

## Positive Tone, Chemically Amplified, Cross-linkable Dielectric

Mueller, B. K. and Kohl, P. A.

School of Chemical and Biomolecular Engineering  
Georgia Institute of Technology  
311 Ferst Dr., Atlanta, GA 30332

In microelectronics packaging, it is often necessary to deposit and pattern permanent dielectric materials. These dielectrics serve to electrically and mechanically separate chip-chip or chip-package interconnects, and they relieve thermally-induced stresses created by thermal cycling. Polymers are the most widely used insulators in packaging, because they are easily deposited and can be made photo-definable by inclusion of a photoactive compound (PAC). Cross-linking of these polymers after photo-patterning provides good mechanical and electrical properties required for device longevity and power-efficient device operation.

Since photolithography is often the most expensive and rate-limiting process, maximizing the sensitivity and therefore minimizing the exposure dose required for patterning will increase device throughput. Chemically amplified photo-chemistries have high light sensitivity due to a catalytic solubility switching mechanism. This chemistry is generally made possible by including tert-butyl ester (TBE) or tert-butylcarboxylate (TBOC) functional groups pendent to the polymer backbone. The films are a mixture of base-polymer and a small amount of photoacid generator (PAG). Exposure to ultraviolet radiation causes the PAG to form a strong acid. This acid catalytically deprotects the TBE or TBOC to form a carboxylic acid or alcohol, respectively. The deprotected polymer is soluble in aqueous base, and a develop step dissolves the exposed regions of the film. Cross-linking of these films is a challenge, because common cross-linking mechanisms react to the PAG. For example, epoxy cross-linkers readily ring-open in the presence of acid. This reaction would interfere with the photo-patterning steps.

In this study, the first working positive tone, chemically amplified, cross-linkable dielectric is demonstrated. The base polymer is a random copolymer of tert-butyl methacrylate (TBMA) and 2-hydroxyethyl methacrylate (HEMA). Photo-patterning is brought on by the traditional deprotection of the TBMA to form a carboxylic acid. Formulations of 1 and 3 parts per hundred PAG were measured to have contrasts of 12.7 and 5.2, respectively, and sensitivities ( $D_{100}$ ) of 50.2 and 32.2 mJ/cm<sup>2</sup>, respectively. Figure 1 shows an SEM image of the film with 3 parts per hundred PAG after photo-patterning. Reported  $D_{100}$  values for common positive tone dielectrics are greater than 350 mJ/cm<sup>2</sup> and often much higher due to inefficient absorption of photoactive compounds in thick films. These lithographic properties are a 10x or larger improvement over existing materials.

After photo-patterning, the TBMA in the remaining film was deprotected by blanket exposure. This deprotection could also be done thermally. The resulting film had carboxylic acids and alcohol functional groups pendent to the methacrylate polymer backbone. These functional groups can be thermally cross-linking via an acid-catalyzed Fischer esterification reaction which

can be carried out at low temperatures. The esterification reaction proceeds at a much slower rate than the deprotection, so photo-patterning is unaffected. The film was cured at 120°C for 10 hours. These conditions were not optimized and were chosen to drive the reaction toward the esterification by removing water produced by cross-linking. The residual stress of the film was measured to be 6.2 MPa prior to cure and 17.9 MPa post-cure. Additionally, the film was insoluble in aqueous base after curing. These changes in stress and solubility are clear evidence of cross-linking.

## References

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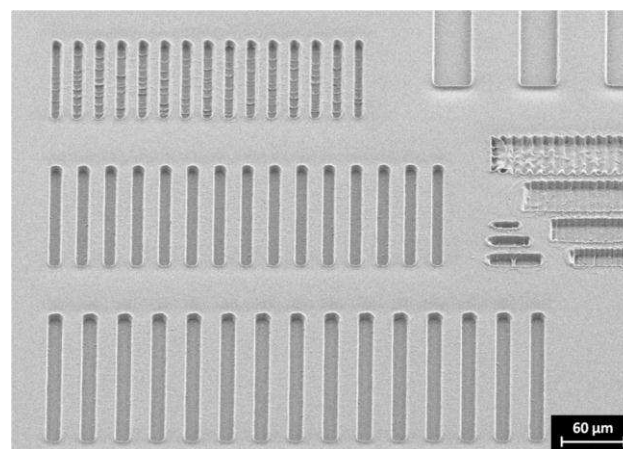


Figure 1: SEM of photo-patterned trenches in TBMA-co-HEMA polymer film