SCIENCE AND TECHNOLOGY OF
ULTRANANOCRYSTALLINE DIAMOND FILMS:
APPLICATIONS TO MACRO, MICRO AND
NANODEVICES

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Industrial Partners
Motorola (DARPA-MEMS)
Second Sight (DOE-Artificial Retina)
Delphi (Fuel Cells)
INTEL (UNCD RF MEMS)
IPLAS (joint development microwave plasma system for large area UNCD films)
MATERIALS ISSUES FOR MACRO-DEVICES, MEMS/NEMS, BIODEVICES, AND BIOSENSORS

APPLICATION TO MECHANICAL PUMP SEALS

APPLICATION TO MEMS/NEMS; MATERIALS INTEGRATION, PROCESS DEVELOPMENT, AND FABRICATION

APPLICATION TO FUEL CELLS

APPLICATION TO BIOSENSORS

APPLICATION OF UNCD TO ARTIFICIAL RETINA AS AN EXAMPLE OF UNCD FOR BIODEVICES

CONCLUSIONS AND FUTURE DIRECTIONS
MATERIALS ISSUES FOR MACRO-DEVICES, MEMS/NEMS, BIODEVICES, AND BIOSENSORS
MOTIVATION FOR APPLICATION OF UNCD TO MACRO-DEVICES, MEMS, NEMS, FIELD EMISSION DEVICES, BIODEVICES, BIOSENSORS

- Si-MEMS
- Poor mechanical & tribological properties!
- Problem of Stiction!

SiC Seal for mechanical pumps exhibit high wear

Antistiction coatings may not help
- SAM need dilution; sensitivity to moisture
- limited thermal stability; HCl by-product H-C chain
- require insulating oxide; large # of fabrication steps
- survivability on surfaces with hard contact

Si or metal surface exhibit high Threshold V for electron emission

Biointercess of UNCD opens way to MEMS/NEMS biodevices (e.g. artificial retina)

Functionalization of UNCD opens way to MEMS/NEMS biosensors

NH₂ NH₂ NH₂

Diamond
# SELECTED PROPERTIES OF Si, SiC, AND DIAMOND

<table>
<thead>
<tr>
<th>Property</th>
<th>Silicon</th>
<th>Silicon Carbide</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Constant (Å)</td>
<td>5.43</td>
<td>4.35</td>
<td>3.57</td>
</tr>
<tr>
<td>Cohesive Energy (eV)</td>
<td>4.64</td>
<td>6.34</td>
<td>7.36</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>130</td>
<td>450</td>
<td>1200</td>
</tr>
<tr>
<td>Shear Modulus (GPa)</td>
<td>80</td>
<td>149</td>
<td>577</td>
</tr>
<tr>
<td>Hardness (kg/mm²)</td>
<td>1,000</td>
<td>3,500</td>
<td>10,000</td>
</tr>
<tr>
<td>Fracture Toughness</td>
<td>1.0</td>
<td>5.2</td>
<td>5.3</td>
</tr>
<tr>
<td>Flexural Strength (MPa)</td>
<td>127.6</td>
<td>670</td>
<td>2944</td>
</tr>
<tr>
<td>Friction Coefficient</td>
<td>0.4-0.6</td>
<td>0.2-0.5</td>
<td>0.01-0.04</td>
</tr>
<tr>
<td>Relative Wear Life</td>
<td>1.0</td>
<td></td>
<td>10,000</td>
</tr>
</tbody>
</table>
## DISTINGUISHING CHARACTERISTICS OF DIAMOND AND DIAMOND-LIKE CARBON FILMS

