Deposition and atomic force microscopy of individual phthalocyanine polymers between nanofabricated electrodes

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Individual chains of the rigid-rod polymer phthalocyaninepolysiloxane (PcPS) have been deposited and immobilized on top of nanofabricated metal electrodes. This is realized by embedding sparsely distributed PcPS polymers in a monolayer of cellulose using the Langmuir–Blodgett deposition technique. Atomic force microscopy was used to study the resulting spatial arrangement of these one-dimensional conducting polymers. Images of the polymer chains were obtained with a lateral resolution of better than 1 nm. Inspection of the polymers near the edges of the electrodes demonstrates that the monolayer structure is not perturbed by the 15 nm high electrodes. With this procedure, it appears to be possible to bridge two closely spaced electrodes with individual PcPS polymer chains. © *1997 American Vacuum Society*. [S0734-211X(97)02803-5]

I. INTRODUCTION

For a variety of experiments in the fields of scanning probe microscopy,[1,2] spectroscopy,[3] sensors,[4] and electronics,[5] there is a strong interest to investigate properties of individual molecules that are dispersed on a substrate. Required for such experiments are deposition methods that lead to molecules that are mutually well separated as well as immobilized on the surface. Various approaches towards this goal have been investigated. For example, special endgroups have been used to attach short oligomers to the surface, leading to self-assembled monolayers (SAMs).[2] In the approach presented in this article, long polymer chains are deposited using a Langmuir–Blodgett (LB) deposition technique resulting in conducting polymers that are embedded in a monolayer of an insulating molecule.[6] We show that this method leads to a controlled deposition and strong immobilization of the polymer chains, even on a surface corrugated with 15 nm high nanofabricated metal electrodes. This allows very reproducible atomic force microscopy (AFM) imaging of the molecules. A lateral resolution of better than 1 nm is obtained. We show high-resolution AFM images of individual polymer chains bridging two nanofabricated electrodes, a configuration that is of interest for measuring the conductance of a single molecule.

II. EXPERIMENT

We have studied phthalocyaninepolysiloxane (PcPS) polymers[7] (Fig. 1). These are 20–100 nm long stacks of Si-phthalocyanine monomers linked by O-atoms. Including the flexible hydrocarbon side chains, the total diameter of the polymer amounts to 2.3 nm. The distance between monomers is 0.33 nm. This small distance accounts for the mechanical rigidity of PcPS as well as for orbital overlap which renders the polymer a one-dimensional semiconductor.[8] In the present investigation, the PcPS molecules are deposited in a unique way. A mixture of PcPS and insulating isopentylcellulose[9] is dispersed on the water surface of a LB trough. The resulting mixed monolayer is then deposited in a single dip at a surface pressure of 19 mM/m at 6 °C. The Si/SiO_2 substrates have a surface roughness of ~0.1 nm as determined by AFM. The role of the cellulose is to separate the PcPS polymers electrically as well as to mechanically immobilize them on the surface. In order to reduce high parasitic tip-substrate forces that can perturb AFM imaging, the ambient AFM is operated in tapping mode (TM).[10] In TM, the cantilever is vibrating at resonance with a large amplitude (~100 nm). Changes in the amplitude resulting from the contact between tip and sample are used as the

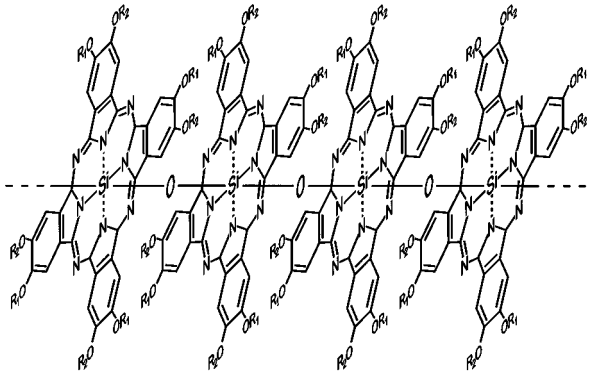

FIG. 1. Schematic drawing of PcPS ($R_1=CH_3$, $R_2=(CH_2)_7CH_3$). The PcPS polymers have a distributed length between 20–100 nm and a diameter of 2.3 nm. Monomer spacing is 0.33 nm. The π-orbitals of the monomers overlap which renders PcPS a one-dimensional semiconductor.

