Moving beyond Molecules: Patterning Solid-State Features via Dip-Pen Nanolithography with Sol-Based Inks

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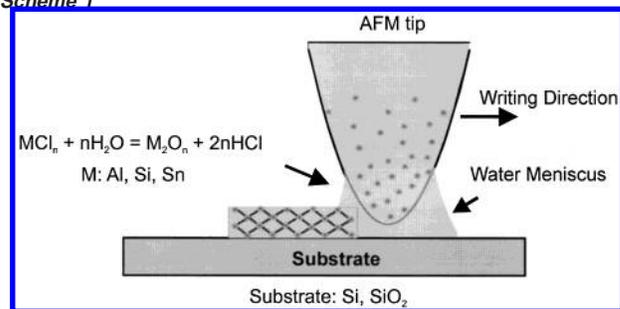
Dip-pen nanolithography (DPN) can be used to generate one molecule thick structures through the controlled movement of an ink-coated atomic force microscope (AFM) tip on a desired substrate.[1] In many cases, the molecular inks transport from the tip to the substrate surface via a water meniscus formed between the tip and substrate under ambient conditions.[2] The method was originally developed for alkylthiol self-assembly on gold, but it was subsequently extended to silazanes on semiconductor surfaces[3] and metal structures on conductive surfaces.[4] In addition, it has been used extensively as a way of making patterns out of simple organic and complex biological molecules which can be used to direct the assembly of higher-ordered architectures.[5] In principle, DPN can be extended to pattern any material on virtually any substrate provided there is a driving force for moving the molecules from the tip to the substrate. In practice, DPN experiments are generally limited by factors such as the solubility of the desired ink, the transfer and stability of the material within the water meniscus, and the adsorption of the material on the substrate surface. Thus, the selection of stable inks that can be transferred from the tip to the substrate is critical to a DPN experiment. Thus far, inks used include alkanethiols,[1] arylthiols, and thiol-functionalized proteins and alkylthiol-modified oligonucleotides[5] for Au substrates, alkylsilazanes[3] and inorganic salts[4] for oxidized Si surfaces, and alkylsilazanes for oxidized GaAs.[3]

Herein, we describe a new method for the direct patterning of organic/inorganic composite nanostructures on silicon and oxidized silicon substrates. The approach works by the hydrolysis of metal precursors in the meniscus according to the reaction $2MCl_n + nH_2O \rightarrow M_2O_n + 2nHCl$. This method was inspired, in part, by the sol–gel chemistry used to make mesoporous structures from inorganic salts and polymer surfactants.[6] Significantly, unlike the original DPN method, this technique allows one to prepare solid-state structures with controlled geometry beyond the individual molecule level.

The inks are hybrid composites of inorganic salts with amphiphilic block copolymer surfactants. We have successfully patterned composite nanostructures consisting of Al_2O_3, SiO_2, and SnO_2 on silicon and silicon oxide surfaces (Scheme 1). After removing the organic moiety, mesoporous metal oxides are the resulting products. Significantly, this method does not require conducting substrates. The role of the copolymer surfactant is to disperse and stabilize the inorganic ink precursor, increase ink fluidity, and act as a structure-directing agent for the materials that comprise the patterned nanostructures (i.e., mesoporosity).

A ThermoMicroscopes CP AFM and conventional silicon nitride microcantilevers (force constant of 0.05 N/m) were used for all

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Scheme 1

$MCl_n + nH_2O = M_2O_n + 2nHCl$
M: Al, Si, Sn

AFM tip
Writing Direction
Water Meniscus
Substrate
Substrate: Si, SiO₂

patterning experiments. In each experiment, the tip was coated by dipping it into the as-prepared sols at room temperature for 20 s. All patterning experiments were conducted under ambient conditions without rigorous control over humidity (∼40%) and temperature (∼20 °C) with a tip–surface contact force of 0.5 nN. To minimize the piezo tube drift, a 90 μm scanner with closed loop scan control was used for all patterning experiments. Subsequent imaging of the generated patterns was done with the ink-coated tip under conditions identical to those used for patterning but at a higher scan rate (6 Hz).

In a typical experiment, an inorganic precursor solution (sol) was prepared by dissolving 1 g of the block copolymer poly(ethyleneoxide)-*b*-poly(propyleneoxide)-*b*-poly(ethyleneoxide) (EO_{20}-$PO_{70}EO_{20}$) (Pluronic P-123, BASF) in 10 g of ethanol and then adding 0.01 mol of the desired inorganic chloride precursor. The mixture was stirred vigorously for 30 min to generate the sol. The as-made sols are transparent fluids. The ethanol slows the hydrolysis of the inorganic precursor (as compared with water),[7] and as a result the gelation normally occurs after several hours and is not complete until several days. This time frame allows one to easily do DPN experiments, which for the ones described herein take only a few minutes.

Dots, lines, and complex patterns comprised of tin oxide and aluminum oxide have been generated on silicon and silicon oxide (>600 nm oxidation layer) substrates, as shown in Figure 1. For example, 155 nm wide parallel lines made of tin oxide have been constructed on SiO_2 by moving a tip coated with the composite ink ($SnCl_4$ and P-123) across the substrate (0.2 μm/s). Similarly, dots consisting of Al_2O_3 could be generated on a Si substrate using a tip coated with $AlCl_3$ and P-123 by successively bringing the tip in contact with substrate for 1 s/dot intervals. These structures maintain their shapes even after repeated imaging (five times) and are indefinitely stable (>1 month) under ambient conditions.

