A HIGH ASPECT RATIO, FLEXIBLE, TRANSPARENT AND LOW-COST PARYLENE-C SHADOW MASK TECHNOLOGY FOR MICROPATTERNING APPLICATIONS

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Abstract: In this paper, we present a flexible parylene-C shadow mask technology for creating microscale patterns on flat and curved surfaces. The smallest feature size of 4 µm is demonstrated and the technology is scalable up to full wafer size. With the addition of SU-8 pillars, we also demonstrate multi mask processing with an alignment accuracy of about 5-6 µm. To achieve the smallest features, a low temperature and high aspect ratio (>8:1) parylene etch process is also developed. Utilizing this shadow mask, we successfully patterned proteins and cells on various surfaces (glass, PDMS, methacrylate) up to 9 times. This technology has potential applications for patterning proteins, cells and organic transistors on conventional and/or unconventional substrates.

Keywords: Parylene-C, Flexible Shadow masks, High Aspect Ratio Polymer Etching

1. INTRODUCTION

The current interest for microscale patterning on “unconventional” surfaces and/or non-IC applications has increased the need for novel patterning technologies. Previously reported microstencils, which are made of rigid and polymeric membranes, have various shortcomings. Si, Si\textsubscript{3}N\textsubscript{4} or stainless steel shadow masks are brittle, require complicated and expensive processing steps, and lack the precise pattern definition and flexibility to create patterns with varying length scales due to the gap between the rigid stencil and the substrate \cite{1,2}. Elastomeric microstencils (such as PDMS) are not easy to handle and have difficulty in allowing mechanical alignment and lack high resolution \cite{3}. Shadow masks made of SU8 polymers are also not suitable for large scale applications since their high residual stress make them buckle. Furthermore, dry lift-off method utilizing parylene as demonstrated by B. Ilic \cite{4} is limited to very thin (~1-2µm) films of single use and is applicable solely to cleanroom compatible substrates such as silicon and glass.

In this paper, we present a flexible, reusable, transparent and biocompatible parylene-C microstencil technology. A novel low temperature polymer etching process utilizing an inductively couple plasma (ICP) tool is developed to create the high aspect ratio (HAR) structures. The potential applications of this stencil technology are numerous including patterning for organic electronics, patterning of proteins and cells and patterning on topographically rough, curved and unconventional surfaces.

\textbf{Fig.1:} The parylene shadow mask being peeled off a wafer after fabrication

Parylene, poly-para-xylene, is widely utilized in the medical and electronics industries as a conformal coating and also increasingly in the MEMS field. Up to a certain thickness (50µm) the
parylene films are flexible and will conform to curved surfaces and also have the high mechanical strength and robustness compared to PDMS stencils and hence are reusable.

2. FABRICATION

To fabricate the flexible microstencil, first, a 10-20 µm thick parylene is deposited on a silicon wafer (PDS2010, Specialty Coating Systems). Then a 2000 Å thick Aluminum hard mask is deposited using sputter deposition. After patternning the Al hard mask, the uncovered parylene areas are etched in an ICP etcher (Plasmaterm 790). After this etch, the Al hard mask is stripped. Next, the parylene shadow mask is peeled off the wafer as shown in Fig.1 and is ready to use. As a side note, prior to parylene deposition, we routinely use HMDS as the adhesion promoter. Using the traditional adhesion promoter (A-174 Silane) tends to create a very strong adhesion between the film and the substrate and hence causes the film to tear while peeling. We have used both 10 µm and 20 µm thick parylene layers, and both work well and both are flexible, yet for large scale applications and for reusability, the 20 µm thick film is recommended even though it is slightly less flexible.

For larger features (dimensions > 100 µm), we fabricate the shadow mask with a room temperature ICP etch since lateral etching is not a major concern. Furthermore, while fabricating stencils with fine features (< 10 µm), one requires the most anisotropic etch and hence, we have developed a novel high aspect ratio parylene etch process which is detailed in the next section.

3. HIGH ASPECT RATIO ETCHING OF PARYLENE-C

Parylene is gaining popularity as a unique low temperature material for many biomedical or non-biomedical applications. It is also being utilized as a flexible substrate [5]. One of the current needs for parylene micromachining is the need for a high aspect ratio etch process. Meng, [6] utilizing a DRIE tool, obtained aspect ratios of up to 3:1, moreover to create stencils with fine features one requires higher aspect ratios.

It is possible to reduce the isotropy of a reactive ion etch process by reducing the etch temperature which is commonly done by etching silicon at low temperatures (~ -100°C). Moreover, for etching polymers such as parylene-C, reducing the etch temperature down to 5°C serves a similar purpose. Using an ICP reactor (Plasmaterm 790), we developed multiple recipes (Table 1) with fast etch rates and anisotropic profiles (>8:1). The parylene film shown in Fig.2(a) with a thickness of 55µm is etched with the recipe “b” in Table 1 and the one shown in Fig.2(b) with a thickness of 10µm is etched with recipe “c” in Table 1 and they both display almost vertical sidewalls. We were able to etch a 55 µm thick parylene film through an opening of 6 µm which is equivalent to an aspect ratio of about 9:1.