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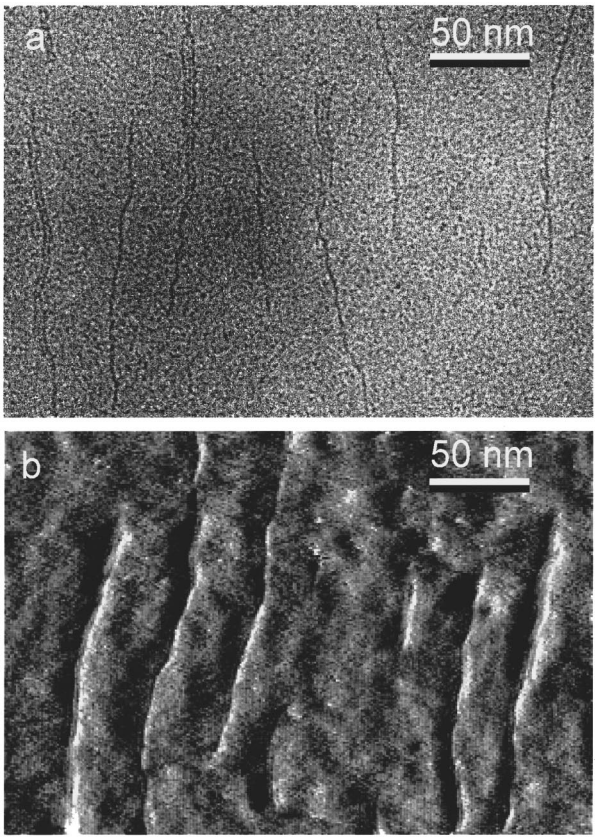

FIG. 2. TEM (a) and amplitude-TM-AFM image (b) of a mixed LB monolayer of PcPS and cellulose with a weight ratio of 1:5. The semiconducting PcPS polymers are embedded in a monolayer of insulating cellulose polymers.

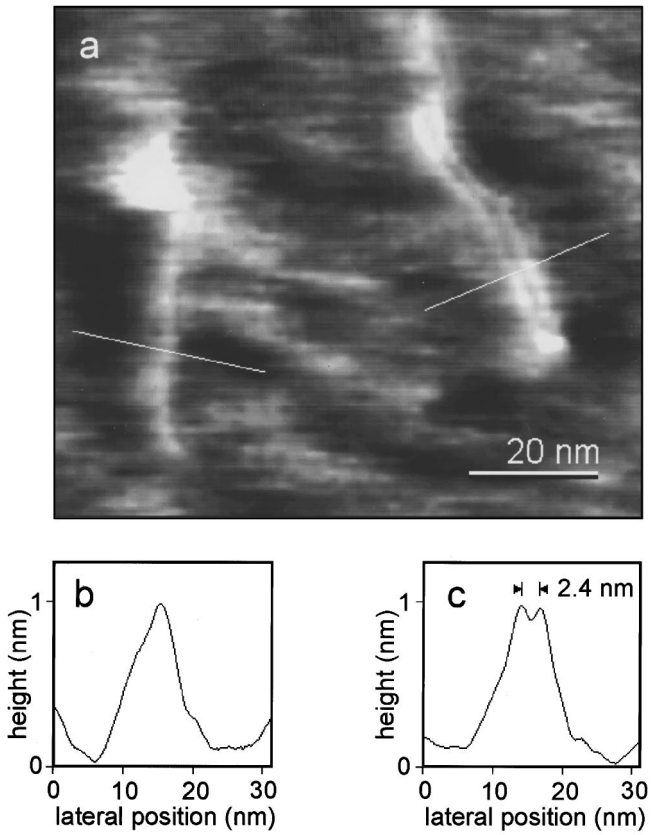

FIG. 3. TM-AFM height-image of an isolated and two adjacent PcPS molecules (a) with height profiles across these molecules (b and c). The displayed curves are the average of ~10 height profiles.

feedback signal. With this method, tip-sample friction forces are greatly reduced as compared to standard contact-mode AFM.