<table>
<thead>
<tr>
<th></th>
<th>Microcrystalline diamond (MCD)</th>
<th>Nanocrystalline diamond (NCD)</th>
<th>UltraNanocrystalline diamond (UNCD)</th>
<th>Diamond-Like Carbon (DLC)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Growth Species</strong></td>
<td>CH$_3$* H$_0$</td>
<td>CH$_3$* H$_0$</td>
<td>C$_2$</td>
<td>C</td>
</tr>
<tr>
<td><strong>Crystallinity</strong></td>
<td>Collumnar</td>
<td>Mixed diamond &amp; non-diamond phases</td>
<td>Equiaxed diamond</td>
<td>Mixed diam. amorphous &amp; amorph phases</td>
</tr>
<tr>
<td><strong>Grain size</strong></td>
<td>~0.5-10 μm</td>
<td>50-100 nm</td>
<td>2-5 nm</td>
<td>variable</td>
</tr>
<tr>
<td><strong>Surface roughness</strong></td>
<td>400 nm-1 μm rms</td>
<td>50-100 nm rms</td>
<td>20-40 nm rms</td>
<td>5 -100 nm rms</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1-30 nm rms</td>
<td></td>
</tr>
<tr>
<td><strong>Electronic bonding</strong></td>
<td>sp$^3$</td>
<td>up to 50% sp$^2$ (second phase)</td>
<td>2-5% sp$^2$ (40-80% at grain boundary)</td>
<td>up to 80% sp$^2$ up to ~40% sp$^2$</td>
</tr>
<tr>
<td><strong>H content</strong></td>
<td>&lt;1%</td>
<td>&lt;1%</td>
<td>&lt;1%</td>
<td>15 - 60%</td>
</tr>
</tbody>
</table>
APPLICATION TO MECHANICAL PUMP SEALS
SiC CHEMICAL PROCESS PUMP SEALS

- Chemical Process Industries
- Pulp and Paper Industries
- Petroleum refineries, gas plants
- Nuclear power generating plants

With development of new applications and Technology.....

- More demands on operating limits
- Ability to perform better in chemical harsh environments
- Uninterrupted service life,
- Increased energy savings
- Reduced cost of maintenance

Search for New Materials With Superior Mechanical, Tribological and Chemical Properties → UNCD
UNCOATED AND UNCD-COATED SEALS (After 21 days Test)

Uncoated SiC Seal

UNCD-coated SiC Seal

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

~0.8 um wear on SiC
No wear
TORQUE REDUCTION IN UNCD-COATED SEALS

Average Torque Vs Face Load

- Uncoated SiC Seal
- UNCD coated SiC seal

Face Load (lb):

Torque (inch-lb):

50 72.5 95 117.5 140

5 5 5 5 5
TORQUE REDUCTION IN UNCD-COATED SEALS

- Summary of UNCD coated SiC tests against a carbon counterface for long time duration under real industrial conditions:
  - NO measurable wear OR delamination on UNCD coated SiC Seal after 21 days test
    - Significant improvement in the operational life-span of the seal, reduced cost of maintenance, reduction in down-time
  - Reduction in torque by 5-6 times
    - increased energy savings
  - No leakage during test
    - NO release of hazardous materials into the environment, Environment friendly!

UNCD is promising material for seal applications!
APPLICATION TO MEMS/NEMS; MATERIALS INTEGRATION, PROCESS DEVELOPMENT, AND FABRICATION
SELECTIVE DEPOSITION OF UNCD FOR FABRICATION OF MEMS COMPONENTS

## COMPARISON OF DIAMOND AND DIAMOND-LIKE FILM CHARACTERISTICS FOR MEMS APPLICATIONS

<table>
<thead>
<tr>
<th></th>
<th>MCD</th>
<th>NCD</th>
<th>UNCD</th>
<th>ta- C</th>
<th>ta- C:H</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Growth Species</strong></td>
<td>CH$_3$</td>
<td>CH$_3$</td>
<td>C$_2$</td>
<td>C</td>
<td>C</td>
</tr>
<tr>
<td><strong>COF</strong></td>
<td>0.1 (polished)</td>
<td>unknown</td>
<td>0.04 (as-deposited)</td>
<td>0.1</td>
<td>0.06</td>
</tr>
<tr>
<td><strong>Conf. Dep. on High Asp. Ratio Features</strong></td>
<td>poor</td>
<td>good</td>
<td>excellent</td>
<td>unknown</td>
<td>unknown</td>
</tr>
<tr>
<td><strong>Internal stress</strong></td>
<td>high</td>
<td>unknown</td>
<td>low (as-deposited)</td>
<td>high</td>
<td>unknown (as-deposited)</td>
</tr>
<tr>
<td><strong>Scaling to large area</strong></td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td><strong>Hardness</strong></td>
<td>87 G Pa</td>
<td>unknown</td>
<td>97 G Pa (practically no dependance on indentation dept)</td>
<td>~80 G Pa</td>
<td>≤ 40 G Pa (substantial hardness decrease w/ indentation dept)</td>
</tr>
</tbody>
</table>
FABRICATION OF 2-D UNCD-MEMS STRUCTURES

