13 Surface Patterning Using Self-Assembled Monolayers: A Bottom-Up Approach to the Fabrication of Microdevices

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13.1 INTRODUCTION

The bottom-up approach to the fabrication of microscale devices requires the ability to successfully pattern surfaces. This patterning can be achieved by the use of self-assembled monolayers. In this chapter, surface patterning results with respect to making photonic crystal devices and strain gauges are presented. Patterning is
achieved using two approaches. For the photonic crystal devices, UV irradiation is used to pattern self-assembled monolayers, and for the strain gauge a photoresist-based process is used. The electrostatic self-assembly method is used to make patterned multilayers on silicon for the photonic crystal devices. Conducting films of gold were deposited on flexible substrates for making strain gauges. The films were deposited using a completely solution-based process. These approaches are very cost-effective compared to present microdevice fabricating technologies, which are discussed next, and the entire procedure can be done on a laboratory benchtop.

One of the most important fabrication technologies in the microelectronics industry is the top-down approach to making microdevices, be it microelectromechanical systems (MEMS), microfluidics, optical systems such as micromirrors, or communication and information storage devices. In this approach, material is first laid down, and it is removed gradually from top to bottom in patterns depending on the application. The conventional microfabrication technologies have limited the choice of materials; silicon is still the most widely used material of choice. This in turn limits the applications of the devices. For example, it would not be possible to make a biocompatible device for use in vivo with conventional materials used for microelectronics. The bottom-up approach to fabricating micro- and nanodevices has been an area of considerable recent research. The advantages of this approach over the conventional top-down approach used in the microelectronics industry are many. For one, it offers considerable versatility in the materials used. Different types of organic materials that are more easily tailorable than ceramics, such as polymers, nanoparticles, and self-assembled monolayers, are commonly studied. This approach also minimizes waste of material and does not require sophisticated equipment, leading to much lower costs and to molecular-scale control in device fabrication.

The key to such an approach is to successfully pattern the substrates and selectively deposit materials forming three-dimensional structures. Patterning of substrates using self-assembled monolayers (SAMs) is an area that has generated much interest. Self-assembled monolayers are long-chain alkanes that spontaneously chemisorb onto the surfaces of appropriate materials. These layers offer control of structure at the molecular level and can act as ultra-thin resists in lithographic processes. Many problems associated with current patterning techniques, such as the limit on the smallest feature size, optical diffraction effects, depth of focus, shadowing, and undercutting can be minimized. Self-assembly leads to equilibrium structures that are at, or close to, the thermodynamic minimum, and as a result these systems tend to be self-healing and defect rejecting.

In order to fabricate functional microdevices, it is essential to form three-dimensional structures on the self-assembled monolayer. These structures can be built if multilayers can be grown in patterns of the desired structure. There are a number of patterning techniques for SAMs that have been studied: soft lithography techniques such as microcontact printing, replica molding, microtransfer molding, selective transformation of terminal functionalities by either photochemical or chemical methods, selective removal of monolayer film by irradiation and micromachining, and selective deposition of polyelectrolytes and nanoparticles. A more recent method of patterning is the use of scanning probe microscopy tips, which has drastically reduced the sizes of the patterns formed and can be so effective that it can be
used to manipulate single molecules. Techniques such as nanografting and dip pen nanolithography use the tip of an AFM probe to selectively remove and deposit molecules onto the surface. Scanning tunneling microscopy probes have also been used to pattern SAMs using electrochemical methods by applying a bias between the conductive probe and the substrate.

In this chapter, results with regard to the fabrication of different types of devices using patterned SAMs using the bottom-up approach are presented. A brief description of the type of prototype devices investigated follows. A first set of representative experiments on silicon substrates was aimed at fabricating spatially periodic photonic crystals. Photonic crystals are a class of periodic composite structures consisting of spatially varying low- and high-refractive-index materials that exhibit a forbidden band, or photonic band gap, of frequencies wherein incident electromagnetic waves cannot propagate. Introducing defects into the ordinarily symmetrical structure disrupts the periodicity of the crystal-defining microcavities, and in some cases waveguides, where incident electromagnetic energy can become localized or allowed to propagate. The creation of patterns on silicon and formation of multilayers using the electrostatic self-assembly process is a possible method of fabricating these devices. Microstrain gauges are other spatially patterned devices that may be fabricated in situ using self-assembly. These can be achieved by patterning conducting films on flexible substrates. The basic theory behind these devices is that a change in the length and geometry of an electrical conductor causes a change in its resistance, and this change can be quantified and used to infer elongation. Using self-assembly, patterned gauges may be formed by depositing conducting gold on substrates such as polyethylene and measuring the change in resistance of the conductor versus strain.

