

Task ID: 425.019

Task Title: Low Environmental Impact Processing of sub-50 nm Interconnect Structures

Deliverable: Report on the development of optimal parameters for synthesizing new sacrificial layer material by photoinitiated CVD and demonstration of etching using plasmas and supercritical CO₂

Summary Abstract:

This project evaluates the performance of gas, liquid, and supercritical fluid processes to clean sub-50 nm structures, fabricate multilevel air gaps, and planarize surfaces without contact. These tasks were chosen because of the potential to reduce resource use and waste production by understanding process limitations. The primary objective of this project is to develop a set of principles to guide the choice of materials and processing fluids to fabricate sub-50 nm structures with the lowest cost of ownership.

Exploiting selective surface reactions, initiated chemical vapor deposition (iCVD) achieved the growth of patterned, rather than blanket, organic thin films, eliminating the need for a series of subtractive lithographic processing steps to achieve patterning. The properties of iCVD films enabled them to be utilized as sacrificial layers for fabrication of prototype air gap structures for high performance interconnect designs. An alternative dry removal method using supercritical CO₂ was tested on the sacrificial polymer films and demonstrated partial dissolution, though further studies are needed to confirm the removal mechanism.

Technical Results and Data:

An existing 200 mm system at MIT was upgraded to allow 300 mm wafers to be accommodated (Fig. 2). A reactor of sufficient size is crucial to being able to send wafers to industrial collaborators for integration testing.



Figure 2. New iCVD chamber capable of accommodating 300 mm wafers.

Thin films of iCVD sacrificial polymers were synthesized using cyclohexyl methacrylate (CHMA) as the monomer and ethylene glycol dimethacrylate (EGDMA) as the cross-linker. The resulting film is composed of only carbon, oxygen, and hydrogen. Although cross-linked, the iCVD sacrificial layer was found to decompose cleanly, leaving behind a maximum of 0.3% of residue by thickness. Cross-linking renders the polymer stable in practically all solvents and results in an onset of thermal decomposition at 270°C, providing compatibility with subsequent microfabrication steps. The high etch rate (0.35 $\mu\text{m}/\text{min}$) in oxygen reactive-ion etching

eliminates the need of a hard mask during etching. Fabrication using conventional lithographic, etching, and deposition techniques resulted in single-level void structures.

The concept of additive processing for sacrificial layers was demonstrated using dip-pen nanolithography to define patterns of initiators onto a silicon wafer surface. The dip-pen lithography was done in collaboration with the group of Prof. Angie Belcher (Material Science and Engineering, MIT) and utilizes an atomic force microscope (AFM) for defining the patterned regions (Fig. 3). Once patterned with initiator, the wafers were loaded into a CVD chamber and then exposed to flowing monomer vapors at partial pressures of 0.1 to 1.0 torr. During the monomer flow, UV exposure of the substrate inside the CVD chamber causes the initiator species to produce a free radical site on the surface to which multiple monomer units can add.

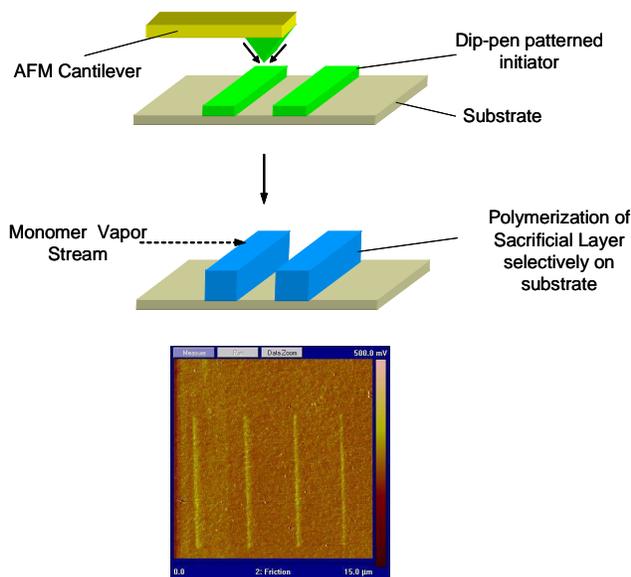


Figure 3. (top) Use of AFM enabled dip-pen nanolithography to apply photoinitiator to a surface. (middle) The polymeric sacrificial layer deposits selectively from gaseous monomers when the surface patterned with initiator is subjected to UV exposure. (bottom) AFM micrograph of the result of additive processing using dip-pen nanolithography.

Using this additive processing scheme permitted growth of directly patterned layers the sacrificial material, poly(cyclohexylmethacrylate).

Preliminary data processing CHMA films with supercritical CO₂ and added cosolvents of IPA, acetone, and hexane are shown in Figure 4. These results were compared to the polymer removal by exposure to pure cosolvents under ambient conditions. Ellipsometry was used to measure film thickness. Fourier transform infrared spectroscopy (FTIR) data of the C-H and C=O absorbance intensities at 3000 and 1720 cm⁻¹ verified ellipsometry data. The amount of polymer removed was calculated from an average of two samples reacted under the same conditions with error bars showing $\pm 1\sigma$.

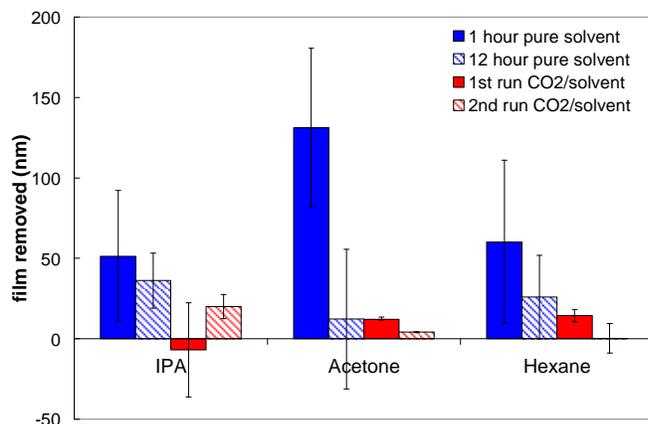


Figure 4. (top) EGDMA polymer film removal by processing in pure solvents of IPA, acetone, and hexane (filled bars) compared to reaction with supercritical CO₂/solvent (striped bars). Error bars show $\pm 1\sigma$.

While the polymer removal did vary significantly between samples under the same reaction conditions, trends indicate that processing with a pure cosolvent removed more CHMA than exposure to the CO₂/cosolvent solutions. It should be noted that exposure to pure solvents was done for a total of 13 hours while each CO₂ processing lasted 16 minutes. A second set of reactions in both the pure solvent and CO₂ mixture (striped bars) generally exhibited lower removal, indicating that exposure to the solvents may have only dissolved lower molecular weight components within the film. Within error, none of the cosolvents appear to perform better than the others and in all cases only partial dissolution was observed. These results demonstrate that the iCVD film was stable in pure liquid solvents as well as when these cosolvents were added to supercritical CO₂ at high pressures, even with rapid depressurization steps.