UNCD - strain gauge ~ 100 nm resolution

UNCD straight released membranes, cantilevers and 2 - D structures indicate low UNCD stress

UNCD Nanocantilevers 200 x 200 nm
FABRICATION OF UNCD-MEMS STRUCTURES TO MEASURE MECHANICAL AND TRIBOLOGICAL PROPERTIES AT THE MEMS SCALE

2-D structures to measure UNCD film stress at MEMS scale (50-100 MPa)

Water contact angle (\(\sim 85^\circ\)) for a UNCD surface exposed to lab environment

Comb drive structure to measure UNCD wear at the MEMS scale (with M. Dugger-SNL)
FABRICATION OF 3-D UNCD STRUCTURES

Conformal growth of UNCD on Si post

Ion bombardment of top of UNCD-coated Si post etches UNCD edge faster than flat

Selective chemical etching of exposed edge of Si core produces UNCD top and separated ring resulting in UNCD ring structure after further etching

Conformal UNCD Coating on Sacrificial Layer

Conformal UNCD Coating on High-aspect Ratio Si Tips

Selective chemical etching of Si core produces hollow 3-D UNCD structure
ENHANCED ELECTRON EMISSION FROM UNCD-COATED Si PLANAR SURFACES AND FIELD EMITTER TIPS

MCD-coated Si tips

UNCD-coated Si tips

J vs. E curves for uncoated and UNCD-Coated Si tips and flat substrate

Emission threshold voltage vs. film thickness for UNCD-coated Si Tips
FABRICATION OF UNCD-BASED MICROTURBINE FOR MICROFUIDICS

Fabrication Process

With Mike Moldovan (ANL, now NU)
CLAMPED-CLAMPED BEAM UNCD RESONATOR

SEM pictures of clamped-clamped UNCD beam

RF RESPONSE FOR UNCD RESONATORS

With P. Zurcher (Freescale)
ALTERNATIVE RESONATOR ARCHITECTURES

- Clamped-clamped beam resonator: (Flexural Fundamental mode: **433 MHz Si-based resonator demonstrated**

- Higher modes enable higher frequencies (**quadruple** frequency by **3rd-mode** operation)

- **High Q**, very low power: Potential for higher performance filters, oscillators, etc.

- **High Frequency (1.5 GHz)-High Q (~14,000) NCD disc resonator demonstrated** (Nguyen et al. 04)
OXIDE/UNCD INTEGRATION FOR MEMS/NEMS/ELECTRONICS
MULTIFUNCTIONAL DEVICES

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

BST/oxygen barrier/UNCD: barrier layer enables oxide/diamond integration

PbZrxTi_{1-x}O_3/Pt/barrier/UNCD: barrier layer enables Piezo/diamond integration

Lack of saturation due to thick film

Polarization (\( \mu \text{C/cm}^2 \))

Voltage (V)

Current (mA)

Volts (V)

Gate leakage
INTEGRATION OF HIGH-K DIELECTRICS AND UNCD FOR MISFET DEVICES

All Metal Contacts are Ohmic

Contact Behavior on Same 20%N UNCD Film


In progress:
Graded doping
Better Gate (ALD Al2O3, etc.)
Photolithography

Collaboration with R. Divan, J. Elam, D. C. Mancini

Simple shadowmasking with non-optimized oxide gate

Lack of saturation due to thick film

APPLICATION TO MICRO/NANOPROBES
Microfabrication of Diamond (UNCD) AFM Tips

Microfabrication of Diamond AFM Tips

Ox., M₁, KOH
Ox. Sharpening
UNCD, Al
M₂, Al etch (wet)
UNCD etch (RIE)
Al removal
M₃, Ox. etch back side
Cr/Ni, M₄, Ni, Cr etch

SU-8, M₅
Ni electroform
Lap/Polish
SU-8 removal
KOH etching
Ox etch


With H. Espinosa’s group (NU)
UNCD Conductive tips

Au layer sputter coated on backside of cantilever to provide good reflection for AFM scanning

Details in:

With H. Espinosa’s group (NU)
APPLICATION TO FUEL CELLS
Materials Issues for Fuel Cells

- Problems with electrodes in PEM-based hydrogen or direct-methanol fuel cells:
  - Pt is expensive
  - Pt also corrodes, and is easily poisoned
    - **Pt-based alloys: Pt-Ru-Os-Ir**
  - Energy efficiency less than the 80% ideal due to slow reaction kinetics