13.2 EXPERIMENTAL PROCEDURE

13.2.1 MATERIALS

Three types of substrates for patterning were studied: silicon (111); Kapton® (DuPont), a polyimide; and polyethylene. The SAMs that were used are octadecyltrichlorosilane (OTS) (Aldrich), heptadecafluoro 1, 1, 2, 2, tetrahydrodecyl trichlorosilane CF3(CF2)7CH2CH2SiCl3 (CF) (Gelest), 3-aminopropyltrimethoxy silane (APS) (Gelest) and 3-mercaptopropyltrimethoxy silane (MPS) (Gelest). The polyelectrolyte used was sodium polystyrene sulfonate (SPS), and the nanoparticles used were silicon dioxide (Nissan Chemical Industries), titanium dioxide, and gold, which was synthesized using a slight modification of previously described methods.

13.2.2 SUBSTRATE PREPARATION

Silicon wafers, cut into small 2-cm side squares, were rinsed thoroughly with dichloromethane and methanol and dried under a stream of nitrogen. The samples were treated with a 7 : 3 v/v mixture of H2SO4/H2O2 for 20 min at 80°C (piranha treatment) and rinsed thoroughly with nanopure water (18 MΩ) from a Barnstead nanopure water system. The Kapton® and polyethylene were plasma treated using a March plasmad plasma etcher in an argon atmosphere for ~2 min at 0.2–0.4 torr and 50 W power.
13.2.3 Deposition of SAM

OTS SAM was deposited in a glove bag under nitrogen atmosphere. The piranha treated silicon substrates were immersed in a 1% (v/v) solution of OTS in dicyclohexyl (Aldrich) for 1 h with stirring. After the reaction was over, the substrates were rinsed thoroughly with dichloromethane. CF SAM was also deposited in a similar manner, with Isopar-G (Exxon) acting as the solvent in this case. The entire deposition process was carried out in a nitrogen atmosphere and dry conditions. The deposition of APS and MPS were carried out in ambient conditions. The substrates were immersed in a 1% (v/v) solution of APS/MPS for 15 m with stirring. After that they were rinsed thoroughly in methanol and heated at 110°C for 1 1/2 h and then dried under vacuum at 50°C. All the SAM depositions were carried out in less than an hour after the substrate preparation.

13.2.4 Patterning

Patterning of the SAMs was carried out by irradiation with an Hg(Ar) lamp (Model 6035, Oriel Instruments) at a wavelength of 184 nm. The OTS SAMs were photolyzed for 1 h, while all the others were photolyzed for 3 h. The masks consisted of meshes used for transmission electron microscopy, and masks were also made on aluminum sheets when larger scale patterns were required. Patterning on the flexible substrates was carried out by using a positive photoresist S1813 (Shipley). Photoresist was spin-coated onto the silane-coated substrates, and then irradiated with broadband UV (350–450 nm) (Oriel Instruments Model no. 92530) through a mask, developed using the Microposit developer 351. Then gold was coated onto the entire substrate and later photoresist was removed using acetone. At that time the gold, which was coated over the photoresist, was also removed leaving a pattern of conducting lines.

13.2.5 Deposition of Multilayers

Multilayers were deposited on silicon using electrostatic self-assembly. TiO₂ and SiO₂ were alternately deposited on patterned OTS, and TiO₂ and SPS on patterned CF. The patterned samples were first dipped in the positively charged solution for 3 min, sonicated in nanopure water for 2 min, dipped in the oppositely charged solution for 3 min and sonicated again, and this cycle was repeated to obtain the desired number of multilayers. On the polymer substrates, gold was deposited using previously described methods.

