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Characterizing the Performance of Rapidly-Degradable Polyaldehydes as Dry-Developing Photoresist

The demand for smaller and portable devices has created a need for more minuscule computer chips, requiring more intricate patterning and features. This patterning process is done by photolithography, which requires the use of polymetric photoresist. To be classified as a photoresist, it must degrade when exposed to light and be resistant to the etching process. This used to create a pattern onto a substrate by transferring a pattern from a photomask onto a substrate. The conventional way to do photolithography is by a wet development process. This involves spincoating a wafer, that is usually silicon, with your desired photoresist. This can be done by using a SCS spin coater. The next step would be to soft-bake the coated wafer, by using a hot plate, to evaporate the excess solvent from the photoresist. After the wafer is soft-baked, the next step would be to use a mask aligner to project the desired pattern form the mask onto the wafer. The exposed part of the photoresist that is not covered by the mask will then undergo a solubility switch, which requires a hard-bake process before the final solution-based development process. This developmental process is done by using a tetramethylammonium hydrodixe solution, which can be very corrosive.

For the past summer I have been working in the Kohl research group where they have created a dry-developing photoresist. The first two steps are the same. Spincoat the wafer with photoresist and soft-baking the wafer to remove the solvent. However, when the wafer is placed under the mask and exposed to light, the exposed photoresist starts to depolymerize into small molecules. This makes the developmental process very easy because the photoresist can evaporate off of the substrate simply by placing the substrate onto a hot plate or into a vacuum oven. Our photoresist is created from low celling temperature polymers which are easily degradable polyaldehydes. Having a low ceiling temperature means that the equilibrium temperature between the monomer and polymer is very low. So when the monomer or polymer is raised above the ceiling temperature it becomes thermodynamically unstable. The monomer we used was *ortho*-Phthalaldehyde which has a ceiling temperature of -40°C. From this monomer we created two polymers, a homopolymer (p(PHA)) and copolymer (p(PHA-PA)). The contents of the photoresist that we have created is diglyme, a photoacid generator (PAG), and either the homopolymer or copolymer. Diglyme is the solution and PAG is light sensitive solvent. When PAG is exposed to light from the mask aligner, it forms super acids which causes spontaneous depolymerization of the polymer due to the super acids reaction with the polymer backbone above its celling temperature. This depolymerization reverts the homopolymer back into the monomer, *o*-Phthalaldehyde, and the copolymer becomes *o*-Phthalaldehyde and propanal. What makes the copolymer special is because it is volatile, this means it can easily depolymerize at room temperature. The goal of this research is to characterize the performance of dry-developing photoresist materials by optimizing the development procedures and measuring the sensitivity and contrast values of the polymer.

The problem that we faced was how to efficiently develop the photoresist, while deriving contrast and sensitivity values that are commercially comparable. The conditions that were varied was the light exposure time, which is the time the light shines through the mask onto the wafer, thermal or vacuum development, what weight percent of PAG, either five or ten percent,

and the choice between the homopolymer or copolymer. Thermal development consists of the temperature and time the substrate was on the hot plate. Vacuum development is how long the wafer is in the vacuum oven and at what pressure the oven was set to. The variables I did not change was the average thickness, 280 nm, and the pre-bake conditions, 3 minutes at 115°C. To accurately calculate the contrast and sensitivity values, a contrast curve must be created. A contrast curve can be created from a contrast mask which allows us to create a contrast curve with one exposure because the mask projects different doses of light onto the substrate creating varying thickness that we are able to measure with the profilometer. The contrast curve is a plot of normalized film thickness vs. light dose. The curve will show D_o, the lowest does in which the photoresist is undeveloped, and D_{100}, the lowest does in which the photoresist is completely developed. D_{100} is also the sensitivity value. We are looking for a low sensitivity value so we do not need a lot of energy to fully clear the photoresist. In order to compare our photoresist to commercial grade photoresist we must come up with the correct variables to derive a contrast number that is in between two and five, which is the contrast range for commercial grade photoresist. The equation to calculate the contrast is:
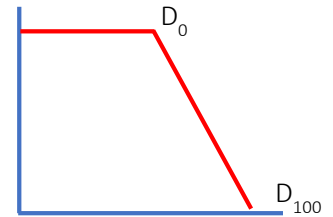
$$\gamma = \frac{1}{\log_{10}\frac{D_{100}}{D_0}}$$

