

Surface Functionalization of Ultrananocrystalline
Diamond Thin-Films: Toward Biomedical Devices
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There has been a growing interest in using hard carbon thin-films, diamond based materials in particular, as impervious coatings for Si based biomedical microelectromechanical systems (bioMEMS). Diamond materials, well known for their high mechanical and chemical robustness and low permeability, are also biocompatible and bioinert, able to fulfill rigorous biocompatibility and long-term operation stability requirements for biomedical devices.

We have been working on a new form of diamond film — ultrananocrystalline diamond, or UNCD.¹ UNCD film, typically grown using microwave plasma chemical vapor deposition (MPCVD) from Ar-rich plasma, consists of crystalline grains of 3-5 nm in size, separated by atomically abrupt (0.5 nm wide), π -bonded grain boundaries (Fig. 1). UNCD differs from other types of diamond materials in low as-deposited stress, low surface roughness and high conductivity while doped with nitrogen. We have demonstrated that UNCD can be used as hermetic coatings to encapsulate silicon chip for retinal implants.² On the other hand, Microfabricated UNCD MEMS can also serve as a platform for biosensors.^{2,3}

Most bioMEMS applications require surface functionalization of microfabrication materials to either promote specific biomolecule interactions or alleviate biofouling. Much work has been carried out to modify diamond surfaces using procedures including plasma treatment, UV irradiation and electrochemical reactions. We present here our attempts to electrochemically modify N-doped UNCD surfaces. The approach involves electrochemical reduction of aryl diazonium cations, which has been successfully employed to modify sp^2 carbon based materials.⁴ Different aryl derivatives can be tethered on UNCD surface via covalent C-C bonding. They serve as a linker for further attachment of biomolecules.

Fig. 2 shows the electrochemical reduction of 3,5-dichlorophenyl diazonium salt (DCPDS) at 5% N-doped UNCD. The experiment was performed in 10 mM DCPDS + 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB), with acetonitrile as the modification medium (nonaqueous). The first sweep gave an irreversible reduction peak at ca. 0.05 V, corresponding to the formation of dichlorophenyl radicals. The cathodic peak decreased to zero upon repetitive scans, indicating the electron transfer was inhibited by grafted dichlorophenyl group.

XPS spectra confirmed the grafting of aryl group to UNCD surface (Fig. 3). The XPS spectrum between 192 and 208 eV showed only noise before the electrochemical reduction. After five potential sweeps, Cl_{2p} peak was observed at about 201 eV. The Cl/C ratio is about 14%.

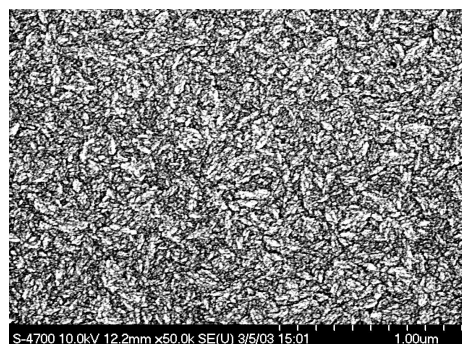


Figure 1. Typical SEM image of UNCD film deposited on single crystal silicon substrate.

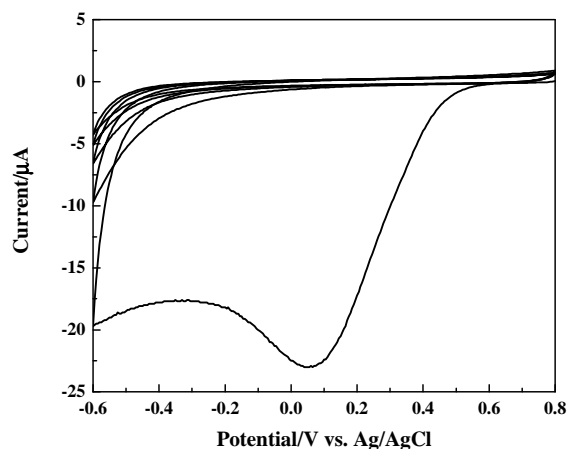


Figure 2. Cyclic voltammetric i-E curves of a UNCD film in 10 mM DCPDS + 0.1 M TBATFB + CH_3CN .

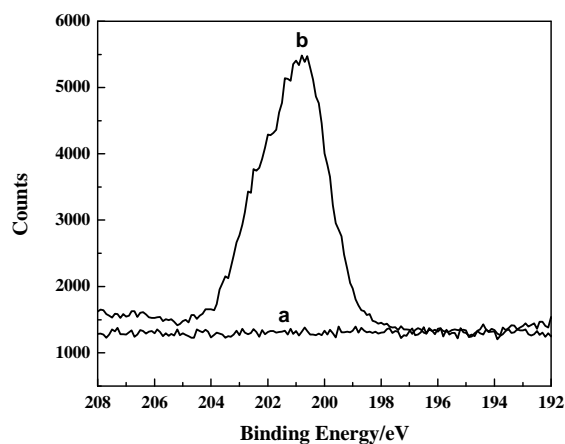


Figure 3. XPS spectra of a UNCD film before (a) and after (b) electrochemical reduction of DCPDS.

References:

1. D. M. Gruen, *Annu. Rev. Mater. Sci.*, **29**, 211 (1999).
2. J. A. Carlisle and O. Auciello, *Interface*, **12**, 28 (2003).
3. W. Yang, O. Auciello, J. E. Buttler, W. Cai, J. A. Carlisle, J. Gerbi, D. M. Gruen, T. Knickerboker, T. L. Lasseter, J. N. Russell Jr., L. M. Smith, and R. J. Hamers, *Nature-Materials*, **1**, 253 (2002).
4. A. J. Downard, *Electroanalysis*, **12**, 1085 (2000).