

Selective placement of templated DNA nanowires between microstructured electrodes

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Abstract: Dip-pen nanolithography is used to selectively modify the SiO_x area between microfabricated electrodes. The modified surface is characterized by atomic force microscopy, X-ray photoelectron spectroscopy, force volume imaging, and adhesion maps. The functionalized complex architecture is used for the localization of DNA coated with magnetic nanoparticles. The strategy reported here can become the basis for the construction of a number of functional devices. The devices can utilize the unique recognition properties of the DNA and the magnetic properties of the nanoparticles that template them.

Keywords: DNA nanowires, microstructured electrodes, nanolithography

Introduction

The need to validate methodologies for the placement of nanoparticles, nanorods and nanowires has been recognized in recent years (Neimeyer 2001). Methodologies to localize such materials on specific surface coordinates are of interest for applications such as (bio)sensors, molecular scale devices and optoelectronic platforms (Djalali et al 2003). Among these methodologies two distinct approaches can be identified: “top-down” and “bottom-up”. The top-down strategies are well established for dimensions above 100 nm, whereas bottom-up strategies are excellent for self-assembly processes of entities in the range of 0.1 to 5 nm. Researchers have identified the need to place biomolecules and nanoclusters with dimensions of 5–100 nm in order to generate functional devices. A combination of bottom-up and top-down approaches can address this need (Neimeyer 2001). A promising way to make this into a well-developed strategy is to come up with a successful recipe that combines microfabrication with self-assembly. Some examples so far include the placement of short DNA strands between electrodes and subsequent metallization with silver (Braun et al 1998) or selective hybridization of functionalized Au nanoparticles using complementary DNA (Chung et al 2005). Keren et al (2003) have also constructed a carbon nanotube-based device using DNA as a scaffold. Such studies have shown the promise of using DNA as a template on microfabricated architectures (Niemyer 1997). There is a need to extend this strategy to methods that do not rely on metallization and use other kinds of promising nanoparticles besides gold. In this work we place pre-formed magnetic wires with DNA cores between microstructured electrodes. We describe a procedure for the selective modification of the SiO_x surface between the electrodes, detail a protocol for the characterization of the functionalized surface, and subsequently localize DNA templated with Fe₂O₃ particles on the same surface.

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Procedure

We utilized a microfabricated substrate, Nanoscale Experimenters Test System (NETS), which is commercially available from NanoInk, Inc. (Chicago, IL, USA, <http://www.nanoink.net>). The substrate was a silicon chip with 35 sets of gold electrodes. The gaps between the electrodes were composed of spin-on SiO_2 . Each chip was cleaned according to the manufacturer's specifications. The quality of the surface was evaluated by atomic force microscopy (AFM) using a Multimode SPM (Veeco Instruments, Santa Barbara, CA, USA). A typical height image is shown on Figure 1a. The distance between the different sets of electrodes on the chip varied from 1 to $3\ \mu\text{m}$. The quality of the SiO_x layer between the electrodes was not affected by the cleaning. Prior to any chemical modification of the surface we performed force volume (FV) imaging in order to assess the properties of the substrate. Adhesion maps were generated using the FV option of the multimode. In a FV image corresponding to a height image, a force curve is plotted across the surface at regular intervals. A typical FV image is a collection of deflection vs distance curves. A FV image can be converted into an adhesion map by calculating the values of the adhesion force that correspond to the location of each deflection vs

distance curve (Poggi et al 2004). Adhesion maps were generated using custom-written MatLab code. The adhesion map of a clean set of electrodes and the area between them is shown in Figure 1b. The adhesion forces between the clean tip and the different materials on the surface are very similar and the contours of the electrodes on the adhesion map can barely be distinguished. This result is expected since both surfaces are hard and similar in roughness. If the gold electrodes and the SiO_x in between them are free of chemical contaminants the tip should experience the same contact area with each type of material on the surface and show no differences in adhesion forces.