- Need to improve catalytic activity
  - Use catalyst support: High surface area, conducting, corrosion resistant

- Carbon-based supports
  - Sp²-bonded carbons: graphitic, glassy carbon, aerogels
  - Graphitic carbon susceptible to corrosion, not dimensionally stable
    - **CO₂ evolution poisons Pt catalyst**
Material Solution for Fuel Cell Electrodes and Approach

- Use high-performance diamond coating integrated with appropriate support material
  - UNCD (Ultrananocrystalline Diamond) coating on appropriate conductor platform
    - Corrosion resistant
    - Conducting
    - Dimensionally stable

- UNCD/metal composite electrodes

- Partnering with Industry
  - Preliminary work underway
  - Initial results encouraging
UNCD AS CORROSION RESISTANT COATING FOR FUEL CELL ELECTRODES AND MEMBRANES

Sample#3 CV abuse

RESISTANCE VS LOAD FOR UNCD FUEL CELL ELECTRODE
APPLICATION TO BIOSENSORS
Combination of UNCD surface functionalization and MEMS devices leads to biosensors.
UNCD-MEMS/NEMS BIOSENSORS BASED ON ELECTRONIC DETECTION

FluorImager confirms the hybridization.

Impedance measurement

With Hamer’s Group (UW-Madison)
APPLICATION OF UNCD TO BIOELECTRODES
AND BIOMOLECULAR INTERFACES

- Need to understand biomolecular interfaces and the mechanism of nerve stimulation
  - Changes in membrane permeability due to electrical stimulation
    - Electrochemical studies
      - Impedance, dielectric spectroscopies
  - Protein conformational changes on diamond/UNCD surfaces induced by applied electric fields
    - Diffuse scattering at the APS
  - Structure, binding, and other properties of biomolecule/nanostructure interfaces
    - Quantum chemical calculations
      - Nanoscience integrated computational environment (NICE) at MCS

Nerve Stimulation

UNCD
E-field

Biomolecule/UNCD interface
APPLICATION OF UNCD TO ARTIFICIAL RETINA AS AN EXAMPLE OF UNCD FOR BIODEVICES
TOWARDS AN ARTIFICIAL RETINA FOR THE BLIND!

RETINA DEGENERATION:
A GLOBAL PROBLEM!

About 25 million people worldwide
RETINA DEGENERATION: What is it?

- **RETINITIS PIGMENTOSA** (begins with vision loss in the peripheral retina)
  - **NUMBER OF BLIND PEOPLE IN THE USA**
    - More than 1 million people in the USA are blind
    - About 12 million people in the USA suffer from irreversible vision impairment
    - About 100,000 blind school age children

- **EARLY ONSET MACULAR DEGENERATION** (loss of central (macular)vision)
  - Children or young adults: ~25,000 to 50,000 in the USA
WHERE IS THE RETINA AND WHAT IT DOES

CONE PHOTORECEPTOR

CYLINDER PHOTORECEPTOR

TO BRAIN FOR IMAGE FORMATION
ARTIFICIAL RETINA BASED ON IMPLANTABLE MICROCHIP

Argonne National Laboratory’s ultrananocrystalline diamond hermetic, corrosion resistant, bio-inert coating technology enables implantation of Si-based microchip onto the human retina via UNCD 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.

1 \( \mu m = 0.0001 \) cm

UNCD microtips could be used for corrosion resistant electrode array

University of Southern California (Doheny Eye Institute)
North Carolina State University
Argonne, Lawrence Livermore, Los Alamos,
Oak Ridge and Sandia National Laboratories
Second Sight
MATERIALS ISSUES FOR ARTIFICIAL RETINA (UNCD exhibit these properties)

- **Hermetic microchip coating**
  - High mechanical strength
  - Low Stress
  - Impermeability
  - High chemical inertness
  - High thermal stability
  - Biocompatible

- **Electrode array**
  - High electrical conductivity
  - High chemical inertness during electrical current transport
  - High mechanical strength
  - High thermal stability
  - Conformal coating of high or low-aspect ratio microtips
  - Bio-functionalization of surface
  - Biocompatible

**Argonne Contribution to the DOE Retina Program**

- **Present**
  - Research and development of UNCD hermetic coating for microchip

- **Future**
  - Research on UNCD/metal composite electrodes
  - Research on functionalized UNCD electrodes
  - Scale up of UNCD film growth process for device fabrication
Good conformal deposition of UNCD on microcircuit features ALL DEVICES FUNCTIONAL AFTER UNCD DEPOSITION
HERMETIC UNCD COATING AND ELECTROCHEMICAL TEST SET UP

Cross-section of specimen

UNCD on Si

Reference electrode
Ag/AgCl

Counter electrode
Pt

5% HF
or 0.5M PBS

Power

V

i

Office of Science U.S.
Department of Energy
UNCD coating grown with Ar/CH₄ plasmas exhibit excellent hermeticity!!!, but leakage current is still high for application to artificial retina!