III. IMAGING OF INDIVIDUAL POLYMERS

Figure 2a shows a transmission electron microscope (TEM) image of a mixed PcPS/cellulose monolayer. Single isolated molecules as well as small aggregates are observed. For the distance between adjacent chains in the aggregates we find 2.25 nm. The PcPS polymers are often organized head-to-tail which accounts for apparent lengths of more than 100 nm. Larger-scale images indicate that the polymers tend to be directed along the LB dipping direction. In contrast to TEM, AFM does allow imaging of samples corrugated with electrodes as well as providing height information. Figure 2b is a TM-AFM image of a similar PcPS/cellulose monolayer. The PcPS polymer pattern observed in the AFM images is consistent with the TEM data. The measured height difference between PcPS and cellulose varies from 0.5 to 1.4 nm. The maximum value of 1.4 nm is in agreement with the difference of the diameters of PcPS and cellulose that amount to 2.3 nm and 0.9 nm,[11] respectively. The root mean square (rms) roughness of the cellulose surface is ~0.4 nm, which is larger than the ~0.1 nm surface roughness of the SiO_2 substrate on which the monolayer is

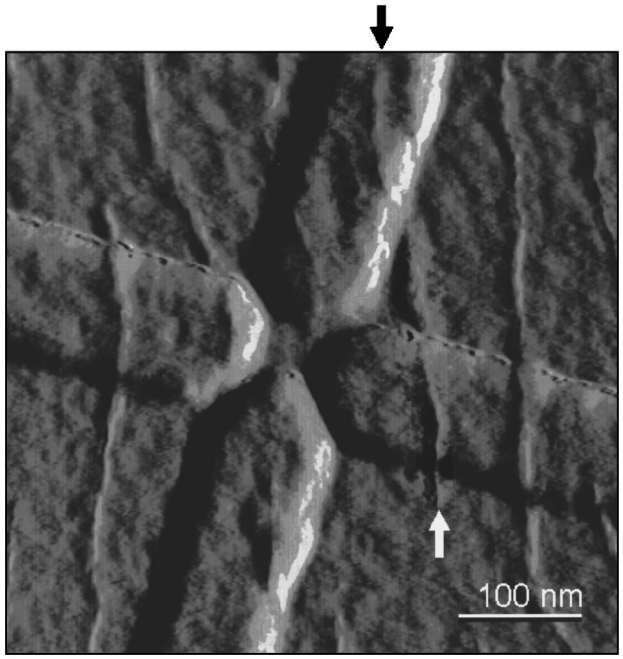

FIG. 4. TM-AFM amplitude-image of a PcPS/cellulose monolayer on top of a cross-shaped electrode structure. The spacing between neighboring electrodes is ~30 nm. The electrodes appear not to perturb the PcPS pattern in the monolayer. The PcPS polymer chain indicated by the two arrows bridges the two electrodes. This illustrates the concept of possible electronic transport measurements through a single polymer.