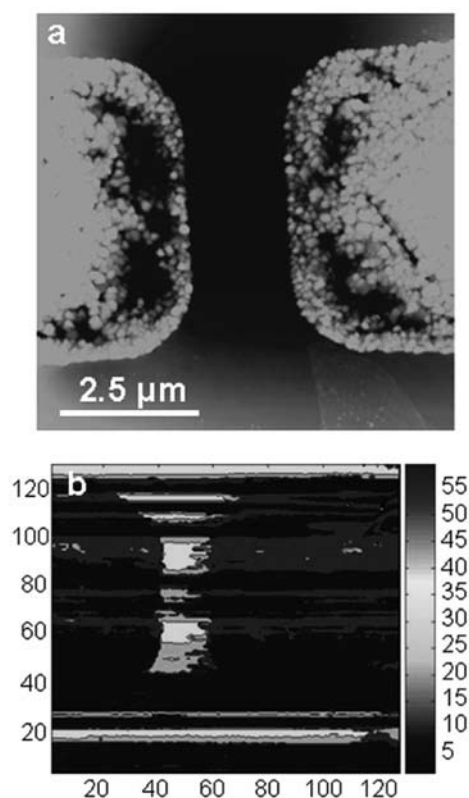


Figure 1 (a) A representative height image of a clean set of electrodes from the NETS substrate. The image has a height scale of 30 nm; (b) An adhesion map generated from a force volume image collected over a set of clean electrodes. The x and y scales show pixel numbers and the color z scale is in nN.

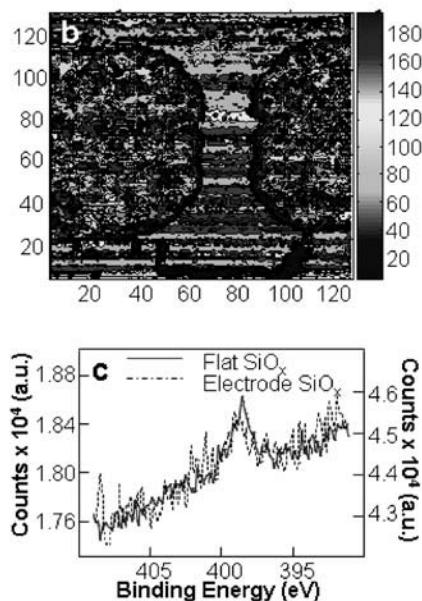
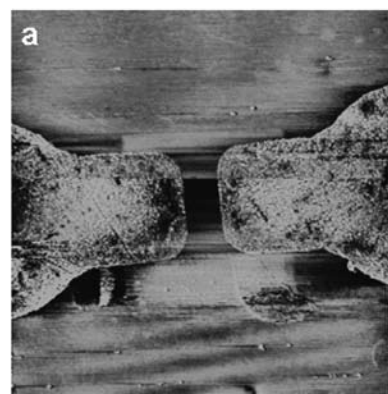


Figure 2 (a) Lateral force microscopy image of a set of electrodes after consecutive modification with poly(allylamine hydrochloride) (PAH) and polystyrene sulfonate (PSS) using dip-pen nanolithography (DPN). The light-colored square in the middle of the image is the area scanned with the coated tips; (b) An adhesion map generated from a force volume image collected over a set of electrodes and an area of SiO_x around them modified by PAH. The x and y scales show pixel numbers and the color z scale is in nN; (c) N 1s binding energy region of a high-resolution X-ray photoelectron spectroscopy spectra. The solid line data were collected from a region of a flat SiO_x surface modified with PAH by DPN. The dashed line data were acquired from a region between the electrodes of a NETS substrate modified with PAH by DPN. The y-axis on the left corresponds to the electrode SiO_x data and the y-axis on the right corresponds to the flat SiO_x data.

A chosen set of electrodes on the chip was modified selectively using dip-pen nanolithography (DPN) (Bullen et al 2004). In a typical DPN procedure performed in air, an AFM tip is used to deliver molecules to a specific location. The molecules of interest are physisorbed on the AFM tip that is brought in contact with the surface. The water meniscus that forms between the tip and the surface due to the ambient humidity is used as a transport media. This procedure has been successfully utilized in the fabrication of various device platforms (Pena et al 2003; Su et al 2003; Li et al 2004a; Maynor et al 2004; Chung et al 2005). We utilized two types of polyelectrolytes in order to specifically modify the area between the electrodes: a positively charged poly(allylamine hydrochloride) (PAH) and a negatively charged polystyrene sulfonate (PSS). The SiO_x surface is negatively charged after the cleaning procedure. One can rely on electrostatic interactions and sequentially adsorb layers of PAH and PSS on a desired location on the SiO_x surface. We have previously reported the details of the DPN writing with PAH and PSS on flat SiO_x surfaces (Nyamjav and Ivanisevic 2004). A typical result on the microfabricated surface is shown in Figure 2a. This lateral force microscopy (LFM) image indicates the presence of a square in between the two electrodes. Prior to obtaining this LFM image a tip modified with PAH was rastered across a $10 \times 10 \mu\text{m}^2$ area. Subsequently another tip modified with PSS was used in the same way. FV imaging verified that the surface properties are changing as a result of the delivery of the molecules to the surface. Figure 2b displays an adhesion map collected with a clean tip and a set of electrodes around a SiO_x surface modified with PAH. This map clearly shows differences in adhesion forces. The tip would be expected to have a larger contact area with the softer surface covered with the randomly oriented chains of the PAH polymer (Nyamjav and Ivanisevic 2004). Additional evidence that the PAH was delivered between the electrodes came from X-ray photoelectron spectroscopy (XPS). High resolution XPS data indicated the presence of nitrogen on the surface when DPN with PAH was performed on flat SiO_x and on a SiO_x surface between the electrodes (Figure 2c). Neither surface shows the presence of nitrogen prior to the modification procedure. Taken in sum the LFM, adhesion maps, and XPS data can be used as positive proof that the surface was selectively modified.

