DISSOLUTION KINETICS OF INORGANIC PHOTORESISTS

Sung Ju Lee, Cameron McGrath, Peter Thompson

Issue & Opportunity

The project goal is to characterize the dissolution behavior of butyltin hydroxide oxide in polar organic solvents.

SEMICONDUCTOR DEVICES & PHOTORESISTS

Modern electronics compute use semiconductor devices made from thin film materials. Patterns are etched in thin films and layered atop one another to form the semiconductor devices. Pattern feature size has a major effect on final device size and functionality.

Patterns can be etched in multiple ways; this project focuses on a photoresist, which changes solubility upon exposure to radiation.

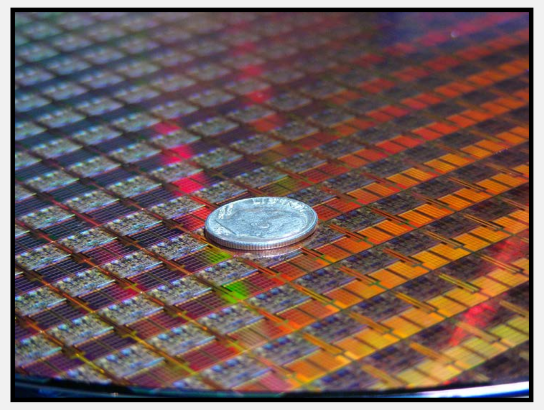
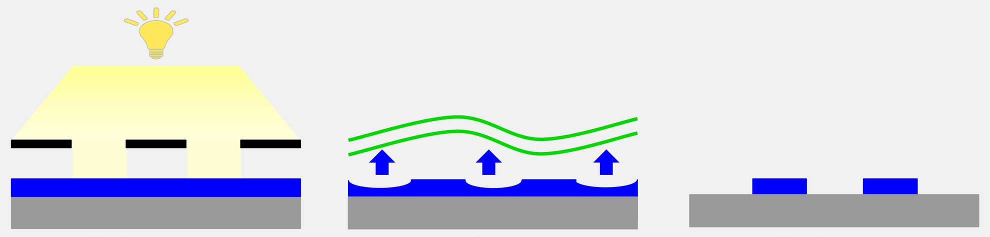
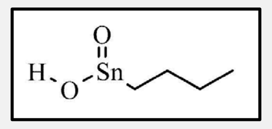


Image: Intel 45 nm Chip

When a pattern is formed by radiation exposure, the parts of the film outside the pattern can be dissolved in a chemical solvent. The remaining film is the desired layer; further layers can be added in the same manner to form a device.



The minimum feature size generated in this manner depends on the photoresist used. Butyltin hydroxide oxide (BuSnOOH or butyltin) shows promise as a high-resolution thin film photoresist.



Its dissolution behavior is not well-characterized, so the optimal solvent for development is unknown. This project was created to characterize the dissolution behavior of butyltin and potentially find an optimal solvent.

Butyltin converts to tin oxide upon exposure to electron-beam radiation making it insoluble in most solvents.

Solubility was tested using a Quartz Crystal Microbalance (QCM), which detects minute changes in film mass using the piezoelectric properties of quartz. Thermal studies are conducted by baking the films to mimic the development process without the use of an electron beam.

Methods & Results

QUARTZ CRYSTAL MICROBALANCE (QCM)

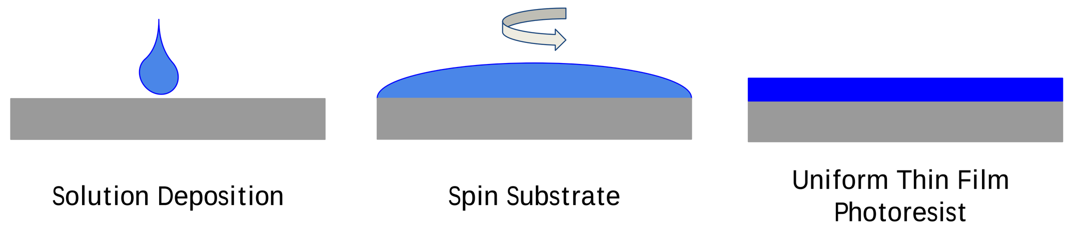
QCM uses the piezoelectric properties of quartz to measure small changes in mass of a substance on top of a uniform quartz crystal.

