Free Radical Polymerization and Imprint Lithography

Microlithography Materials and Processes
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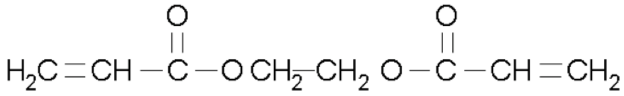
1. INTRODUCTION

Nanoimprint Lithography (NIL) is a low cost, high resolution, large area patterning process. NIL differs from optical lithography in that the mask is not optically binary (i.e. not composed of clear and dark areas) but contains relief structures (topography that protrudes or depresses on the mask face). NIL allows for patterning down to the sub-100nm regime while also ridding the need for the expensive lenses used in optical lithography. The goal of our exploration in NIL is to achieve equal lines and spaces using a wafer nanoimprinting process.

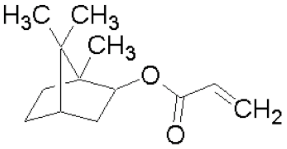
2. CHEMISTRY



$$H_2C{=}CH-\overset{O}{\overset{\|}{C}}-O\,CH_2-CH_2\,O-\overset{O}{\overset{\|}{C}}-CH{=}CH_2$$

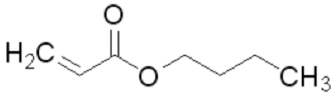
Source: http://www.sigmaaldrich.com/ (Sigma-Aldrich)

.274 grams ethylene glycol diacrylate (30%wt) – liquid (Aldrich)
Crosslinking monomer



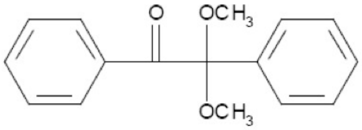
Source: http://www.sigmaaldrich.com/ (Sigma-Aldrich)

.343 grams isobornyl acrylate (37.5%wt) – liquid (Aldrich)
Matrix polymer -- increases glass transition temperature



Source: http://www.sigmaaldrich.com/ (Sigma-Aldrich)

.274 grams butyl acrylate (30%wt) – liquid (Aldrich)
Reactive diluent – reduces viscosity



Source: http://www.cibasc.com/ (CIBA Specialty Chemicals)

.035 grams Irgacure 651 (2.5%wt) – solid powder (Donated by CIBA)
Photoinitiator – sensitive to i-line radiation

The acrylate precursor used in this experiment undergoes free radical polymerization. Upon the absorption of 365nm radiation, the center bond of the Irgacure molecule breaks; each end is then free to attach to either side of a diacrylate molecule by breaking one of the double carbon-carbon bonds. With one of the carbon atoms now only sharing three single bonds with three other atoms, it is possible for a free radical to occupy the empty bond site; if that free radical is another diacrylate molecule, the crosslinking process may continue to build upon the length of the polymer.

3. PROCEDURE

3.1 Compressed air (no mask)

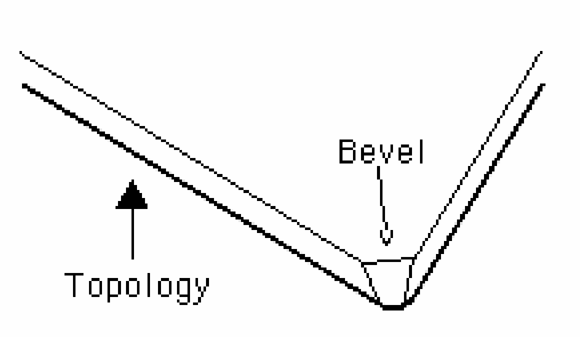
1. Make sure to have the proper chemical-handling protection (goggles, face shield, gown, and gloves). Avoid inhalation of the precursor vapors.
2. Fill glove bag with compressed air and allow bag to slowly deflate.
3. Extract and place a 2μL drop of imprint resist on a wafer while under a fume hood. Do this while the precursor is cool, because resist spreading slows down.
4. Once bag has almost fully inflated, place the wafer in the glove bag.
5. Let compressed air fill the glove bag and close all opening in glove bag; once closed, turn off the compressed air.
6. Let the wafer sit for 10 minutes to allow oxygen to diffuse out.
7. Deflate the center of the bag by opening one of the smaller holes so that the top is close to the wafer
8. Measure the irradiance with the photodiode inserted into a glove bag.
9. Calculate the correct exposure time and expose for 150mJ/cm^2 of dose.
10. Once exposed, examine. Has it polymerized? If so, to what extent?

3.2 Nitrogen (no mask)

1. Make sure to have the proper chemical-handling protection (goggles, face shield, gown, and gloves). Avoid inhalation of the precursor vapors.
2. Fill glove bag with nitrogen and allow a slow leak to replace the air with nitrogen gas.
3. Extract and place a 2μL drop of imprint resist on a wafer while under a fume hood. Do this while the precursor is cool, because resist spreading slows down.
4. Once bag has almost fully inflated, place the wafer in the glove bag.
5. Let nitrogen fill the glove bag. Pinch shut all of the openings when you are confident that nearly all of the ambient air has been replaced with pure nitrogen gas; once closed, turn off the gas flow.
6. Let the wafer sit for 10 minutes to allow oxygen to diffuse out of the precursor.
7. Deflate the center of the bag by opening one of the smaller holes so that the top is close to the wafer – this lets the bag be closer to the wafer during the exposure.
8. Measure the irradiance with the photodiode inserted into a glove bag.
9. Calculate the correct exposure time and expose for 150mJ/cm^2 of dose
10. Once exposed, examine. Has it polymerized? If so, to what extent?

3.3 Karl Suss MA150 contact aligner

1. Make sure to have the proper chemical-handling protection (goggles, face shield, gown, and gloves). Avoid inhalation of the precursor vapors.
2. Insert the i-line filter in the optical column of the Karl Suss
3. Measure the irradiance and calculate the correct exposure time for 150mJ/cm^2 of dose
4. Load ImprintLit program
5. Modify the "exposure time" to the one calculated and modify the "hard contact delay" to 22 seconds.
6. If the 6-inch chuck is installed (NOT the 4-inch chuck), disregard steps 8 through 13 and instead follow the "Short Program Procedure' on page 7 in the Karl Suss MA150 Operating Instructions Manual, and use the mask holder labeled "Special 5" Mask Holder"
   a. Make sure the vacuum hose to the special mask holder is firmly attached, and be cautious when inverting the fixture after mounting the mask to prevent accidental release.
7. When loading the mask, remember that the topology is etched into the face opposite the one containing a beveled corner.



8. Extract and place a 2μL drop of imprint resist on a wafer while under a fume hood.
9. Place wafer in the Karl Suss' loading boat.
10. Press "Start/Stop" button and wait for wafer to be loaded onto the chuck.
11. If its light is on, press "Cont. Sep." button on the right joystick
12. When it lights up, press "Exposure".
13. Wafer may not unload from chuck. If this occurs, press "Reset" twice and wait for Suss to move to its default position. Remove the mask holder and then wafer.
14. Examine the polymer's physical properties, and evaluate its topology using microscopy, profilometry, SEM, etc…
    a. Note that the tip of the profilometer's stylus may have a radius as large as 12.5μm, and the relief mask was etched in HF, which is an isotropic etch; this will affect the drawn profile.

REFERENCES

http://www.sigmaaldrich.com/
http://www.cibasc.com/
http://www.nilcom.org
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