The first polymer tested was the homopolymer, p(PHA). For five weight percent PAG the first development process used was thermal. Changing the conditions I could not find the correct variables to develop the photoresist and get a good gradient of thickness from the contrast mask. This is because the heat from the hot plate caused to much acid diffusion which created poor pattern fidelity. However, the vacuum development worked much better because, the lower the pressure in the vacuum oven, the better the patterns developed. While analyzing the results of figure 1, we tested the reproducibility of the photoresist and created three contrast curves from the same conditions, three different times, and got the
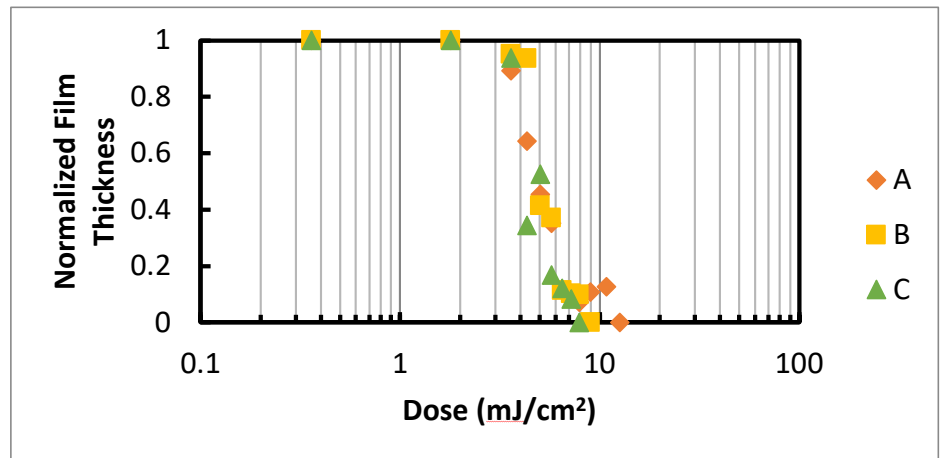

Figure 1. P(PHA) 5% PAG Vacuum Development- Reproducibility Test

same contrast number of 2.7, for each of the three curves which is in between the commercial range of 2 to 5. The time in between the light exposure and vacuum development was also tested to see if it effected the contrast number. The results from figure 2, show that the longer amount of time in between light exposure and development, the more the contrast number decreased. Letters A,B, and C, represent when the substrate was put directly into the vacuum oven the corresponding contrast number for all three was 2.7. When we waited 10 and 30 minutes in between the light exposure and development the contrast numbers dropped to 1.8 and 1.4,
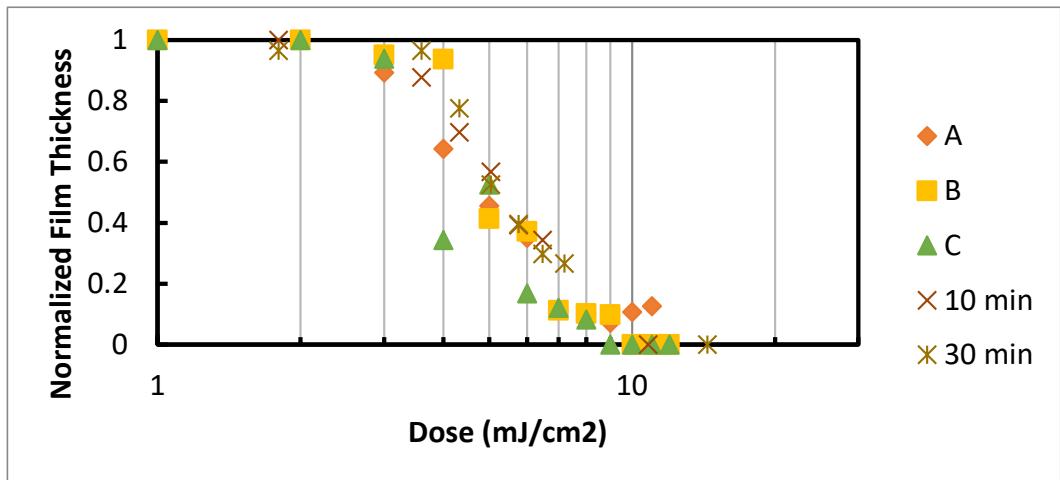
Figure 2. P(PHA) 5% PAG Vacuum Development- Wait Time In-between Light Exposure and Vacuum Development Test

