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SCANNING TUNNELING MICROSCOPY AND ATOMIC FORCE MICROSCOPY OF THIN POLYMER FILMS

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Abstract Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) have the potential of giving the three dimensional morphology of polymer surfaces with atomic resolution. We have imaged doped and undoped polyacetylene, poly(3-hexylthiophene), and polystyrene. Both these techniques are well suited to study the fibrillar nature and growth of these films. STM shows that the fibrils of the free side of iodine doped polystyrene are flat to within less that 10 Å. The fluctuations in the surface conductivity of polyacetylene and the thermally induced motion of the polymer side groups limit the potential of these techniques to give atomic resolution.

Keywords: Scanning tunneling microscopy, atomic force microscopy, polyacetylene, polystyrene, poly(3-hexylthophene), morphology

INTRODUCTION

Conducting polymers are of interest for a number of reasons, one being that they may obtain conductivity approaching that of copper. The transport of charge in these materials is limited by a variety of defects, including ends of the polymer chains, residual catalyst, and undoped regions. Characterization of the type and distribution of the defects is needed for an understanding of the nature of charge transport. Polyacetylene is an interesting conducting polymer not only because it has a simple chain structure, but also because it has been determined that motion of chain deformations - solitons and polarons - play a role in transport.

Scanning Electron Microscopy (SEM)[1] and Transmission Electron Microscopy (TEM)[2] have found that polyacetylene consists of bundles of fibrils, with fibril diameters ranging in diameter from 100 to 1000 Å, depending on the preparation method.

In this paper we discuss the application of Atomic Force Microscopy (AFM)

and Scanning Tunneling Microscopy (STM) to study polyacetylene, polystyrene, and poly(3-hexylthiophene). These microscopies complement other probes of the material in a number of ways. The resolution of STM is higher than the 50 Å attainable in SEM. Both techniques probe not only the lateral extent of surface features, but also give their height. AFM can probe nonconducting surfaces, so conducting polymers in their undoped state and nonconducting polymers can be probed without a gold overlayer required for SEM examination.

We have imaged both Shirakawa[3] and new polyacetylene[4] films with AFM and STM. AFM can resolve the fibrillar structure in undoped material, and with STM we could probe details of the fibril structure on doped films with finer resolution. However, the instability of the conductivity limited our vertical resolution to 10 Å, which did not allow single chains to be resolved. We therefore were motivated to study submonolayer coverages of polymer films on graphite, which gave more stable tunneling current. We present images of these surfaces, demonstrating that the growth of individual fibrils can be characterized.

INSTRUMENTATION

STM images were obtained with a Nanoscope I. The height of the sample is fed to the computer, translated to a gray level, and plotted as a function of the lateral position of the probe tip. The atomic force microscope is a home-built modification of the Nanoscope STM. The detection of the displacement of the cantilever in the AFM is made with the beam bounce method.[5] The AFM operates both in a noncontacting (low resolution) attractive mode,[6] and a contacting (high resolution) repulsive mode.[7] The tip in both instruments is a tungsten wire etched in potassium hydroxide.

UNDOPED POLYACETYLENE

We used AFM to measure the fibrillar morphology of undoped polyacetylene. The polyacetylene was prepared as a free-standing film using the Naarmann-Theophilou synthesis method.[4] The film had been stretched before examination. A section of the polyacetylene film was attached to an aluminum substrate with epoxy before examination. The sample had been exposed to air for a number of days and was imaged in air.

In Figure 1 we show an AFM image of the sample. The horizontal lines in the image are an artifact. In this image the fibrils of the polyacetylene are clearly seen. They have a diameter of approximately 400 to 800 Å. In addition, examination of the digital data in cross section shows that the

height of the fibrils is of the same order, implying that they are rounded. The shape of the fibrils depends on the conditions under which the film was grown.[1]

DOPED POLYACETYLENE

When polyacetylene is doped it becomes conductive and can thus be examined under higher resolution with STM. The sample was prepared using the Shirakawa method.[3] A thin film was polymerized onto a glass slide using a modification of the synthesis used for thick films.[8] Doping was performed by placing the sample in a solution of iodine in carbon tetrachloride for two hours.[9] After doping, the sample was immediately examined with STM.

The vertical resolution of the STM images of polyacetylene was rarely better than 10 Å, even though STM images of many other materials in air can have a vertical resolution as high as 0.1 Å. We attempted to improve our resolution by tunneling through different media. The surface was imaged both in air, in an inert argon atmosphere, while immersed in carbon tetrachloride, and while immersed in glycerine. The image quality did not depend on the medium through which the electrons tunneled. The instability of the tunneling current under this variety of conditions indicates that the the surface of the fibrils is either insulating, or that dopants are moving.

In Figure 2(a) we show a typical STM image. We found that the fibrillar structure is also easily imaged with STM. The fibrils in this film were found to have a width of 100 Å over much of the film. In Figure 2(b) we display a cross section through one of the fibrils indicated by the line drawn in Figure 2(a). One can see that within the 10 Å vertical resolution the tops of the

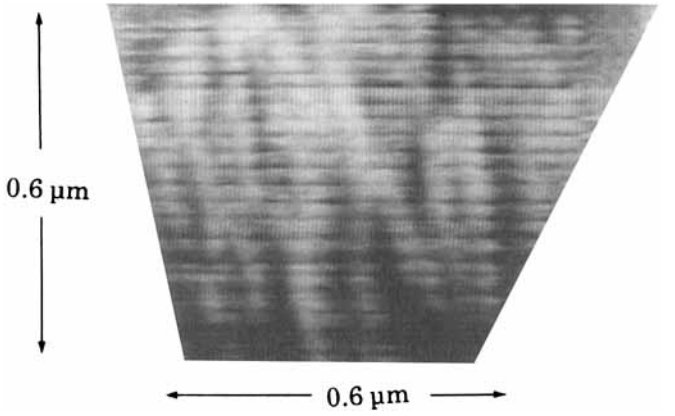

FIGURE 1 AFM image of new-polyacetylene

fibrils could be atomically flat. This flatness was seen over much of the surface. SEM images show that the side of the polyacetylene which is attached to the flask wall on which it grows has flattened fibrils, but the STM image is of the free surface. X-ray diffraction measurements show that polyacetylene highly doped with iodine can have a structure consisting of alternating planes of polyacetylene and iodine.[10] The surface of the crystalline structure would thus be atomically flat, in accordance with our observations.