The DNA templated structures were prepared by mixing λ -phage DNA (*E. coli* host strain GM119, from Sigma-Aldrich, St Louis, MO, USA) and Fe_2O_3 magnetic nanoparticles (Li et al 2004b). Details regarding these structures and their properties have been previously published

(Nyamjav et al 2005). The procedure for the preparation of these nanowires offers several advantages over previously reported metallization strategies (Mertig et al 2002). The diameter of the wire can be more easily controlled, the spacing in between the particles can be governed by their surface properties, and nanoparticles can be placed along specific segments of the DNA if the Fe_2O_3 is functionalized with complementary short DNA sequences. The coated magnetic wires were placed in between the PAH–PSS functionalized electrodes using a molecular combing procedure (Bensimon et al 1994). A drop of solution containing the templated DNA was stretched across the surface using a receding meniscus protocol (Bensimon et al 1995). The chip was rinsed with

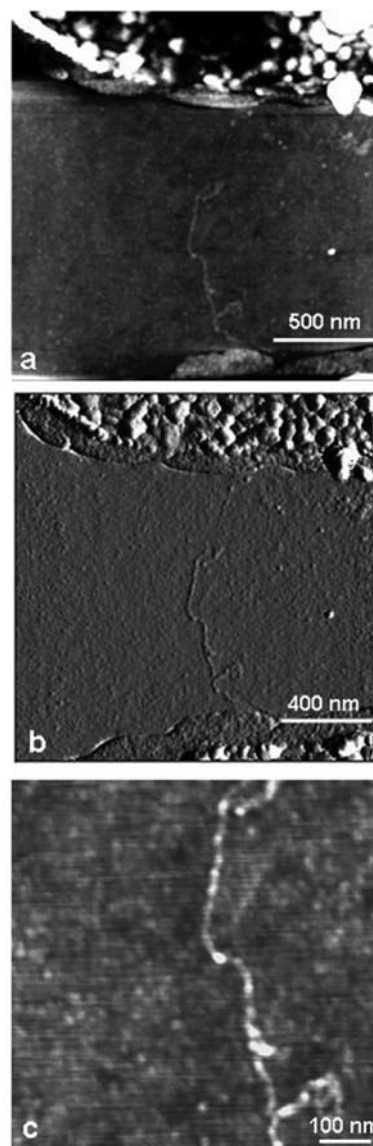


Figure 3 An area between two dip-pen nanolithography-modified electrodes after the templated DNA was stretched via molecular combing. (a) is a height image and (b) is an amplitude image. The height scale is 12 nm in (a) and 0.1V (1.475 nm) in (b). (c) shows a high resolution height image of the templated DNA strand imaged in (a) and (b). The height scale in (c) is 3 nm.

water to remove loosely bound structures and excess salt. The electrode surface was imaged by AFM and a typical result is shown in Figure 3. The templated wires are terminated on Fe₂O₃ nanoparticles which are capped with positively charged pyrrolidinone. The negatively charged surface, owing to the presence of PSS, allows the wires to be localized because of electrostatic interactions (Figures 3a, 3b). High resolution height images can resolve the individual particles on the DNA (Figure 3c). The height of the structure across the electrodes was 2.35 ± 0.33 nm extracted from 5 randomly drawn height profiles.

Summary

In summary we have demonstrated the following: (i) a DPN procedure to modify microfabricated structures with polyelectrolytes; (ii) a protocol to characterize the modified surface in between the electrodes; and (iii) a methodology to localize and stretch DNA coated with magnetic nanoparticles between specific sets of electrodes. These proof-of-concept experiments will be utilized in the construction of devices with small electrode gaps. Such gaps will be generated by cutting the DNA in specific locations using restriction enzymes (Kinsella and Ivanisevic 2005).

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