13.3 RESULTS AND DISCUSSION

13.3.1 Patterning on Silicon

The piranha treatment cleans the surface exposing the hydroxyl groups on the surface of silicon. The deposition of silanes on these surfaces occurs by the hydrolysis of the alkoxy- or trichloro- groups on the silane and subsequent reaction with the surface hydroxyl groups. The deposition of OTS and CF was characterized by
contact angle measurements. After the piranha treatment the silicon substrate was completely wetted with contact angles as low as ~10°. The deposition of OTS or CF raised the contact angles. For OTS it was between 90° and 115°, and for CF the contact angles were slightly higher, around 120°. This is expected because CF has a much lower surface energy than OTS due to the presence of fluorine groups. After irradiation with UV light at 184 nm, both the SAMs are degraded and are removed from the substrate. This is evidenced by the drop in contact angles to ~10° upon photolysis. The CF took a longer time than OTS to photolyze completely and this can be attributed to the strong C–F bonds. Figure 13.1 illustrates the photolysis process on OTS.

On OTS and CF, the multilayers were formed by electrostatic self-assembly. Electrostatic self-assembly involves dipping a charged substrate alternately into solutions of an anionic charged species and a cationic charged species; the electrostatic force between oppositely charged molecules acts as the binding force holding the molecules together. Patterning on OTS and CF creates regions of charge and regions where there is no charge and the charged molecules get selectively adsorbed on the charged regions. TiO₂ was the positively charged nanoparticle for OTS and CF; SiO₂ was the negatively charged nanoparticle for the patterned OTS, and SPS was the negatively charged polyelectrolyte used for CF. After the photolysis the negatively charged substrate is exposed and the charged particles selectively adsorb on the charged regions and are bound by electrostatic interactions. Figure 13.2 is an SEM image of the patterns formed on OTS- and CF-coated substrates. The size of the patterns was 7.5 × 7.5 µm square holes with a center-to-center spacing of 12.5 µm. The lengths of all the scale bars in the figure are 10 µm. The dark regions are the regions of deposition in all the images except in Fig. 13.2(a), where it is the opposite. This is probably due to some differential charging effect when imaging the samples.

The deposition of the polyelectrolyte, SPS, was successful for the CF, while on the OTS good patterns were not obtained. This can be explained by the fact that the negatively charged groups on the polyelectrolyte are repelled by the electronegative fluorine atom on the CF and are thus selectively deposited on the regions where CF
is absent. On the OTS SAM there is no such interaction and SPS, being a large molecule, may get attached on the OTS regions also due to some hydrophobic interactions. These selectively grown ESA nanocomposites represent 2-D photonic crystal structures composed of high refractive index pillars suspended in air. Measurements on a Rudolph Auto EL ellipsometer revealed that the TiO$_2$/SiO$_2$ corresponded to high index pillars with an average refractive index of 1.6.

13.3.2 PATTERNING ON POLYETHYLENE AND KAPTON®

Polyethylene and Kapton® are flexible polymers suitable for making patterned electrodes to fabricate microstrain gauges in situ. This requires selective deposition of conductive layers, and gold was the material of choice because of the ease of deposition of a conductive film using a completely solution-based process. The resistance of a conductor is dependent on its length and cross-sectional geometry, and a change in the geometry would lead to a change in the resistance and this can be measured quantitatively. This principle is used in strain gauges also, where a change in the length will cause a change in the resistance and the strain can be measured. In order to increase the device sensitivity, the length of the conductor should be made long and this can be done using geometry as shown in Fig. 13.3.

The surface of the polymers is plasma treated to deposit the silanes. Plasma treatment of the polymers creates free radicals on the surface, which when exposed to air form oxygenated species. These can then react with the silanes to form a monolayer on the surface. Table 13.1 shows the contact angles for substrates after
plasma treatment and SAM deposition. Figure 13.4 shows the X-ray photoelectron spectroscopy (XPS) data corresponding to the different treatments on Kapton®. A comparison of the untreated and the plasma-treated surfaces shows that there is an increase in the oxygen concentration, as expected. The deposition of the SAM on the substrate gives rise to a polysiloxane backbone. Figure 13.4(c) shows the siloxane peak at 102.4 eV, which confirms the formation of the SAM. Similar results were also obtained for polyethylene.