SUBMONOLAYER POLYMER FILMS

AFM and STM of polyacetylene were not able to resolve the individual chains. We investigated whether individual strands of a polymer placed on a suitable substrate would allow this possibility. Graphite was chosen as a substrate since it is inert in air and can be imaged with atomic resolution.[11] Conduction can occur through monolayer coverages of a insulator,[12] so STM can be used to examine these surfaces.

Submonolayer coverages of the conducting polymer poly(3-hexylthiophene) and the nonconducting polymer polystyrene were solution cast from chloroform and toluene respectively onto a graphite substrate. Polyacetylene could not be examined since it is insoluble. The coverage of the polymer on the graphite could be adjusted by changing the concentration of the polymer in solution.

An image of poly(3-hexylthiophene) is shown in Figure 3. Two steps are seen in the image; each one is approximately 3 Å in height and corresponds to a monolayer of polymer. From this image one learns that STM can be used to

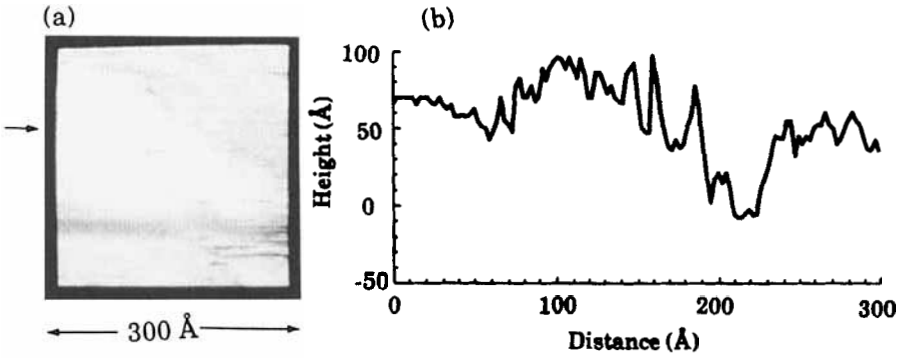

FIGURE 2 (a) STM image of iodine doped polyacetylene. (b) Horizontal cross section of image at location of arrow. Note that the height is relatively flat from 0 to 50 Å and from 240 to 300 Å.

study the growth of the polymer on the surface. On this image one can identify areas from which fibrils are beginning to emanate. In addition, the polymer is forming a uniform coverage instead of conglomerating into islands.

Individual fibrils can also be studied, an example being shown in Figure 4. Imaged here is a fibril of polystyrene on graphite. It has a width of 70 Å and a

FIGURE 3 STM image of poly(3-hexylthiophene). Image is 600 Å by 600 Å.

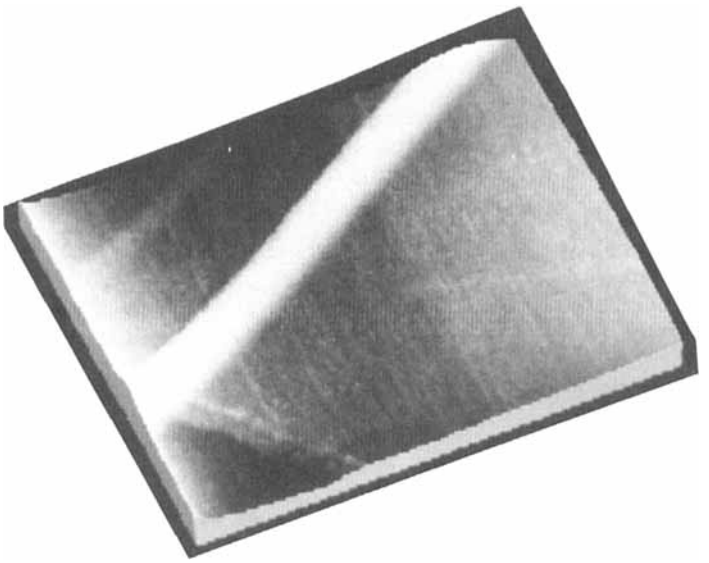

FIGURE 4 STM image of polystyrene. Image is 600 Å by 600 Å.

vertical height of 6 Å. The apparent height may not correspond to the topography, but to the distance the tip must withdraw in order to maintain a constant tunneling current. The image does show that the fibrils are growing as single layers on the graphite substrate.

While STM images of other organic films has shown molecular resolution, it has not been obtained here. This may be due to the freedom of the molecular side groups to diffuse at room temperature. Molecular resolution for other organics has been obtained only for closed pack structures.[13]

CONCLUSIONS

We have demonstrated here the capabilities AFM and STM have for characterizing thin polymer films. They complement other imaging techniques in that they give the full three dimensional structure of the surface and have higher resolution. However, stability of the conductivity of surfaces and diffusion of the molecules is limiting the potential of these techniques to give atomic resolution images. Despite these limitations, these techniques provide important new tools for the study of polymer growth. Restricting surface motion and stabilizing the tunneling current may allow study of polymer films on an atomic level.

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