A Si sol (comprised of $SiCl_4$ and P-123) was patterned onto a silicon oxide substrate in the form of parallel lines. The composition of the lines is expected to be a mixture of SiO_x and the polymer.
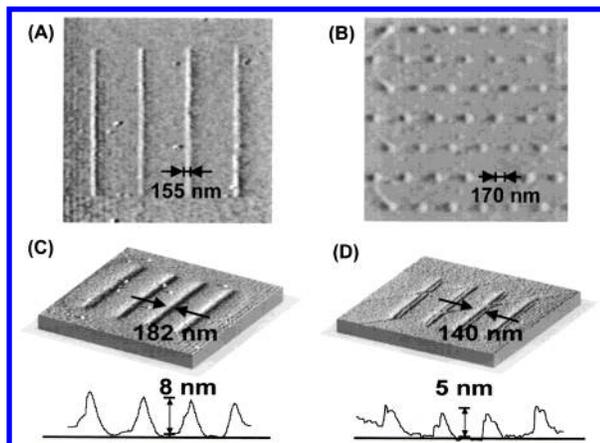
Figure 1. (a) Topographic AFM image of composite tin oxide/P-123 nanostructures on silicon oxide; the writing speed for each line is 0.2 μm/s. (b) Lateral force microscope (LFM) image of a dot array of aluminum oxide/P-123 composite nanostructures formed on silicon; the holding time for each dot is 1 s. AFM images collected before (c) and after (d) heating silicon oxide/P-123 composite nanostructures in air at 400 °C for 2 h; the writing speed is 0.1 μm/s. Note the lateral dimensions are enlarged due to tip convolution.

When heated in air at 400 °C for 2 h, the copolymer surfactant is expected to combust leaving a SiO_2 nanostructure. Consistent with this hypothesis, an AFM image collected from the same area postheating indicates that the pattern height decreases from 8 to 5 nm, Figure 1c and d.

The types of oxide structures that can be formed seem only limited by the availability of sol precursors. Indeed, tin oxide structures have been prepared from $SnCl_4$ and P-123 on SiO_2; energy dispersive X-ray (EDX) analysis of a 4 μm SnO_2 dot formed by holding the ink-coated tip for 30 s shows the expected peaks for tin, silicon, and oxygen, confirming the chemical identity of the microstructure (Figure 2a−c). The copolymer used here is well known as a structure-directing agent for mesoscopic ordered solids. Transmission electron microscope (TEM) images of bulk as-prepared products (used as a control), after being heated at 400 °C for 2 h, show that the pore size for SiO_2 is about 10 nm, Figure 2d. These patterned nanostructures are believed to be chemisorbed to the underlying substrate. Indeed, others have shown that when sols hydrolyze on oxide substrates, they form thin films that are adsorbed to the substrates through silicon−oxygen−metal bonding.[8] Finally, it is assumed that the nanostructures in Figure 1 undergo the same structural transition as that observed for the bulk material.

The work reported herein is important for the following reasons. (1) This novel process allows one to pattern solid-state materials, rather than organic molecules, onto substrates via a straightforward modification of the conventional DPN process without the need for a driving force other than chemisorption (e.g., an applied field). This could open up significant opportunities in areas ranging from high-resolution mask fabrication to the evaluation of solid-state nanoelectronic structures and devices fabricated by DPN. (2) The diffusion coefficients of the sol inks are qualitatively comparable to those of alkanethiols on gold (e.g., octade-canethiol), enabling relatively fast patterning by DPN. (3) The composite nanostructures have large surface areas that are important
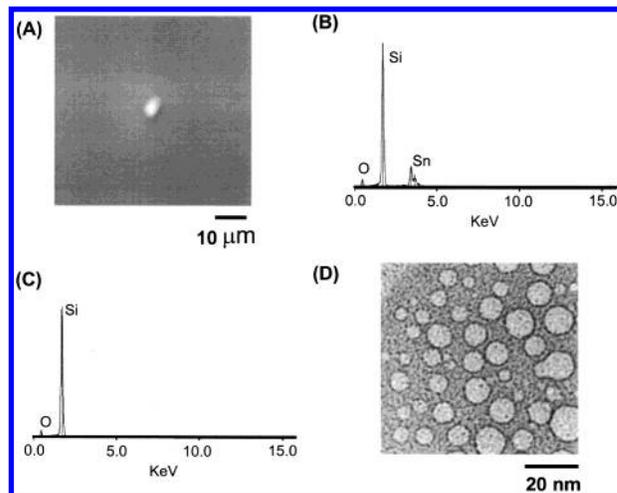

Figure 2. (a) Scanning electron microscope (SEM) image of a 4 μm SnO_2 dot formed by holding an ink-coated tip on the substrate for 30 s. (b) EDX analysis of the SnO_2 dot. (c) EDX of the SiO_2 substrate outside of the dot. (d) TEM image of the mesoporous SiO_2. The image was collected from heated samples with a Hitachi HF-2000 TEM.

for catalyst and waveguide applications. Functional materials can be added quite easily into sol inks.[9] For example, in the case of catalysts, these types of structures could be very important for initiating the growth of larger structures (e.g., nanotubes) from a surface patterned with these materials. Finally, it is important to note that this sol patterning process complements the larger scale micromolding techniques[10] by offering substantially higher resolution and the ability to make multicomponent nanostructures with ultrahigh registry.[1b]

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