Quartz crystal with gold layers used in QCM

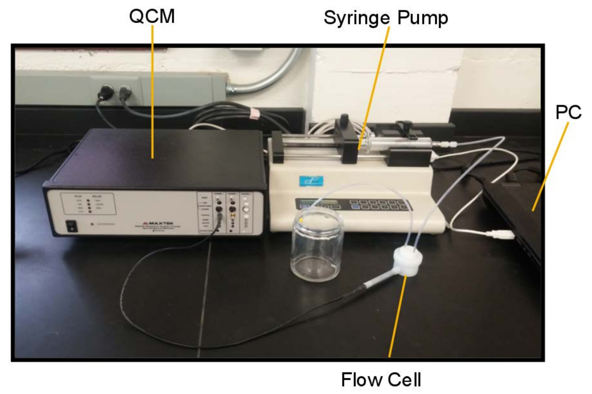
The resonance frequency of a piezoelectric material is dependent on its mass. The addition of a film on top of a quartz crystal increases its mass and decreases its frequency. By measuring the resonance frequency change as the film is dissolved, the mass removal rate can be determined by Sauerbrey equation.

SOLUBILITY EXPERIMENTS

Experiments were performed on thin films of butyltin created with spin coating directly on the QCM crystals.

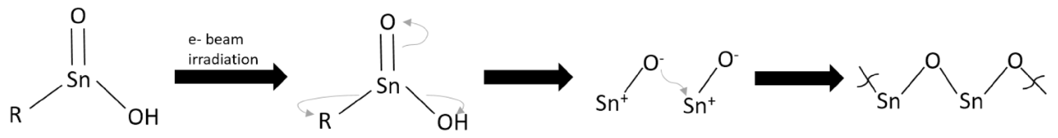


The QCM device is connected to data-collection software on a PC. The crystal is contained in a flow cell. Solvent is pumped through the flow cell with a syringe pump.



THERMAL BEHAVIOR

Butyltin can be developed using electron beam radiation. When butyltin develops it reacts to form tin oxide, an insoluble semiconductor material. The reaction mechanism is shown below:

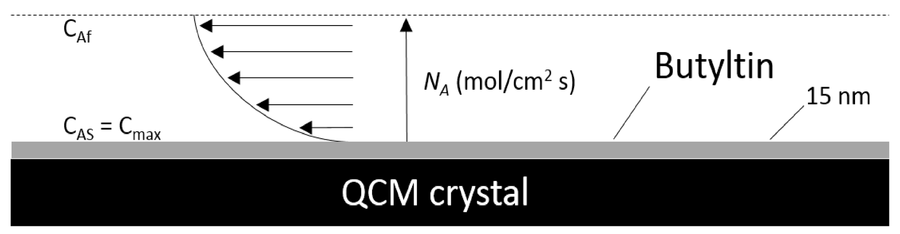


Baking the films mimics development due to electron beam radiation. Butyltin films were baked at 70, 100, 125, 150, 175°C to remove residual solvents. Films were not heated above 200°C because butyltin fully reacts at that temperature. Heating the films slows the dissolution rate allowing for clearer understanding of dissolution behavior. The films have the potential to partially develop during baking, which would cause an insoluble layer of tin oxide to form. This layer would remain behind after the dissolution trial.

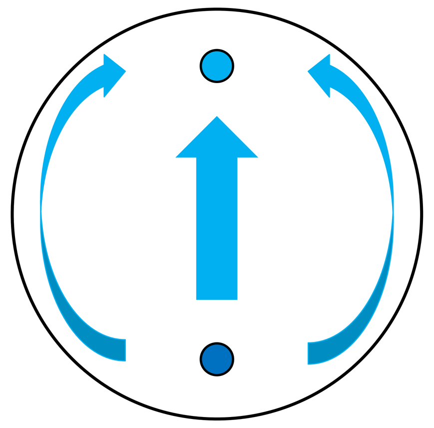
FLUID FLOW PATTERN

The solvent has a laminar flow pattern and the concentration gradient determines our driving force. Dissolution behaves according to the following mass transfer correlation:

$$N_A = k_c(c_{AS} - c_{Af}) \qquad k_c = \frac{D_{AB}}{L} \times 0.664\,\mathrm{Re}^{\frac{1}{2}}\,Sc^{\frac{1}{3}}$$

