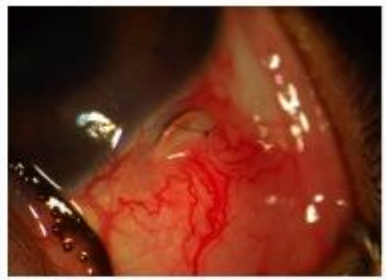


New UNCD-Coated Grid (3 mm diameter) Draining Concept

UNCD-Coated Cu Grid implanted in rabbit eye for ~ 12 months (NO bio-rejection at all)



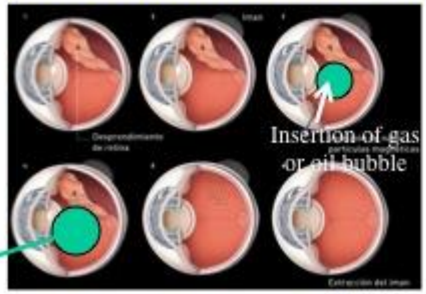
PATENT PENDING



Uncoated Cu Grid implanted in rabbit eye for ~ 24 hrs (strong bio-rejection)

Product in Advanced State of Development for Treatment of Retina Detachment (Pre-clinical Trials in Animals Close to Completion) (with UBA/Hospital Austral-Argentina)

Schematic Conventional Treatment for Retina Detachment



Gas or oil bubble
Push retina back

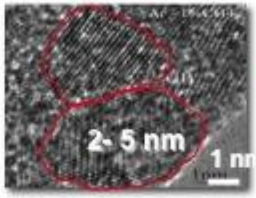
Gas or oil bubble injected in eye to push retina back into place

Serious problems:

- does not work for inferior detachment
- temporary impair vision
- low rate of success

New Treatment for Retina Detachment

Patent Pending (2012)



UNCD-coated magnet outside rabbit eye provides magnetic field

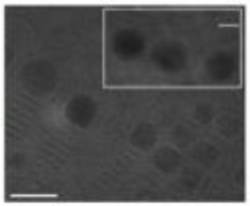


Imagen HRTEM
Nanopartículas
superparamagnéticas

Super-paramagnetic nanoparticles injected in rabbit eye attracted by magnetic field press retina back into place

Nanoparticles are latter absorbed

Advanced Diamond Technologies Development of UNCD Coating for Jarvik 2000 Heart Pump

UNCD® as an anti-thrombotic coating for ventricular assist devices

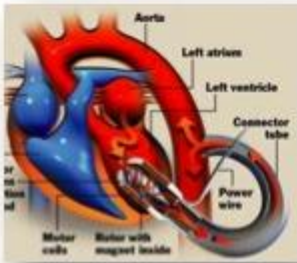
- Recent results show UNCD is highly effective at inhibiting adsorption of clot-forming proteins.
- UNCD can be further improved by adjusting its surface roughness and chemistry. Virtually zero adsorption observed in laboratory experiments.
- Current application of VADs is for temporary use (2 years) until patient can receive permanent heart replacement from donor.
- ADT is now working with Jarvik Heart to develop VADs that will last for ten years (chronic implants) based on combined wear resistance, anti-clot properties.
- **Started NIH SBIR I (2011) to finish development of UNCD-heart valve looking at FDA (1-2 years)**

OBI (Original Biomedical Implants)

Founders: O. Auciello, B. Geras, C. Davis, P. Gurman, A. Berra

UNCD Bio-coatings for Near Future Biomedical Products

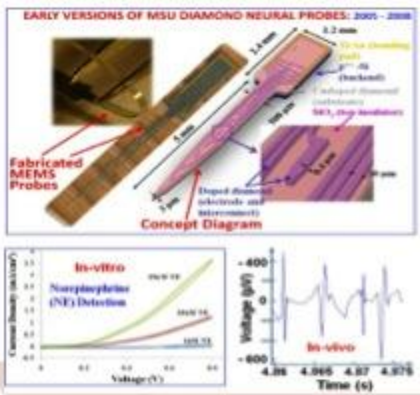
Stent



Artificial Hips

Artificial knees

New Polymer composite including diamond
(Patent Pending)



Neural Electrodes

£ 290

£ 300

£ 555

Dental Implant

The Future of Nanocarbon-Based Biotechnology

"Nanocarbon-Enabled Biomedical Implants"

Neural Disorders
(NINS Testbed)

MSU (with D. Aslam)

Flexible NCD electrode array

ANL (Auciello)

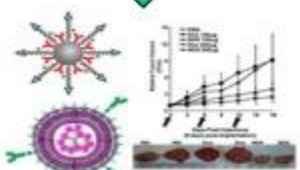
UNCD electrode array w/ 10 nm top diameter

Epilepsy Treatment by RFID controlled electrical pulses
(U of Colorado-Colorado Springs, (with Waziri)

(a) Chronic neural recording in epileptic rate and elimination of seizure via electric pulse controlled by RFID technology
(b) Intra-cortical insertion of a commercial platinum electrode array in an epileptic patient.

Cancer
(Functionalized NCD Nanoprticles
UCLA (with D. Ho)

1/3 lungs, 2 spine, 4 ribs, 5 aorta, 6 spleen, 7/8 kidneys, 9 liver.



Targeted nanodiamond delivery to reduce tumor size in mice.

Developmental Biology
ANL-MSU-NU

Embryonic Stem Cells Growth on UNCD and Differentiation

Conclusions

- THE FUNDAMENTAL AND APPLIED SCIENCE ON MULTIFUNCTIONAL OXIDES ULTRA-NANOCRYSTALLINE DIAMOND (UNCD) FILMS PROVIDE MATERIALS WITH UNIQUE COMBINATION OF PROPERTIES, INCLUDING EXCELLENT BIOCOMPATIBILITY FOR A NEW GENERATION OF INDUSTRIAL, MICRO/ NANOELECTRONICS, AND IMPLANTABLE BIOMEDICAL DEVICES

- THE NEXT BIG STEP FORWARD, UNDERWAY, IS TRANSLATING THE SCIENCE AND TECHNOLOGY OF MULTIFUCNTIONAL UNCD INTO A NEW GENERATION OF MULTIFUNCTIONAL DEVICES AND SYSTEMS FOR INSERTION INTO THE MARKET

- THE MARKET IS RIPE FOR A NEW GENERATION OF BIOCOMPATIBLE UNCD AND OXIDE-BASED IMPLANTABLE BIOMEDICAL DEVICES AND INDUSTRIAL COMPONENTS AND MICRO/NANOELECTRONIC DEVICES