# Electrochemical Properties of Nitrogen-doped Ultrananocrystalline Diamond (UNCD)

D.M Gruen, J.A. Carlisle, M.Q. Ding, O. Auciello, G.W. Swain (Michigan St. U.)

## SCIENTIFIC ACHIEVEMENT

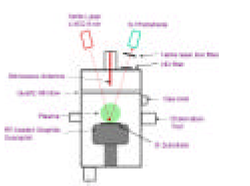
Boron-doped microcrystalline diamond film electrochemical electrodes have been known for some time to have superior properties because they span a potential window of ~ 4 eV in aqueous solutions compared, for example, to platinum electrodes with a potential span of ~ 1.5 eV. The reason is that diamond electrodes have a high overpotential for the evolution of both $H_2$ and $O_2$. The morphology of microcrystalline diamond films, however, is such that thicknesses of several microns are required to obtain pinhole-free films, which in any event do not conformally coat microtip electrode arrays required for certain biomedical and sensor applications. The recent development at Argonne of n-type-doped ultrananocrystalline diamond films displaying conductivities that rival those of boron-doped microcrystalline films suggests the possibility of using this unique material as electrochemical electrodes, which can overcome the limitations enumerated above.

We have recently demonstrated that nitrogen-doped ultrananocrystalline diamond (UNCD) thin films can in fact function as excellent electrodes. Electrically conductive UNCD films (~1 µm thick) were deposited on conducting Si and W substrates from $CH_4/N_2/Ar$ gas mixtures using microwave plasma CVD. Such films are continuous even at thicknesses of ~100 nm. The grain size is 3 to 10 nm, and the grain boundaries are 0.2 to 0.5 nm wide (two carbon atoms). Nitrogen appears to substitutionally insert into the grain boundaries and the film concentration (~$10^{20}$ atoms/$cm^3$) scales with the $N_2$ added to the source gas mixture up to about the 5% level. The nitrogen-doped films are void of pinholes and cracks, and electrically conducting due in part to the high concentration of nitrogen impurities and or the nitrogen-related defects ($sp^2$-bonding). The films possess semi-metallic electronic properties over a potential range from at least -1.5 to 1.0 V *vs.* SCE. The electrodes, like boron-doped microcrystalline diamond, exhibit a wide working potential window, a low background current, and high degree of electrochemical activity for redox systems such as $Fe(CN)_6^{-3/-4}$, $Ru(NH_3)_6^{+3/+2}$, $IrCl_6^{-2/-3}$, and methyl viologen ($MV^{+2/+}$). More sluggish electrode kinetics are observed for 4-methylcatechol, presumably due to weak adsoption on the surface. Apparent heterogeneous electron transfer rate constants of $10^{-2}$ to $10^{-1}$ cm/s are observed for $Fe(CN)_6^{-3/4}$, $Ru(NH_3)_6^{+3/+2}$, $IrCl_6^{-2/-3}$, and $MV^{+2/+}$ at films without any pretreatment.

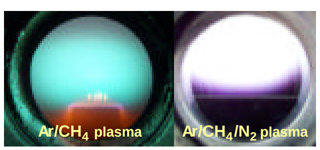
## SIGNIFICANCE

The full significance of this result is realized when one considers that diamond is a highly biocompatible material. This result thus opens the door for a number of potential applications of UNCD as a *biochemical electrode*. UNCD should show several advantages over platinum electrodes (which lead to redox reactions) in a number of biological contexts, such as nerve stimulation. Work just starting in our group is a broad collaborative project funded by DOE biomedical engineering program to develop an *artificial retina*, with the key challenge being the development of biocompatible electrodes to stimulate ganglion and bipolar nerve cells in the retina in people suffering from retinitis pigmentosa without leading to deleterious redox reactions (UNCD has a high overpotential for O2, H2 evolution), degradation of the electrode, or damage to the nerve cells. UNCD may also be used as a hermetic coating for the retinal implant developed in this project.