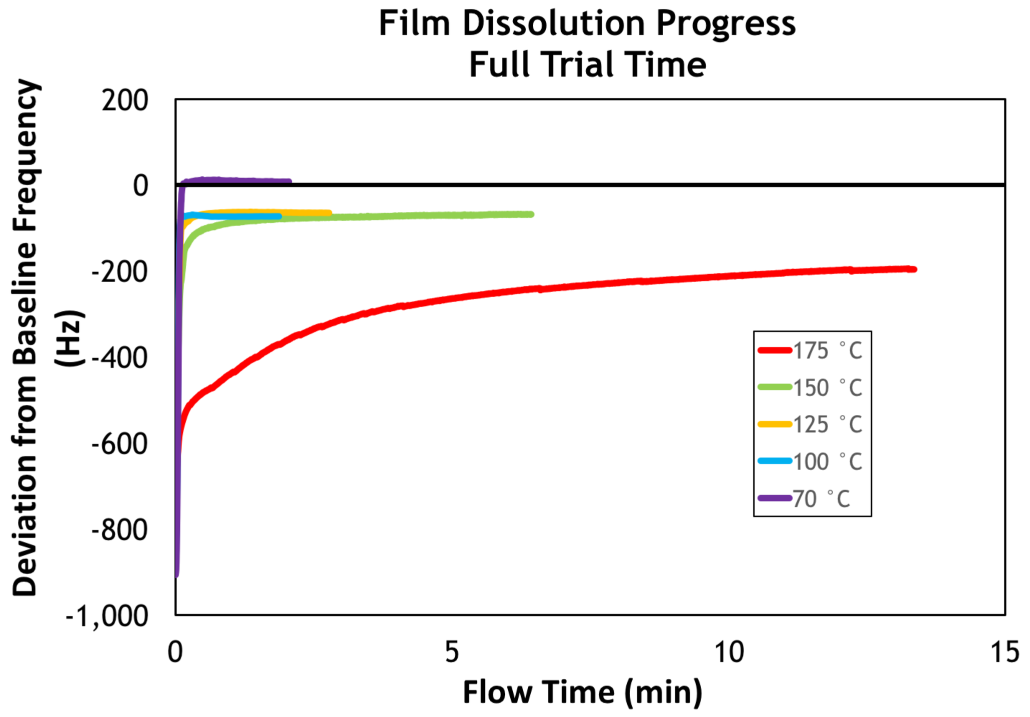


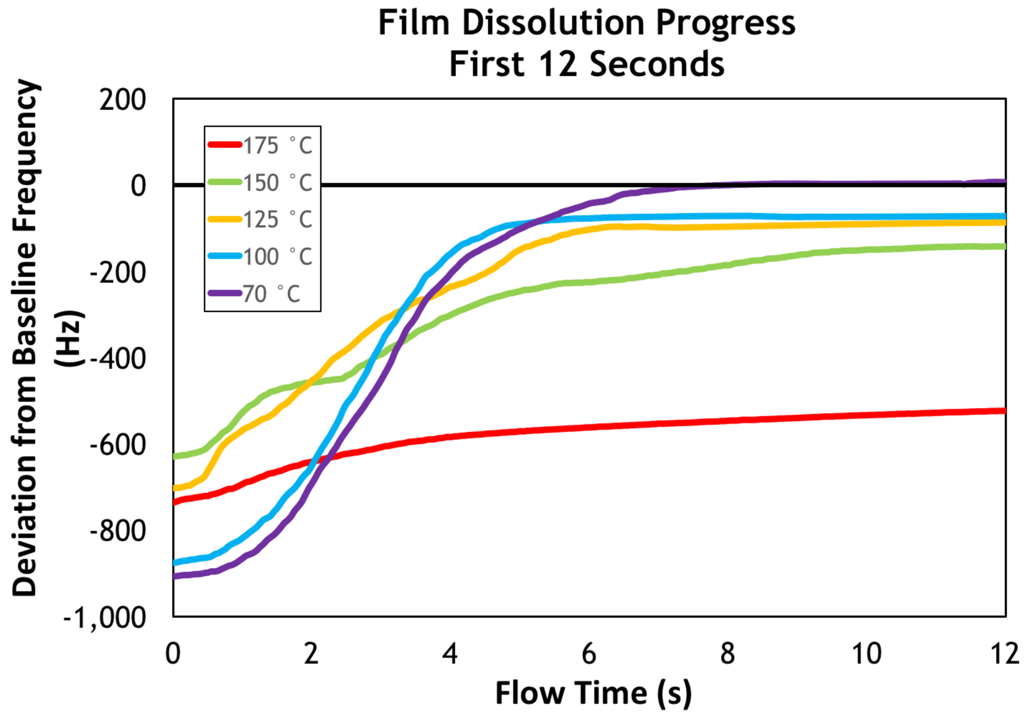
The flow pattern is more complex when viewed from above. The fluid flows fastest between the inlet & outlet, and slowest at the edges, as shown in the figure on the right.



