Sacrificial Polymers and Their use in Patternable Air-Gap Fabrication

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Abstract:
Patternable air-gaps are added to electrical and mechanical structures in semiconductor and MEMS devices as a means to decrease the dielectric constant, add mechanical compliance, and facilitate microfluidics. In this study, sacrificial polymers and standard photolithographic techniques were used as a way to create air gaps. A photodefinable sacrificial polymer was created by adding photoacid generator (PAG) to the sacrificial polymer mixture. Air gaps were made by patterning the sacrificial polymer into the desired structure, covering it with an overcoat polymer, and decomposing the remaining sacrificial material. There are three problems associated with this fabrication technique: (i) the patterning resolution was coarse, (ii) residue was produced during the decomposition of the polymer, and (iii) wide structures tended to collapse. These problems were investigated through process optimization, quartz crystal microbalance (QCM), and overcoat modification, respectively. In addition, a new sacrificial polymer, PDM-1088, was investigated. PDM-1088 increased the resolution of the pattern, QCM measurements indicated the amount of remaining residue, and hardening the overcoat allowed the fabrication of structures several hundred micrometers wide. Micrometer scale air gaps were successfully fabricated through common photolithographic techniques, permitting the integration of these structures into semiconductor processing.

Introduction:
Air-gaps have yet to be created using standard electronics processing techniques. They are desirable for use in semiconductor and MEMS devices as a means to decrease dielectric constant, add mechanical compliance, and facilitate microfluidics. In this study, photopatternable air-gaps were successfully fabricated by improving each of the three major problems associated with sacrificial polymers: i) difficulty patterning the sacrificial polymer, ii) residue after decomposition, and iii) wide structure collapse.

Experimental Procedure:
Sacrificial polymers were used to create patternable air gaps. First, a new polymer, PDM-1088, was mixed with a photoacid generator (PAG) so that it could be patterned. The PAG released a proton upon heating or by exposure to 248 nm UV light. The acid significantly decreased the decomposition temperature of the sacrificial polymer.

As shown in Figure 1, PDM-1088 mixed with PAG has a lower decomposition temperature (170°C) than the next polymer (260°C) and the exposed polymer/PAG mix has an even lower decomposition temperature (85°C).

Through standard photolithography, as explained in Figure 2, PDM-1088 was spin-coated onto a copper (Cu)-sputtered...
silicon wafer and a pattern was exposed. Upon heating to 120°C, the exposed portions decomposed. An overcoat material was then spin-coated onto the sample. Two different overcoat polymers were used in this study; polyimide and Avatrel 8000 (polynorbornene). The overcoat was then exposed to 365 nm UV light to activate the polymer cross-linkers and was cured at 150°C for one hour. Finally, the sample was exposed a second time at 248 nm, activating all remaining PAG, followed by a six hour cure at 150°C to decompose the remaining PDM-1088.

Results:
There are three major issues associated with this processing technique: i) patterns are coarse due to polymer reflow and proton diffusion, ii) the polymer leaves behind a notable residue after decomposition, and iii) wide structures tend to collapse in the center due to surface tension. These problems were solved systematically by modifying the processing approach in three ways.

PDM-1088 has a glass transition temperature of 90°C, which is higher than previous sacrificial polymers. Decreasing the processing temperature increased control of the polymer reflow resulting in the fabrication of clean patterns.

Quartz crystal microbalance (QCM) was used to measure the mass left behind after polymer decomposition. This quantification of the residue allowed modification of the processing techniques, polymer choice, and PAG loading to achieve minimal residue. Polymer samples were spin-coated onto quartz crystals. The crystal was allowed to equilibrate to its resonant frequency in the QCM, and then the residue was washed off without removing the sample from the instrument. Finally, the solvents were evaporated at room temperature and the crystal equilibrated again to its resonant frequency. The change in frequency allowed us to use the Sauerbrey equation [1] to calculate the mass of the residue left on the crystal. Figure 3 shows the linear relationship between polymer thickness and residue, meaning the residue is dependent on the composition of the formulation.

Wide air-gap structures were successfully fabricated by modifying the overcoat material. Avatrel 8000 was not strong enough to hold up air-gaps wider than 100 µm as the surface tension pulled the overcoat onto the substrate. To strengthen the Avatrel, extra trimethylolpropane triglycidyl ether (TMPTGE) was added to the polymer. TMPTGE is a trifunctional polymer crosslinker used with Avatrel 8000, and the addition significantly increased the hardness, as seen in Table 1. By increasing the hardness, the resulting polymer was able to withstand surface tension pull, even at a thickness of 7 µm. Adding TMPTGE worked significantly better than several other attempted methods, including the addition of surfactant (Triton X-100) and the addition of a second, glass-like polymer (epoxycyclohexyl polyhedral oligomeric silsesquioxane, or POSS).

Conclusions:
By modifying processing methods and incorporating the use of PDM-1088, we successfully fabricated air gaps several hundred micrometers wide and only 5 µm tall. For the first time, such structures were achieved with an overcoat thickness less than 10 µm.

Future Work:
The fabrication method we developed can now be used in direct applications including electronic interconnects, MEMS, and microfluidics. More work needs to be completed to increase resolution, reduce residue, and create wide structures for certain applications.

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References:

![Figure 3: QCM results of mass residue vs. polymer thickness (PDM-1088 with PAG).](image)

<table>
<thead>
<tr>
<th>Overcoat</th>
<th>Elastic Modulus (GPa)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avatrel</td>
<td>2.44</td>
<td>0.155</td>
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<tr>
<td>Avatrel + TMPTGE</td>
<td>3.19</td>
<td>0.199</td>
</tr>
<tr>
<td>Avatrel + POSS</td>
<td>1.49</td>
<td>0.169</td>
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<tr>
<td>Air Gap</td>
<td>0.71</td>
<td>0.121</td>
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Table 1: Hardness and elastic modulus values of modified Avatrel 8000 overcoats.