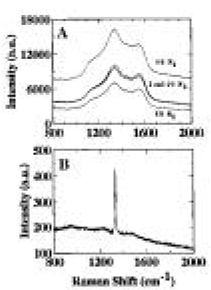
## Synthesis of Nitrogen-doped Ultrananocrystalline Diamond

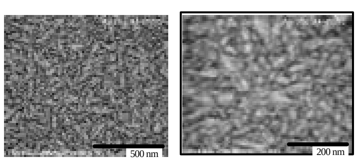


Microwave $C_{60}$/Ar or $CH_4$/Ar plasmas are used to produce undoped UNCD films




Nitrogen is added to Ar/CH4 plasmas to produce UNCD thin films with greatly enhanced conductivity

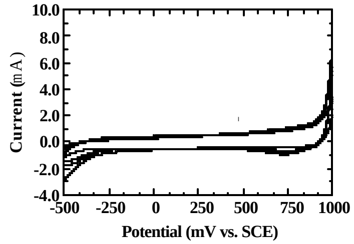



High-resolution SEM micrographs of nitrogen-doped UNCD thin films. Nitrogen-doped UNCD films are pinhole free and can function as an electrochemical electrode as thicknesses much less than boron-doped Microcrystalline diamond.

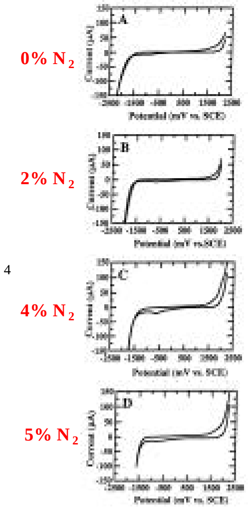
Visible Raman spectra of (A) nanocrystalline diamond films deposited from 0, 2, 4, and 10% $N_2$ in the source gas mixture and (B) a microcrystalline, boron-doped diamond film.

## Electrochemical Properties of Nitrogen-doped UNCD



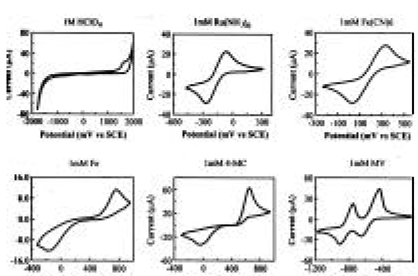

Cyclic voltammetric *i-E* curves for nanocrystalline diamond thin films deposited from 1% CH 4 /1% N 2 /98% Ar, 1% CH 4 /2% N 2 /97% Ar, 1% CH 4 /4% N 2 /95% Ar and 1% CH 4 /5% N 2 /94% Ar. Electrolyte: 1 M KCl. Scan rate: 0.1 V/s.

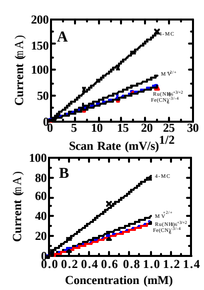
- Ultrananocrystalline diamond (UNCD) films doped with nitrogen are highly conductive and function as superb electrochemcial electrodes:
  - High overpotential for $H_2$ and $O_2$ evolution
  - Wide potential window (4 eV in aqueous soltuion desirable for inducing action potential in nerve tissue)
  - Low thickness (100 nm) for pinhole free, conformal coatings on microtip arrays




Cyclic voltammetric *i-E* curves for nanocrystalline diamond thin films deposited from (A) 1% CH 4 /99% Ar, (B) 1% CH 4 /2% N 2 /97% Ar, (C) 1% CH 4 /4% N 2 /95% Ar, and (D) 1% CH 4 /5% N 2 /94% Ar. Electrolyte: 0.1 M HClO 4 . Scan rate: 0.1 V/s.