Comparison of UNCD coated Si samples

UNCD coating deposited on Si at different substrate temperature
Hydrogen incorporation into grain boundaries satisfy dangling bonds resulting in reduction of leakage current.
Optimization of $H_2$ Content in Plasma Results in UNCD Coatings with Lower Leakage Current

UNCD deposited with 2 % Hydrogen content in plasma at different substrate temperatures

UNCD deposited at 400 °C with different hydrogen content in plasma

Low hydrogen content in plasma and low deposited temperature results in higher hydrogen incorporation into UNCD coatings and decrease in leakage current to the range required for hermetic coating for artificial retina

IN VIVO BIO-INNERTNESS TEST FOR HERMETIC UNCD COATINGS

• 5 x 5 mm² Si chips wholly coated with UNCD were implanted into rabbit eyes for bio-innertness test (6 months).

• Surface analysis of UNCD implant showed no degradation nor reaction of UNCD with the eye saline solution suggesting that UNCD might be bioinert in the eye environment.
AFM ANALYSIS OF UNCD SURFACE IMPLANTED IN RABBIT EYE

AFM topographical image of UNCD surface exposed to rabbit eye for 6 months

AFM magnified view

AFM force curves show that there is no soft matter on the surface of the UNCD exposed to rabbit eye
UNCD AS AN ELECTRODE MATERIAL?

Highly conductive (semimetallic UNCD doped with nitrogen) or with embedded Pt nanoparticles
CONCLUSIONS

- VARIOUS APPLICATIONS HAVE BEEN DEMONSTRATED FOR UNCD COATINGS FOR FABRICATION OF MULTIFUNCTIONAL DEVICES

- THE TWO FRONT RUNNER APPLICATIONS ARE:
  - HARD, LOW FRICTION, CORROSION-RESISTANT COATING FOR MECHANICAL PUMP SEALS (ANL AND ADT ARE WORKING WITH A COMPANY THAT CONTROLS 95% OF THE WORLD MARKET)
  - HERMETIC, BIO-INNERT/BIOCOMPATIBLE COATING FOR MICROCHIP ENCAPSULATION FOR AN ARTIFICIAL RETINA TO RESTORE SIGHT TO PEOPLE BLINDED BY RETINA DEGENERATION

FUTURE DIRECTIONS

- OPTIMIZATION OF FUNCTIONAL UNCD-MEMS DEVICES (e.g., DEMONSTRATION OF RF SWITCHES AND RESONATORS)
- DEMONSTRATE BIOSENSOR
- DEMONSTRATE OXIDE/UNCD MEMS/NEMS DEVICES
THE FUTURE AT ARGONNE:
Welcome to the Center for Nanoscale Materials (CNM)!

- Create and study novel multifunctional nanoscale materials and structures
- Access APS, Intense Pulsed Neutron Source & Microscopy Center

CNM Scientific Themes

- **BioNanocomposites**
  
  D. Tiede, T. Rajh, M. Firestone,
  Electronic and Magnetic Materials & Devices
  S. Bader, O. Auciello
  S. Streiffer, A. Hoffman,

- **Nanophotonics**
  
  G. Wiederrecht, S. Gray

- **Theory and Simulation**
  
  S. Gray, P. Zapol

- **Nanopatterning**
  
  L. Ocola, D. Mancini

- **X-Ray Imaging/Nanoprobe**
  
  J. Maser, B. Stephenson

Open for users beginning 2007, Universities and Industry
Collaborations open NOW!

www.nano.anl.gov

- $36 mill from Illinois for building
- $36 mill from DOE for equipment
- $18 mill/ Y operating budget from 2007

Unique 30 nm diameter synchrotron X-ray beam

MPCVD for carbon

E-beam Lithography

LEO 1560XB CrossBeam

FIB/SEM