A pplications of Conductive A tomic Force M icroscopy

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ABSTRACT
Atomic force microscopy has proven its merit in the study of a variety of phenomena at the micro- and nanoscales. While its main use has been obtaining accurate surface morphology data, new imaging modes are expanding the functionality of this technique by correlating morphological information with other sample properties. This article explores the adaptation of AFM to obtain information about the local conductive properties of a sample by using a conductive probe tip connected to a current meter. Conductive AFM (CAFM) has been applied mainly to solid state materials with heterogeneous transport properties, but is also used to measure electrochemical transport through conductive buffers. We present a selection of recent contributions to this field, and discuss both the strengths and the limitations of this technique.

KEYWORDS
atomic force microscopy, conductive AFM, conductive polymer, electrochemical AFM

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INTRODUCTION
Based on a remarkably simple principle of operation first proposed in 1986 [1], atomic force microscopy (AFM) has grown into a widely employed technique for characterizing sample morphology at the micro- and nanometer scales. Since AFM traces the sample morphology by measuring the mechanical interaction between a sensitive cantilever probe and the sample surface directly, it has at least two major advantages compared to other high-resolution microscopes. First, AFM is capable of performing a direct measurement of the three dimensional morphology of conductive or non-conductive, soft or hard, homogenous or composite materials, i.e. almost any sample type. Second, AFMs can operate under fluid, such as a physiological solution, which is especially relevant to the observation of biological phenomena.

In the last decade, additional functionality has been assigned to the scanning tip in order to extract matching information from the samples. Mechanical properties of the sample such as Young's modulus and surface energy can be extracted by using either force mapping (the acquisition of z-position vs deflection curves over a raster of points on the sample) or phase imaging (the recording of phase shift between drive frequency and cantilever oscillation). The interaction of electromagnetic radiation with the sample surface (i.e. fluorescence phenomena) can be correlated to morphology by integrating an optical fiber into the AFM tip. Magnetic sample properties can also be probed by applying a magnetic coating to the tip, so that the tip-sample coupling force is modulated in the presence of a localized external magnetic field.

In this article, we explore the emerging field of conductive atomic force microscopy (CAFM), a collective name for experiments using conductive AFM tips in which both sample topography and current flow from the sample surface to the tip are recorded simultaneously. Early efforts in this area used either a current measurement apparatus [2] or custom-built current-to-voltage amplifiers [3] to create surface-current density maps. Currently, most AFM manufacturers offer modules capable of CAFM measurements. In the light of this increased availability, we will review outstanding examples of successful applications while discussing the inherent limitations of the method and thus the data obtained.

Figure 1: A multiwalled nanotube imaged by CAFM. Morphology (A) is presented along with a current map (B). Current as a function of distance along the nanotube length is shown in (C). Reproduced from [4] with permission.
CAFM APPLICATIONS

Nanostructures

Charge transport in conductive nanostructures such as carbon nanotubes was an early and pertaining problem in nanotechnology. Determining the conductivity of nanotubes has been a long-standing experimental challenge, largely because of the difficulty in establishing reliable contacts with the nanotube. For most experimental setups, measured resistance is dominated by contact resistance at the nanotube ends. This makes it hard to measure the resistivity of the nanotube itself, and experiments may yield conflicting results.

To solve this problem, the conductive AFM tip can play the role of a moving electrical probe that can be positioned at will along objects which are micrometers long and nanometers wide. This is advantageous because it yields a measurement between a reference point and a point at a distance x along the nanotube, R(x). Here, the contact resistances can be subtracted so that the resistance of a length of nanotube, d = x₂ - x₁, is simply equal to \( R_{\text{contact}}(d) = R(x_2) - R(x_1) \). The contact resistance at one end of the nanotube is therefore factored out. Dai et al. [4] have used this methodology in order to show that nanotube conductivity, while ohmic in nature, is increased by as much as an order of magnitude by defects in nanotube structure (Fig 1). While it is clear that low resistivity regions coincide with the nanotube, and that resistivity increases with length (Fig 1C), some of the limitations of the technique are also apparent: the thick linear conductive region of Fig 1B is also accompanied by a thinner parallel conductive line, which is caused by imperfect contact between the tip and nanotube.

These experiments have proven that CAFM is a very powerful method for nanometer scale conductivity measurements. It provides data for which the only chief assumption is that the tip-nanotube contact resistance remains constant during the scan, without the need to measure its value.

