Nanoscale patterning of gold nanoparticles using an atomic force microscope

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Abstract

We report on the use of the tip of an atomic force microscope to remove selectively, and subsequently to deposit, nanoparticles of gold passivated with tri-n-octylphosphine oxide (TOPO)/octadecylamine. The study has revealed a minimum feature size of 50 nm in the removal experiment, while lines of 180 nm could be drawn with the gold nanoparticles, limited by the quality of the substrate surface.
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1. Introduction

The development of new and novel nanolithographic techniques is essential if the aspirations of nanotechnologists are to be realised. Current microlithographic methods, exploited extensively by the electronics industry, rely on patterning of a resistive film, followed by a chemical etch of the substrate. Dip-pen nanolithography (DPN) has been introduced and developed by a group in Northwestern University [1–3]. An AFM tip is used to 'write' suitable materials, e.g. alkanethiols, onto an appropriate substrate, e.g. gold, in a manner similar to that of a fountain pen. Thus, DPN provides a means for creating and functionalizing nanoscale devices. The DPN method complements that of microcontact printing, using an elastomeric stamp [4], as it can be used to place different types of molecules at specific sites within a nanostructure. For example, DPN might be used for fabricating nanoparticle-based electronic memories [5].

The chemisorption of 'ink' to the substrate is the driving force that moves the ink from the AFM tip to the substrate as the tip is scanned across this surface. Adjusting the scan rate and relative humidity can control line widths, although there is currently some debate about the influence of humidity [6,7]. Recent developments of DPN have included an overwriting capability that allows one nanostructure to be generated and the areas surrounding that nanostructure to be filled with a second type of ink [2]. Furthermore, an eight-pen nanoplotter capable of doing parallel lithography has been reported [3]. There have also been a number of theoretical models developed to describe the DPN process [8–10]. Most of the inks used in the DPN process have been based on long-chain alkanethiol molecules. Some recent success has also been achieved with Au(III) complexes [11], magnetic nanoparticles [12], proteins [13] and conductive polymers [14]. In a recent paper, an AFM tip was successfully used to deposit small islands, about 50 nm in diameter, of gold nanoclusters at a predefined position on a surface [15].

Here, we report on the use of DPN to pattern organically capped gold nanoparticles. Depending on the conditions used, the AFM tip could be used either to remove selected areas from a thin cast film of the nanoclusters or to write these as lines on a hydrophobic substrate.

2. Experimental

The gold nanoparticles (Q-Au) were of nominal diameter 10 nm passivated with tri-n-octylphosphine oxide/octade-

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cylamine; a schematic diagram of their structure is shown in Fig. 1. This capping makes the nanoparticles soluble in various organic liquids, but mainly insoluble in water. The organically passivated nanoparticles were prepared as previously described using Schlenk line techniques [16]. In a typical preparation, 10 g octadecylamine, 25 g technical grade tri-*n*-octylphosphine oxide (TOPO) and 0.0325 g $NaBH_4$ were charged to a Schlenk flask, the atmosphere evacuated and back flushed with dry nitrogen three times. The organic ligands and reducing agent were then heated under vacuum to 100 °C for an hour, and finally flushed with dry nitrogen. The temperature was increased and stabilised at 190 °C. A solution of $HAuCl_4$ (0.07 g, 2.0×10^{-4} M) in 5 ml of 4-tertiary butylpyridine was injected directly into the hot organic ligands, causing an immediate deep red colouration. The solution was allowed to grow for 30 min under dry nitrogen, and then removed from the heating source. The reaction cooled to 60 °C, removed from the Schlenk line and ca. 50 ml of methanol added, causing a precipitate. This was isolated by centrifugation, giving a dark red powder, which could be dispersed in non-polar organic solvents, such as toluene. Filtration of the toluene solution yielded a dark red solution of gold nanoparticles with a cubic crystalline core, capped with a mixture of TOPO and octadecylamine.