worsening as the time increased between the light exposure and the vacuum development. For one weight percent PAG thermal development the results showed crisp features and good pattern fidelity. The lower the temperature was on the hot plate the crisper the features became. This was proven from figure 3, which compares thermal development at 40° C and 50° C. The contrast numbers were 2.02 and 1. 45. This is because the monomers melting point is 55° C. The closer the hot plate temperature is to the the melting point the worse the patter fidelity becomes. However, the homopolymer one weight percent PAG vacuum development did not allow me to create a contrast curve because the photoresist never fully developed. This was because not enough acid was being produced to react with the polymer backbone.
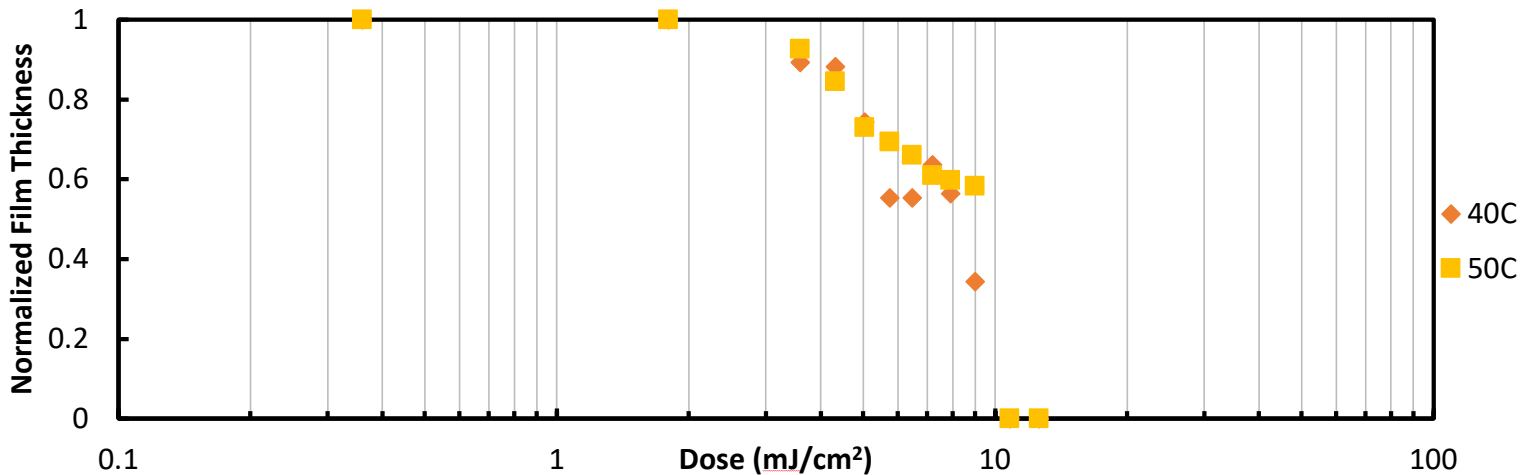

Figure 3. P(PHA) 1% PAG Thermal Development Test

The second polymer that was tested was the copolymer, p(PHA-PA). For five weight percent PAG the first development process I used was thermal. While changing the testing parameters I quickly determined that vacuum development would result in crisper features. This is because thermal development resulted in a large amount of acid diffusion. Therefore, similarly to p(PHA), higher vacuum pressure resulted in porter quality patterns. Figure 4, shows the results of the best testing parameters, resulting in a contrast value that was determined to be 2.2. However, for one weight percent PAG neither thermal or vacuum development was successful in

creating a D_{100} value. This was due to the low molecular weight of the polymer required more acid to fully develop the film. Since there was no D_{100} value we could not derive a contrast value.
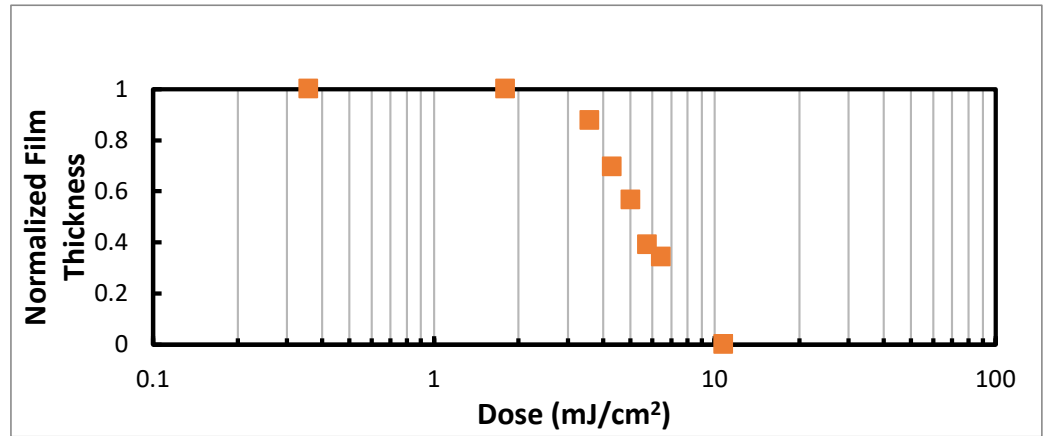

Figure 4. P(PHA-PA) 5% PAG Vacuum Development Test

In conclusion, dry-developing photoresist can produce crisp features depending on the developmental procedures. The homopolymer, p(PHA), with five weight percent PAG exhibited crisp and reproducible features with vacuum development. However, the longer you wait to develop the photoresist the worse of a contrast value you will receive. In contrast, p(PHA), with one weight percent PAG developed better thermally but the lower the developmental temperature, the better the contrast value became. The copolymer, p(PHA-PA), with five weight percent PAG developed the best with the same vacuum developmental procedures as the homopolymer. However, the one weight percent PAG did not develop thermally nor in the vacuum oven because of the low molecular weight of the copolymer, which required more acid to react with the polymer backbone to completely clear the photoresist. The next step in this research would be to access the resolution limit of polyaldehydes. This would allow us to know how small of features we can we reliably print. Overall, rapidly-degradable polyaldehydes as dry-developing photoresist can produce quality results comparable to commercial grade photoresist.