# Chemical and Biochemical Modification of Nanocrystalline Diamond Surfaces

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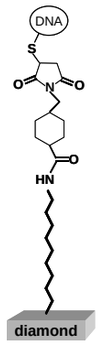
Recent developments have placed increase emphasis on the development of real-time, continuous-monitoring chemical sensor technologies. While the unusual electronic, mechanical, and thermal properties of diamond have received great attention, the high chemical and electrochemical stability of diamond make it an attractive substrate for biological sensing.

We have developed new methods for chemically- and biochemical modification of diamond surfaces and have investigated the stability and selectivity of the resulting interfaces.[1,2] Two types of diamond were investigated: (1) Nanocrystalline diamond[3] (NCD) produced via microwave discharge in a $H_2$-rich environment, and (2) Ultrananocrystalline diamond[4] (UNCD), produced in a $H_2$-deficient atmosphere. Diamond samples were first treated in a hydrogen microwave plasma to produce H-termianted diamond surfaces. These surfaces were then functionalized using a photochemical reaction in which the diamond is covered with a suitable organic alkene that also bears a protected functional group (such as an amine group).[5] Upon illumination at 254 nm, these molecules link to the surface primarily through the alkene (C=C) group. This method provides a means of producing diamond surfaces that are covalently linked to a homogeneous layer of amine groups, which can then be used as the starting point for attachment of DNA, proteins, and other biological molecules.

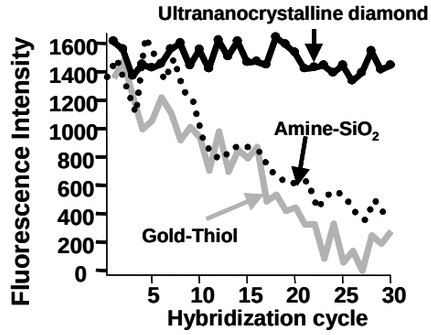
X-ray photoelectron studies were performed to probe the chemical changes occurring at the surface. These studies show that the photochemical functionalization is self-terminated, producing a dense monolayer film with approximately one amine group per four carbon atoms at the surface.

Once the diamond is functionalized with amine groups, standard biochemical methods (optimized for surface conditions) can be used to covalently link DNA to the diamond substrate.




To test the ability of the DNA-modified diamond surfaces to discriminate between different sequences, experiments were conducted in which diamond substrates were functionalized with two different sequences of DNA, and the hybridization of fluorescently-labeled DNA in solution to the surface-bound sequences was investigated using fluorescence imaging. These experiments show that DNA-modified diamonds surfaces show a high degree of selectivity.

For real-time, continuous biosensing, stability of the biologically-modified surfaces is of paramount importance. Most alternative substrates such as gold and glass exhibit serious degradation when repeated hybridized and denatured. However, we have exposed samples of diamond to more than 30 repeated cycles, with no measurable decrease in performance. The graph below shows a comparison of several different materials that were covalently linked to DNA using nearly identical chemistry. While amine-terminated glass (Corning GAPS II) and amine-modified gold surfaces both show a rapid decrease in fluorescence intensity upon repeated hybridization-denaturation cycles, DNA-modified ultrananocrystalline diamond samples show no change.




Similar results have been obtained on both free-standing and thin-film nanocrystalline diamond films prepared in a hydrogen-rich atmosphere.

The high stability of diamond, when exposed to aqueous environments for long periods of time, makes it ideally suited for biological sensing applications. Diamond also has a very wide region of electrochemical stability.[6] This characteristic also makes diamond an an ideal candidate for direct electronic sensing of biological binding processes. To test this, we have fabricated a microfluidic cell that, when combined with an impedance spectroscopy system, can be used to probe the changes in electrochemical impedance of the DNA-modified diamond surfaces. If highly-conductive diamond is used, there is an easily-measurable change in the dielectric properties of the interface upon hybridization. While the mechanism of this is not yet completely understood, the results demonstrate the feasibility of using diamond thin films as the basis for highly-stable biochemical sensors able to achieve direct electronic detection of biological binding events.

Collaborators on this work include W. Yang, W. Cai, T. Knickerbocker, T. Lasseter, T. Strother, and L.M. Smith of the University of Wisconsin-Madison, , D.M. Gruen and J.A. Carlisle of Argonne National Laboratory, and J.N. Russell, Jr. and J.E. Butler of the Naval Research Laboratory

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