## Cyclic Voltammetric Data for Nitrogen-doped UNCD



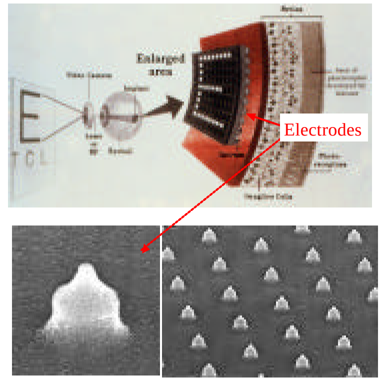



- UNCD electrodes exhibit a wide working potential window, a low background current, and a high degree of electrochemical activity for redox systems such as $Fe(CN)_6^{-3/-4}$, $Ru(NH_3)_6^{+3/+2}$, $IrCl_6^{-2/-3}$, and methyl viologen ($MV^{+2/+}$).
- Heterogeneous electron transfer rate constants of $10^{-2}$ to $10^{-1}$ cm/s are observed at films without any pretreatment.

Cyclic voltammetric data for nanocrystalline diamond thin films. (A) Plots of the oxidation peak current *vs.* the scan rate 1/2 . Analyte concen-tration: 1 mM. Electrolyte: 1 M KCl. (B) Plots of the oxidation peak current *vs.* the analyte concentration. Electrolyte: 1 M KCl. Scan rate: 0.1 V/s.

## Future Work: UNCD as Bioelectrodes for Artifical Retinas [DOE Biomedical Engineering Project]

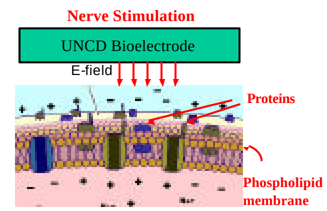
- Nerve Stimulation via implanted retinal chip key issue to be resolved for artificial sight
- Platinum electrodes do not work (redox reactions cause degradation)
- Ultrananocrystalline diamond may offer solution to electrode problem
- Advantages of UNCD:
  - Electrically conductive (via nitrogen-doping)
  - High overpotential for $O_2$, $H_2$ evolution
  - Resistant to corrosion
  - Biocompatibility



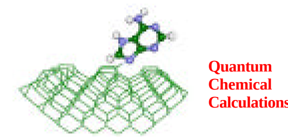

UNCD-coated microtip arrays

## Key Challenge: Fundamental understanding of biomolecular/inorganic interfaces

- Clear need to understand biomolecular interfaces and the mechanism of nerve stimulation on a more fundamental level
  - 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




Biomolecule/UNCD interface




## CONCLUSIONS

Electrically conductive nanocrystalline diamond films (approximately 750 to 1000 nm thick) were deposited on conducting Si and W substrates from $CH_4/N_2$ /Ar gas mixtures using plasma-enhanced chemical vapor deposition. Such films are continuous over the surface and nanometer smooth. The grain size is 3 to 10 nm, and the grain boundaries are 0.2 to 0.5 nm wide (two carbon atoms). Nitrogen appears to substitutionally insert into the grain boundaries and the film concentration ($10^{20}$ atom/$cm^3$ ) scales with the $N_2$ added to the source gas mixture up to about the 5% level. The nitrogen-incorporated films are void of pinholes and cracks, and electrically conducting due in part to the high concentration of nitrogen impurities and or the nitrogen-related defects ($sp^2$ bonding). The films possess semimetallic electronic properties over a potential range from at least 21.5 to 1.0 V *vs.* SCE. The elec-trodes, like boron-doped microcrystalline diamond, exhibit a wide working potential window, a low background current, and high degree of electrochemical activity for redox systems such as $Fe(CN)_6^{-3/-4}$, $Ru(NH_3)_6^{+3/+2}$, $IrCl_6^{-2/-3}$, and methyl viologen ($MV^{+2/+}$). More sluggish electrode kinetics are observed for 4-methylcatechol, presumably due to weak adsorption on the surface. Apparent heterogeneous electron transfer rate constants of $10^{22}$ to $10^{21}$ cm/s are observed for for all the above redox systems at films without any pretreatment.

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