SCIENCE AND TECHNOLOGY OF ULTRANANOCRYSTALLINE DIAMOND FILMS FOR MULTIFUNCTIONAL MEMS/NEMS DEVICES

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The objectives of this project are to investigate microstructure-mechanical-electronic transport property relationships of a new multifunctional material designated as *ultrananocrystalline diamond* (UNCD), and to utilize this material in microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS). Through interdisciplinary research and educational efforts of the team members from Northwestern University (NU), University of Illinois at Chicago (UIC) and University of Missouri-Columbia (UMC), in collaboration with Argonne and Sandia National Laboratories (ANL and SNL), an integrated experimental, analytical and computational program has evolved with the following approaches:

1. Scan probe microscopy approaches, including conductive atomic force microcopy and ultra high vacuum scanning tunneling microscopy/spectroscopy, for nanoscale characterization of surface structure and conductivity of UNCD films, that will enable the microstructure to be ascertained for films made with various dopings;
2. Investigation of mechanical properties, such as Young's modulus, hardness, plasticity, and fracture, of UNCD with varying degrees of doping at the microlevel using a recently developed membrane deflection experiment, and at the nanolevel by means of a novel MEMS loading device that can operate within various microscopes; and
3. Multiscale model-based simulation of the film deposition and growth process, and the relationship between microstucture and electro-mechanical properties of UNCD films, by using combined ab initio, molecular dynamics, kinetic Monte Carlo and continuum methods.

The new methods of chemical vapor deposition (CVD) recently developed by this team make possible the manufacturing of the UNCD films that exhibit *unique and outstanding properties* such as high hardness, high fracture strength, high Young's modulus, extremely low friction coefficient and high wear resistance, low residual stress in as-deposited thin films, unique field electron-emission properties, a wide range of conductivity controlled by microstructure and doping, and highly conformal films, which are all critical to MEMS/NEMS applications. The integrated experimental, analytical and computational study of the unique properties of UNCD films, via the above interdisciplinary approaches, is the first of its kind and we expect it to make an important intellectual impact on the understanding of the relationship between grain size-grain boundary chemistry and *electro-mechanical* properties of UNCD at the nanoscale. In particular, the atomic-scale information suitable to unraveling the electronic conduction mechanism in UNCD and the effect of its microstructure on this phenomenon could be positively used to design MEMS/NEMS devices. The preliminary results obtained from this project since it was funded in September 2003 are summarized as follows.

Nanoscale Characterization of UNCD Film Growth and Properties
(Auciello's, Espinosa's and Hersam's Groups)
The research focus has been on growing undoped and nitrogen-doped UNCD thin films using microwave plasma CVD techniques developed at ANL [2]. Both undoped and nitrogen-doped

UNCD films were grown on SiO_2/Si substrates, using the SiO_2 film as a sacrificial layer to release bridges and cantilevers patterned on the UNCD, via chemical etching SiO_2. The films were characterized by Raman spectroscopy for quick determination of C atom bonding, by TEM for microstructural studies, and by near-edge x-ray fine structure spectroscopy (NEXAFS) for high-resolution determination of sp^2 vs sp^3 bonding in the films. The films produced at ANL have been used for: (a) fabrication of microbridges and cantilevers to measure the mechanical properties of UNCD at the microelectromechanical system (MEMS) scale using the MDE technique developed by Espinosa, and (b) study of the top and bottom surfaces of the UNCD layer using the potentiometric STM technique developed by Hersam, as further discussed below.

Synthesis of UNCD Films to Study Mechanical Properties of UNCD at the MEMS Scale

Studies of microstructure and growth rate vs. temperature and nitrogen content in the plasma were performed to establish correlations with the mechanical properties measured at the MEMS scale. It was demonstrated that both the high and low temperature undoped UNCD films exhibit similar microstructure (3-5 nm grains and ~.4 nm wide grain boundaries). The elastic modulus and fracture strength (FS) were measured using microcantilever and membrane deflection techniques developed by Espinosa's group. Undoped UNCD yielded elastic modulus of ~ 960 GPa and FS of ~ 5 GPa, while N-doped UNCD yielded modulus of ~880 GPa. and FS of ~ 3 GPa. These values are lower than expected based on the intrinsic properties of UNCD, and are attributed mainly to a combination of bulk microstructural defects and/or microstructural changes for N-doped films. Work is in progress to produce thinner UNCD membranes to minimize bulk defects and to test the bulk defect hypothesis.