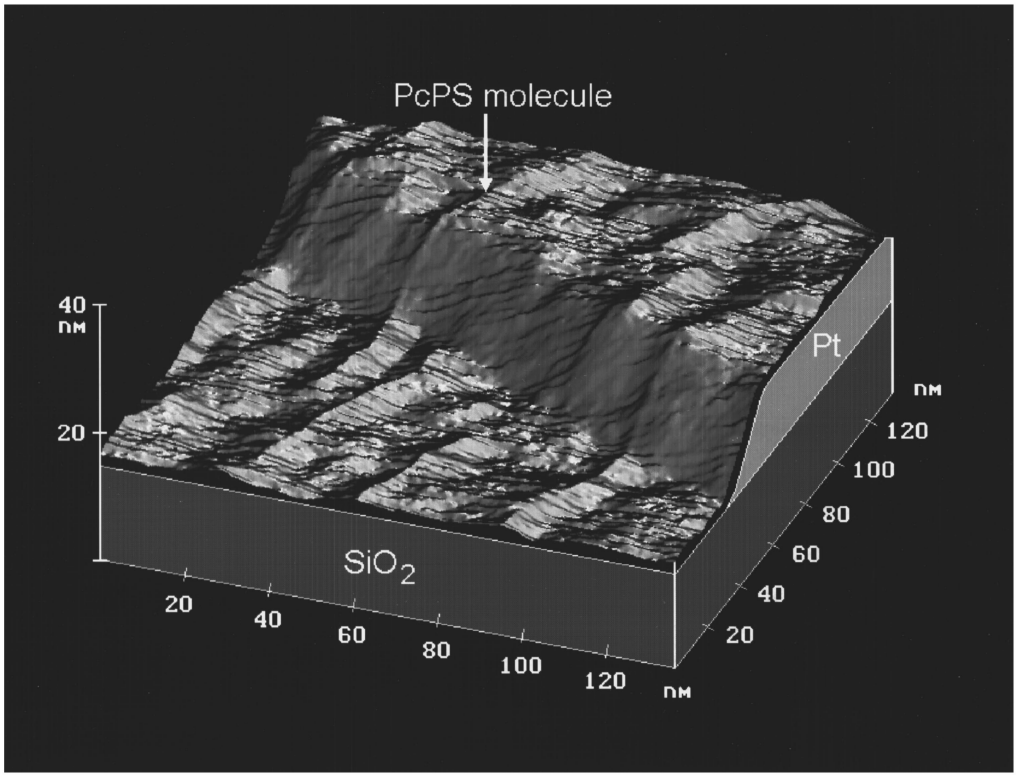

FIG. 5. Three-dimensional rendering of a TM-AFM height-image of the edge of a metal electrode covered with a PcPS/cellulose monolayer. The individually distinguishable PcPS polymers run unperturbed from the 15 nm high electrode down to the substrate.

deposited. Imaging is very stable and nondestructive. This is attributed to the immobilization of the embedded PcPS molecules and the use of the TM technique. Contact-mode AFM yielded a drastically poorer imaging quality.

The TM-AFM image of Fig. 3 indicates that it is possible to distinguish between an isolated PcPS molecule (left side of Fig. 3a) and an aggregate of two directly adjacent molecules (right side of Fig. 3a). One can discern the individual polymers within the aggregate. The distance between adjacent polymers can thus be determined. From data of various aggregates, we find an average distance of 2.4 ± 0.2 nm, which is consistent with the TEM and Bragg reflection results.[6] From the sharp features in the cross sections (Figs. 3b and 3c) one can infer a lateral resolution of better than 1 nm. For the definition of this resolution we take the minimum peak distance for which the dimple between peaks is larger than the noise.[12] The intra-aggregate resolution shown here can only be attained with very sharp tips[13] and for limited time (about 1 h), which is probably due to tip wear. The height profile of the isolated molecule (Fig. 3b) illustrates the tip-convolution effect. Its base, ~ 15 nm wide, is much broader than the actual polymer width of 2.3 nm. Deconvolution leads to an estimate of the tip radius of ~ 7.5 nm.

IV. PcPS POLYMERS ON ELECTRODES

We now look at the molecular configuration of PcPS as deposited onto metal electrodes. Figure 4 shows a TM-AFM image of a PcPS/cellulose monolayer deposited on a cross-shaped contact structure with four Pt electrodes. The amplitude signal is displayed rather than the height signal to provide optimum contrast on both the substrate and the electrodes. The electrodes are defined with e-beam lithography in a double layer of poly methylmethacrylatemethacrylic acid (PMMA) based resist. A ~ 200 nm thick bottom layer supports a ~ 50 nm top layer, that serves as the actual mask. Through this mask, a 5 nm Ti adhesion layer and 10 nm of Pt are evaporated. The spacing between neighbouring electrodes is ~ 30 nm. Despite the ~ 1 nm corrugation of the bare Pt surface, single PcPS polymers can still be discerned easily on Pt. The pattern of the PcPS polymers appears not to be altered by the presence of the 15 nm thick electrodes. The electrodes do not induce disordered regions in the PcPS/cellulose monolayer. The polymer layout at the edge of an electrode is displayed in Fig. 5. From the sharpness of the PcPS features in the image, the chains can be identified as isolated PcPS polymers. Starting on the SiO_2 surface, the chain indicated by the arrow appears to run straight and unperturbed over the Pt electrode edge and ends on top of the electrode.

These TM-AFM images also illustrate the concept of possible future electrical measurements. In covering the electrodes with a PcPS/cellulose monolayer there is a chance that an isolated molecule—or a small aggregate—bridges two electrodes. This in fact is the case with the PcPS chain indicated by the two arrows in Fig. 4. Electrical transport measurements on such samples have shown that the current through a single PcPS polymer in the undoped state is undetectable. From studies of larger-scale samples,[14] the conduc-

tivity of intrinsic PcPS in the undoped state appears to be of the order of 10^{-10} S/cm. This implies a current as low as 10^{-18} A for a single PcPS polymer at 1 V bias voltage. Obviously, it is necessary to address the issue of increasing the conductivity, for example by chemical doping, before successful transport experiments on single chains of these semiconducting molecular wires can be realized.

V. CONCLUSIONS

This study shows that by use of cellulose as an insulating matrix, individual chains of a rigid-rod polymer can be deposited in a controlled way onto nanofabricated electrodes. AFM inspection appears reliable and straightforward because of the strong immobilization of the individual molecules on the surface. This technique may be useful in realizing possible electronic transport experiments on molecular wires.

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