NIRT: Synthesis, Characterization and Modeling of Aligned Nanotube Arrays for Nanoscale Devices and Composites

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With potential applications ranging from molecular electronics and field-emission displays to nanocomposites, carbon nanotubes offer tremendous opportunity in the development of nanotechnologies. As we seek to make practical materials and devices from nanostructures, a basic understanding of the nanoscale behavior across length scales from the atomistic level to the macroscopic level and how nanostructures interact with each other is required.

This multi-disciplinary research program addresses fundamental issues in the processing and mechanics of carbon nanotube arrays for use in nanoscale devices and composite materials. A model system of aligned carbon nanotubes in a 1-D or 2-D array grown via chemical vapor deposition forms a basis for our modeling and characterization work. The primary objectives of this research program are to (1) develop and improve techniques for synthesis of aligned nanotube arrays with controlled structure, nanotube spacing and interface structure/chemistry, (2) develop novel experimental techniques and methodologies to probe the mechanics of nanotube arrays and to investigate the interfacial properties and load transfer mechanisms in nanocomposites and (3) implement atomistic computational modeling of long-lived physical and mechanical phenomena in carbon nanotubes and establish linkages among atomistic, micro-scale and macro-scale modeling through a unified simulation.

For creating large-scale aligned nanotubes for our characterization and modeling research and eventual scale-up for applications, a number of technical issues must be overcome. A 4-inch back heated plasma-enhanced chemical vapor deposition (PECVD) system has been set-up to overcome gradients in thermal and plasma fields that result in non-uniformities in the as-grown carbon nanotube structures within the array. With the new PECVD system, a detailed study of growth parameters to achieve aligned arrays has been accomplished.[2] Using this system, we demonstrated that nanotube arrays can act like radio antennas for detecting light at visible wavelengths.[3] Potential applications of these antennas has generated large media interest.

We can vary the nanotube structure, from single or double-walled nanotubes to multi-walled tubes with complex structures, by controlling the synthesis conditions. For applications in composite materials, double-walled nanotubes and multi-walled nanotubes with nanoparticles grafted to the tube sidewalls (nano-lumps) are of particular interest. With our recent successes in producing double-wall nanotubes, samples have been provided for mechanical characterization.

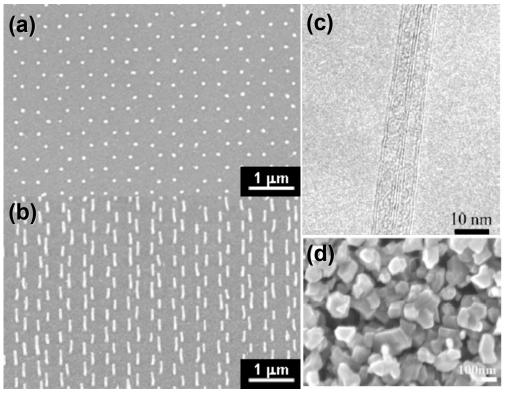

Figure 1: SEM micrographs of (a) patterned catalyst and (b) aligned, periodic arrays of nanotubes, (c) TEM micrograph of double-walled nanotubes and (d)SEM micrograph of large quantities of B_4C nanoparticles

During our research in synthesis of multi-wall carbon nanotubes with boron carbide (B_4C) nano-lumps, we found that large quantities of B_4C nanoparticles could be produced when different ratios of nanotubes and magnesium diboride were used. We have initiated efforts to consolidate nanotubes and nanoparticles into bulk nanocomposites samples for mechanical property studies.

In order to make large arrays of aligned carbon nanotubes with both controlled structure and periodicity, techniques for patterning catalyst need to be studied. We have developed two new methods to make triangular dots of Ni catalyst using a novel sphere self-assembly technique. Two papers reporting these methods have been recently submitted for publication.[4, 5]

For characterization of the nanotube arrays, custom-built AFM testing stages that operate within electron microscopes to enable measurement of deformation behavior and real-time observation of fracture mechanisms are being used. To efficiently characterize carbon nanotube arrays and develop novel methods for probing properties of nanotube-reinforced composites, efficient methods must first be developed to clamp these structures for testing. Electron beam-induced deposition (EBID) methods used previously rely on residual hydrocarbons in the SEM vacuum chamber to generate carbonaceous deposits. This method is slow and unstable.