Heterogeneous materials

A natural application of CAFM imaging is the characterization of material structures where charge-transport properties vary on the nano- to microscales and are correlated to sample morphology. Morphology-transport relations often account for complex macroscopic material properties and are important for improvements in microdevice performance.

Silicon is by far the most widely used material in microelectronic applications. Rezek et al. [5,6] have used CAFM in order to study the nucleation of Si microcrystallites in a layer of hydrogenated microcrystalline silicon as a function of growth conditions. Fig 2A shows surface morphology (error mode), while the current map of the sample is presented in Fig 2B. The topography of the two draws a parallel between the morphology of the Si surface and its composition; most large raised hillocks are identified to be poly-Si (and therefore more conductive) while the rest of the sample (amorphous Si) has a lower conductivity. The dual section in Fig 2C shows some exceptions from this general rule, however: while the larger hillock at x = 600-700 nm is insulating, the small hillock at x = 500-550 nm is highly conductive, indicating the presence of a newly nucleated poly-Si crystal.

A number of new materials are also benefiting from this experimental approach. In conductive polymer blends, for example, structure is self-organized into molecular scale sheets [7]. Work in our group has recently shown this structure to be well correlated with charge injection efficiency at the polymer surface [8]. Large scale CAFM images of a conductive polymer blend surface (PEDOT-PSS, Fig 3A) reveal the presence of regions where charge injection is highly efficient, and regions where charge injection is inhibited (10⁻¹⁰¹⁰ fold lower). Here the current data were superimposed onto the 3D plot of the surface as a color scale.

Despite the fact that roughness is higher in the high-current regions, it does not explain the large difference in current. The explanation lies in the molecular transport model for PEDOT-PSS. Aasmundtveit et al. [7] had shown by X-ray scattering measurements that PEDOT blends self-organize into lamellar structures, and macroscopic measurements showed a large conductivity along patterned polymer films. High-resolution AFM imaging (Fig 3B) confirms the expected supramolecular struc-
ture of the blend. AFM morphology imaging of the conducting regions shows the presence of a large number of edges with a well-defined lamellar spacing (Fig 3B), showing the correlation between the presence of lamellar edges on the surface and efficient charge injection.

As these examples highlight, CAFM can be effectively used to correlate nanometer scale morphological features with charge transport properties, thus providing the underlying mechanisms for macroscopic conductivity anomalies.

Fluid-phase transport
While in the previous section heterogeneity resulted from the solid state superstructure of the sample materials, another example of conductive heterogeneity is an insulating porous structure filled with a conductive fluid. The conductive tip acts as an electrochemical electrode and ions are extracted from the conductive fluid by the field applied. Such an approach was taken by MacPherson et al. [9] in order to observe ion diffusion in nanoscale pores. A CAFM scan of an ultrafiltration membrane filled with a conductive fluid is shown in Fig 4. While the membrane surface morphology shows the pore locations (Fig 4A), current measurements show the amount of charge conducted at each pore site in the presence of a constant bias (Fig 4B).

An extension of this technique has been used in our group to demonstrate combined measurements on another type of fluid filled porous structure - a microfluidic network [11]. Here the fluid-filled channel is a microfabricated fluidic trench that is partially closed, leaving behind access ports at determined positions along the channel (Figs 5A, 5B). Current recording measures the resistivity of a well-determined fluidic path from a reference electrode to the CAFM tip, along with the local morphology of the wafer surface (Fig 5C).

The importance of this approach lies in its ability to verify connectivity between various points in a complex microfluidic network with high spatial resolution. Also, in applications requiring the integration of microelectrodes with fluids, the CAFM tip may act as a rapid prototyping tool (i.e. a mobile test electrode).

CONCLUSIONS
Conductive AFM is a rapidly developing area of research, offering combined information on electronic properties and sample morphology at the nanoscale. While for quantitative resistance measurements the uncertainty in the contact resistance pertains, it can be addressed by careful calibration, improved characterization of this phenomenon, and control of experimental conditions. While CAFM has been mostly used for the characterization of structure-function relationships in heterogeneous materials, recent applications include the measurement of transport through nanoscale and local electronic properties. Such correlation is also important in the validation of transport theories for nanodevices. From a commercial point of view, besides material optimization, the technique is useful for locating circuit defects in microfabricated devices and for mapping out complex fluidic connectivity on sub-micrometer length scales where the use of dyes and optical microscopy is impractical.

REFERENCES