METHANOL RESULTS

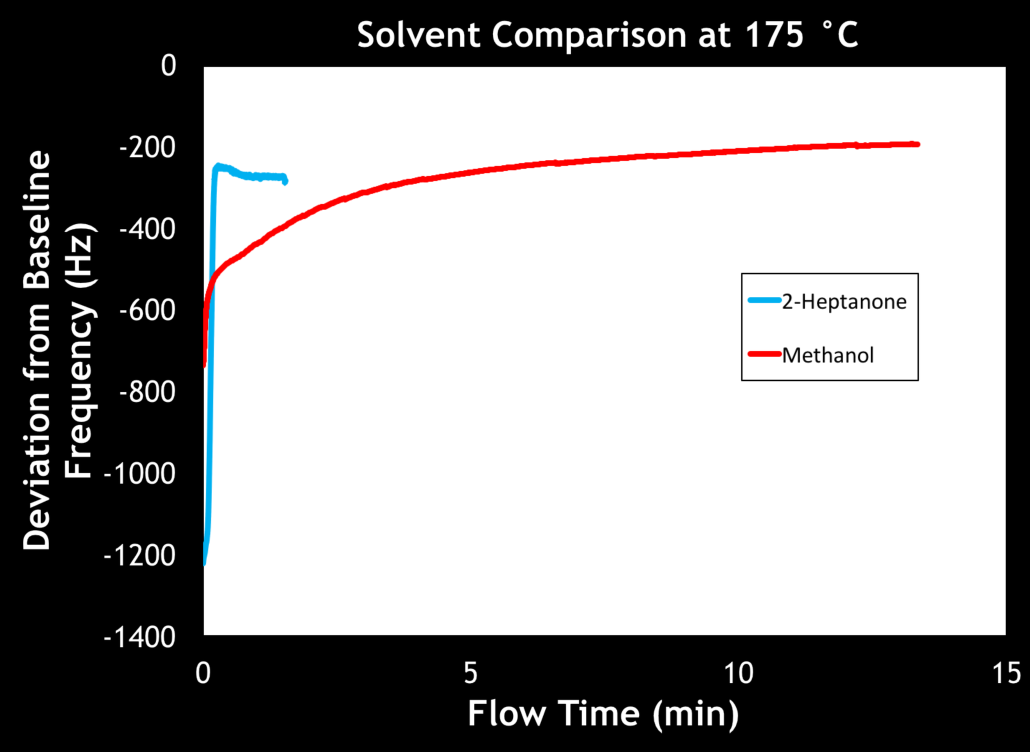
The plot below shows the different frequency changes for films baked at different temperatures then dissolved in methanol flowing at 2 mL per minute.





Results & Conclusions

RESULTS



The graph above demonstrates the difference between 2-heptanone and methanol as solvent. When the butyltin films were baked at 175 °C methanol took around 13 minutes to completely dissolve the film, while 2-heptanone only took about 1 minute. The greater deviation from baseline frequency for 2-heptanone is assumed to be due to a greater dampening effect when the solvent contacts the crystal. Both solvents appear to leave some residue behind, shown by the frequency deviation not reaching zero .

CONCLUSIONS

The effectiveness of 2-heptanone confirms the hypothesis that larger polar organic solvents will more effectively dissolve the butyltin films. The effect of other factors such as the strength of the molecular dipole could be tested in future work.

Further thermal trials would determine if the remaining mass was due to baking, and if so, what the temperature dependence was.

An SOP for the QCM has been developed for current and future researchers to reference when continuing this project.

ACKNOWLEDGMENTS

- Professor Greg Herman (Project Sponsor, OSU)
- Dr. Sumit Saha (Project Sponsor, OSU)
- Jenn Amador (Experiment Guidance, OSU)
- Dr. Philip Harding (Project Mentor, OSU)
- NSF Grant CHE-1102367 for providing additional funding for this work

CSMC center for sustainable materials chemistry

Oregon State UNIVERSITY