Synthesis of UNCD Films on Flat Surfaces and AFM Tips for Potentiometric Studies

Another focus on the synthesis of UNCD films is to explore the electrical characteristics of these films with the use of AFM potentiometric methods developed by Hersam's group. These studies require the synthesis of UNCD films both on flat surfaces and on AFM tips. Initial results have demonstrated that AFM tips can be coated conformally, as shown in Fig. 1. However, further work is needed to produce sharp tips.

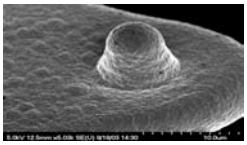

Figure 1. AFM dielectrophoretically-seeded Si tip coated with UNCD film for 120 min at 800 ˚C. It is clear that the growth time and resulting film thickness is too much and that there is a need to reduce the growth time, thus film thickness in order to achieve sharp UNCD-coated AFM tips.

The investigation of UNCD film morphology and conductivity as a function of the growth substrate and nitrogen doping levels has resulted in interesting findings. Both silicon and tungsten substrates have been studied thus far with tungsten proving to be especially effective for producing UNCD films with low surface roughness. Although AFM is generally limited to studying the terminal growth surface, the initial stages of growth have also been assessed by etching away the substrate and then imaging the bottom surface of the UNCD films. Through this procedure, surface roughness as low as ~ 1 nm has been achieved for UNCD. In addition to UNCD surface characterization with scanning probe microscopy, the Hersam's group has explored the possibility of using doped diamond as a low wear coating for cAFM tips. The extended tip lifetimes enabled by doped diamond coatings has enabled the development and innovation of novel cAFM techniques. For example, nanoscale impedance microscopy (NIM) has recently been implemented for the characterization of nanoelectronic devices and circuits [3].

Multiscale Model-Based Simulation of UNCD Film Properties
(Belytschko's, Chen's and Schatz's Group)

With the use of combined ab initio, molecular dynamics (MD) and kinetic Monte Carlo(KMC) methods, we are investigating the film deposition and growth process, and the relationship between microstructure and electro-mechanical properties of UNCD films, in collaboration with ANL and SNL. By using ab initio methods, Belytschko's and Schatz's groups have investigated the mechanical properties of UNCD, including the effect of doping with nitrogen and other atoms on the modulus, and on fracture stress and strain. There are several length scales that are important to UNCD mechanical performance. At the smallest scale we are interested in grain boundaries between diamond crystallites that are a few nm in diameter. The grain boundary width has been found to be only 0.5 nm, so for the most part the crystallites are in direct contact. At a larger scale, several of these crystallites appear to form clusters, and the boundaries between clusters are several nm. The form of carbon associated with these cluster boundaries is not yet known, so we put our initial attention to modeling diamond crystallite interactions. To do this we have developed electronic structure methods that enable us to describe two or more interacting diamond crystallites, to determine stress-strain curves and related information.

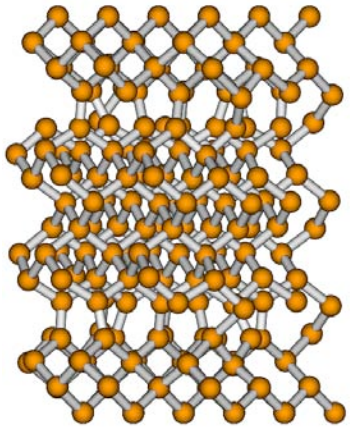

Figure 2. Diamond grain boundary structure used in electronic structure studies.

Figure 2 shows a typical structure that we have studied. In this structure, two grain boundaries are formed by twisting the central portion relative to the others by 67.4°. In this case the minimum size system that we can study consists of 16 planes of 13 atoms each (208 atoms total). We have chosen to use a semi-empirical quantum chemistry method known at MSINDO to determine electronic energies for various values of the strain. From this calculation, the lowest energy paths involve "abrupt" geometry displacements from equilibrium structures. Based on these paths we have derived a peak fracture stress of 73 GPa, which is about 10 times larger than is found in the experiments. This suggests that fracture involves breaking weaker bonds than are contained in the model, which is consistent with experimental observation in which it is the inter-cluster boundaries rather than grain boundaries that show fracture. To develop an effective multiscale simulation procedure, Chen's group has performed combined MD and KMC simulation to investigate the UNCD film growth and resulting mechanical properties. The simulated elastic modulus is similar to the experimental observation, and the fracture strength is close to that predicted by Belytschko's and Schatz's groups via *ab initio* methods. A hyper-surface in both temporal and spatial domains has been proposed by Chen's group to model the growth and multiscale properties of UNCD films, based on the recent work on the interfacial molecular potential during heteroepitaxial film growth [4].

References

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