The atomic force microscope used in this work was a Digital Instruments Nanoscope E contact mode instrument. Silicon nitride cantilevers with a spring constant of 0.15 N m^{-1} were used for all the experiments. The humidity was not found to have a major influence in our preliminary study. The various patterning experiments were undertaken in a Class 10,000 microelectronics grade clean room *in air* (i.e. no environmental chamber was used). The relative humidity of the ambient was approximately 40%. Fig. 2 illustrates the two modes of patterning used in this study. In the first, Fig. 2(a), the AFM tip was used to selectively remove Q-Au particles from a region of the substrate that had previously been coated with the material by solution
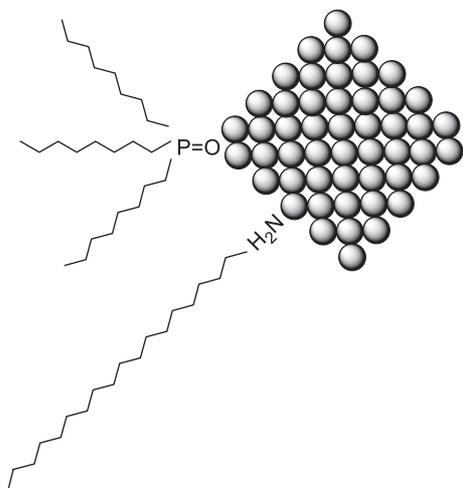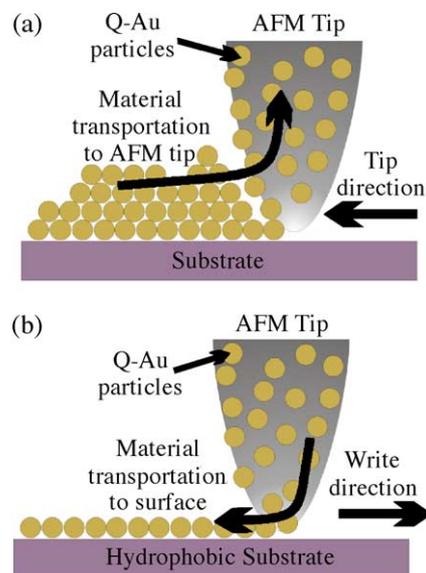
Fig. 2. Schematic diagram showing the use of an AFM tip to: (a) remove Q-Au particles from a substrate; and (b) to deposit Q-Au onto a substrate.

casting. The coated-tip could then be scanned across a different substrate to effect the transfer of the Q-Au from AFM tip to the substrate, Fig. 2(b).

All the silicon substrates used in this work were p-type, (100) orientation. Prior to use, the silicon was soaked in chloroform, followed by acetonitrile for 2 min each, rinsed with water and finally blown dry with nitrogen. Due to the presence of a native oxide layer, the silicon surface tended to be slightly hydrophilic, with an average static contact angle of 40–50°. Glass slides with a thermally evaporated layer of gold were also used as substrates; a layer of chromium (60 nm thick) was deposited between the glass and gold (225 nm thick) to aid adhesion of the Au. To achieve hydrophobic surfaces, both the silicon and gold substrates were dipped in a 2% solution of dimethyldichlorosilane in 1,1,1-trichloroethane for 2 min, rinsed with *iso*-propyl alcohol and then dried for 10 min before use.

3. Results and discussion

3.1. Removal of Q-Au to AFM tip

The Q-Au particles, dissolved in chloroform, were cast onto the substrates using a microsyringe; the solvent was then allowed to evaporate. This left a 'solid' layer of the nanoparticles on the substrate surface. Fig. 3 shows a cluster of the Q-Au particles on an untreated (slightly hydrophilic) gold surface. A layer-type morphology is evident; the Q-Au particles appear to self-organize into a multilayer architecture. A step height analysis using the line scan showed that the layer thickness is about 10 nm, consistent with that expected from the diameter of the individual particles. We have previously shown that the Q-Au forms an insoluble

Fig. 1. Structure of Q-Au nanoparticle.