The deposition of gold on the SAMs takes advantage of the fact that gold has a large affinity for groups such as amino-, mercapto-, and cyano-27 The choice of the SAMs was based on this, and amino- and mercapto- terminated SAMs were used in our experiments. The formation of conductive layers of gold nanoparticles is done by a seeding method as described in a previous study.28 In brief, the SAM-coated substrates are dipped in colloidal gold solution for 2–3 h wherein gold particles get attached to the substrate. Then more gold is reductively deposited on the gold already attached, leading to complete coverage. Figure 13.5 shows the SEM images of the formation of complete coverage gold on Kapton®. All scale bars are 100 nm.

### TABLE 13.1
Contact Angles for the Polymers after Plasma Treatment and SAM Deposition

<table>
<thead>
<tr>
<th></th>
<th>Kapton®</th>
<th>Polyethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>71°</td>
<td>94°</td>
</tr>
<tr>
<td>Plasma treated</td>
<td>18°</td>
<td>41°</td>
</tr>
<tr>
<td>After SAM deposition</td>
<td>84°</td>
<td>95°</td>
</tr>
</tbody>
</table>
FIGURE 13.4 XPS spectra of (a) untreated (b) plasma treated, and (c) Si peak of APS-deposited Kapton®.
The resistance of the samples was measured using a four-point probe. The resistivities on both polyethylene and Kapton® were about 1 ohm/sq. The thickness of a layer of gold was found to be ~300 nm using cross-section SEM. Table 13.2 depicts the strain-resistivity data for gold on Kapton®, and as expected the resistance is found to increase as a function of length.

The patterning on these substrates is done to generate conductive lines, as shown in Fig. 13.3. Patterning was done using a method developed by Hua et al. Table 13.2 depicts the patterns generated on Kapton®, which consists of alternate

<table>
<thead>
<tr>
<th>Load (N)</th>
<th>Resistivity × 10⁴ (Ω-cm)</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.95</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>1.28</td>
<td>0.078</td>
</tr>
<tr>
<td>20</td>
<td>1.26</td>
<td>0.17</td>
</tr>
<tr>
<td>70</td>
<td>3.2</td>
<td>1.875</td>
</tr>
</tbody>
</table>

FIGURE 13.5 SEM images of (a) gold monolayer, (b) one-layer seeded gold, and (c) two-layer seeded gold on Kapton®.

FIGURE 13.6 Patterned gold on Kapton®.
conducting lines. The size of the lines is about 1 mm. Although the patterns shown here are of a big size, with masks of smaller size, patterns of 1 µm or less can also be made. The conductivity of the film was not affected by the patterning process and was the same as for the unpatterned substrates.

13.4 CONCLUSIONS AND APPLICATIONS

It has been possible to selectively deposit and create three-dimensional structures on silicon using a combination of patterned self-assembled monolayers and electrostatic self-assembly. The size of the smallest patterns created was 7.5 µm, which was the smallest mask utilized. However, with appropriate masks the pattern size can be reduced even further. It was also possible to deposit conducting layers of gold on polymer substrates such as polyethylene and Kapton® for the fabrication of strain gauges. Patterning was also successfully achieved to fabricate conducting lines. These results show that fabrication of microdevices can be achieved by methods that are more economical and easier than conventional microfabrication technologies that use sophisticated equipment, increasing costs. This method is so simple that it can be performed on a laboratory benchtop. Future efforts are being directed toward decreasing the size of patterns and the use of a maskless approach to patterning.

PROBLEMS

1. List the important trade-offs when considering bottom-up and top-down fabrication technologies.
2. Perform a literature search on the subject of patterning of substrates using self-assembled monolayers and list any new advances in techniques that have been made relative to the technique in this chapter.
3. Think of some new possible applications for surface patterning using the SAM technique and list what might be the benefits.

ACKNOWLEDGMENTS

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