Table 1: ICP etch recipes for low temperature (5°C) parylene etching

<table>
<thead>
<tr>
<th>Etch #</th>
<th>Etch Rate (µm/min)</th>
<th>RF Bias Power (W)</th>
<th>Source Power (W)</th>
<th>O2 (sccm)</th>
<th>Ar (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>1.7</td>
<td>250</td>
<td>400</td>
<td>20</td>
<td>0</td>
</tr>
<tr>
<td>b</td>
<td>1.0</td>
<td>100</td>
<td>400</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>c</td>
<td>0.5</td>
<td>100</td>
<td>150</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

Aluminum is used as the hard mask during ICP etching which worked well, yet the fact that Al gets sputtered during etching and creates residue as
seen in Fig.2(b), we are currently investigating means to address this problem.

4. SURFACE PROPERTIES OF PARYLENE

As-deposited Parylene-C, similar to PDMS displays hydrophobic properties with a contact angle of \(\approx 98^\circ\). Furthermore, with a short \(O_2\) plasma treatment becomes hydrophilic and it stays hydrophilic for many days. The hydrophilic parylene surface seals extremely well to other hydrophilic surfaces, moreover, the hydrophilic surface does not adhere well to other surfaces, a property that is important while using the parylene-C as a shadow mask. Accordingly, we have characterized the contact angle and the stability of parylene sheets in aqueous environments over time. As seen in Fig.3, submersing the parylene sheet into DI water for 3 days (which may be the case for multiple rinsing experiments) did not change the surface properties significantly. Moreover, Al is used as the hard mask while etching parylene and to improve its adhesion to the parylene surface, we routinely roughen the parylene surface prior to depositing the Al metal which makes the top parylene surface hydrophilic, and hence our stencil to be single sided (one side sticks better than the other side).

5. PATTERNING PROTEINS AND CELLS WITH PARYLENE SHADOW MASKS

Patterning of proteins and cells are previously demonstrated with a parylene-C film by Takeuchi [3] and Craighead [4] on traditional surfaces for single use. Since both groups utilized a very thin to traditional surfaces onto which parylene can be deposited and etched from (silicon and glass). In our approach, we remove the parylene shadow mask from the surface it is deposited and then utilize it on any desired surface.

Parylene-C is a well known biocompatible material utilized heavily to coat implantable devices. Utilizing our parylene stencil, we successfully patterned proteins on polystyrene and methacrylated glass surfaces as seen in Fig.4. Since parylene is a very inert material, one can wash away the protein solutions and can reuse the parylene stencil multiple times. We were able to pattern FITC-BSA on PDMS surface for up to 9 times and the patterns retained their integrity during this time as seen in Fig.5(b).

We next explored applications of the parylene stencil in tissue engineering and have successfully patterned NIH-3T3 fibroblasts (as seen in Fig.6) and other cells types including AML12 hepatocytes and mouse embryonic stem cells on PDMS surfaces.

![Fig.4: Fluorescent images of proteins patterned on polystyrene (a) and methacrylated glass (b) surfaces](image)

![Fig.5: FITC-BSA was patterned on PDMS for (a) 1st use and (b) 9th use](image)

We next fabricated a cylindrical PDMS slab and utilizing our flexible parylene stencil, patterned fluorescent proteins on top. As displayed in Fig.7, due to the flexible nature of our stencil, one can quite readily pattern curved surfaces.
6. MICRO PATTERNING FOR UNCONVENTIONAL MATERIALS

Parylene stencil can also be utilized to create patterns with varying dimensions (pattern flexibility) on any surface. In Fig.8(a), we demonstrate a minimum feature size (4μm) deposited over a 10μm thick parylene stencil using sputtering. Fig.8(b) displays a large scale pattern generated using this technology. By utilizing SU-8 pillars (260μm in height), one can create mechanical alignment posts to house the parylene shadow masks, and with these posts, we were able to achieve multi mask processing with an alignment tolerance on the order of 5-6 μm.

7. CONCLUSIONS

In this paper, we present a flexible, reusable, biocompatible parylene-C shadow mask technology. The minimum feature size of 4 μm is demonstrated while using a 10 μm thick parylene stencil. A low temperature (5°C) parylene etch process was also developed to fabricate the structures with anisotropic profiles. Utilizing this flexible shadow mask technology, we demonstrate patterning of proteins and cells on polystyrene, glass and PDMS surfaces. The parylene shadow mask is biocompatible, chemically inert and reusable. Multi mask processing is demonstrated with the addition of SU-8 support pillars. The shadow mask technology is versatile and will find potential patterning applications in multiple fields including organic electronics and biotechnology.

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