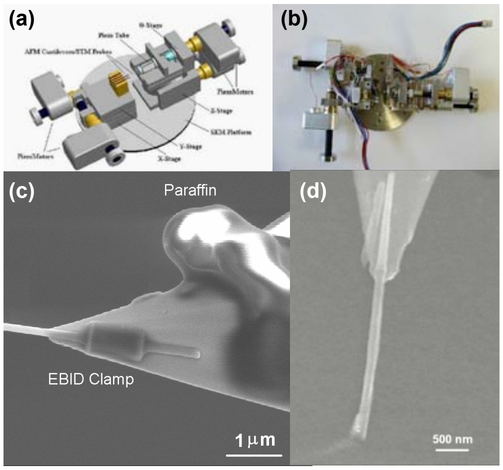

Figure 2: Schematic (a) and photograph (b) of the AFM testing stage. SEM images showing (c) formed EBID clamp with nearby paraffin source and (d) testing of a nanotube in the array.

To overcome this challenge, we developed a simple method to increase EBID clamp production rates by introducing a paraffin source near the clamping region. The paraffin is deposited onto the AFM tip surface, and nanostructures can be clamped to the AFM tips at locations close to the paraffin using the EBID method. The paraffin provides a local carbon source and the EBID clamp deposition rates are greater than twenty times faster. A series of tests were performed to examine the deposition process. The chemical composition and structure of the deposited material was obtained with EELS, SIMS, Micro-Raman and high resolution TEM. The mechanical response was characterized with nano-indentation, and the hydrogenated amorphous carbon film has hardness and elastic modulus values of 3.6 and 34 GPa, respectively. One paper reporting this work has been submitted.[6]

With capability to create large-scale arrays and repeatable clamps, testing of nanotube arrays has been initiated to study their deformation and fracture behavior in tension. Initial experiments show that the nanotubes fracture at one location and across the whole cross section, not in the sword-in-sheath manner as observed for arc-produced multi-wall nanotubes. With the assumption that the inner diameter of the nanotube is half the outer diameter, the fracture strengths were calculated to be in the range of 100-200 MPa.

Owing to the tremendous difficulties of characterization at the nanoscale close synergy between modeling and experimental research is vital. Computational atomistic modeling is essential toward optimization of nanotube structures for applications. Major progresses have been made in the development of molecular structural mechanics for establishing the fundamental elastic properties of carbon nanotubes and exploring their applications in nanoscale devices.

Elastic deformation of single-walled carbon nanotubes under hydrostatic pressure was modeled using the molecular structural mechanics method.[7] Computational results indicate that the radial elastic modulus decreases with increasing tube diameter. The elastic modulus in the circumferential direction is insensitive to tube diameter. The hydrostatic pressure for tube buckling has been determined.[8]

The potential application of carbon nanotubes as ultrahigh frequency nanomechanical resonators in nanoelectromechanical systems has been explored. Both single-walled[9] and double-walled[10] carbon nanotubes are considered and the significant difference in the vibration behavior between them has been identified. The individual tube walls are treated as frame-like structures and simulated by the molecular structural mechanics method. The interlayer van der Waals interactions are represented by Lennard-Jones potential and simulated by a nonlinear truss rod model.

Using the knowledge of vibrational behavior, we have examined the potential of single- walled carbon nanotube as ultra-sensitive mass sensors.[11] Both cantilevered and bridged nanotubes are investigated. The relation between the resonant frequency of a carbon nanotube resonator and the attached mass was established. The results indicated that the mass sensitivity of carbon nanotube-based nanobalances can reach 10^{-21} gram.

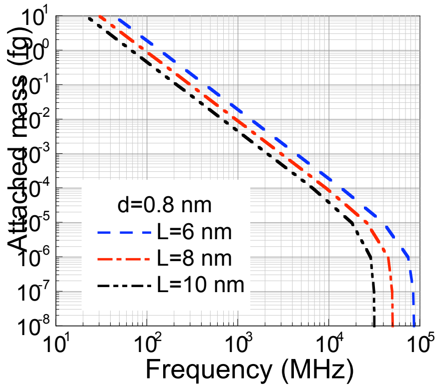

Figure 3: Frequency of cantilevered nanotube resonators versus attached mass, showing a logarithmically linear relationship.

Finally, we have examined the potential of carbon nanotubes as resonant strain and pressure sensors for the purpose of enhancing sensitivity at the nanoscale. The principle of sensing is based on the resonant frequency shift of a carbon nanotube resonator when it is subjected to a strain resulted from external loading. The resonant frequency shifts were shown to be linearly dependent on the applied axial strain and the applied pressure.[12]

References

[1] For further information about this project link to **<http://www.me.udel.edu/chou/nirt>**
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