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# Polymeric Mac-Imprint Stamp Materials for High-Density Defect-Free Patterning of Semiconductors

Metal-assisted chemical imprinting (Mac-Imprint) is a contact-based wet etching process that combines metal-assisted chemical etching (MACE) and nanoimprint lithography (NIL). Mac-Imprint processes have been used for semiconductor patterning with arbitrary and complex 3D micro- and nano-structures. While porous catalytic metal thin-films can be used to reduce limitations with etching fidelity, this approach has several drawbacks: (i) the smallest pattern feature size is restricted by pore diameter, and (ii) high surface area of porous catalytic films leads to excessive hole generation and injection, resulting in semiconductor porosification outside contact areas. Moreover, the thickness of the porous catalyst layer is also a limiting factor for reducing reactant depletion and improving etchant storage. Thus, the scalability of Mac-Imprint can be restricted by the limited mass-transport of the reactants towards a catalytic metal-coated stamp-substrate contact interface. Several approaches have been implemented to promote diffusion through interconnected porous networks embedded into either substrate or in the catalyst thin layer of the stamp. However, these approaches are unable to sustain large-area patterning on blank wafers and etching of deeper features (e.g.,  $>1\text{ }\mu\text{m}$ ) due at least in part to limited volume for etchant storage at the micrometric gaps between stamp and substrate.

Researchers at Arizona State University have developed polymeric stamp materials for Mac-Imprint that are fully porous (i.e., the porosity extends throughout the thickness of the material) and thus support greater storage volume and a diffusion pathway to the bulk of the etchant solution. Due at least in part to the (i) interconnected pore structure and (ii) precise control over the stamp pore size in the sub-100 nm range, these materials allow Mac-Imprint of nano- as well as micro-scale features (e.g., in silicon) with high patterning fidelity and greater depths.

The implementation of porous polymer-based Mac-Imprint stamps allows large-area uniform patterning of blank semiconductors (i.e. without pre-patterning) with densely packed defect-free 3D features. Large-area imprinting is facilitated by mass-transport through a bicontinuous porous polymer network, and defect-free feature patterning is controlled through hole generation and injection rate suppression. Patterning resolution is related to the porosity of the used membrane and can be as low as 5 nm.

Potential Applications:

- Anti-reflective layers in solar cells
- Optoelectronics (visible and near-IR anti-reflective surfaces, self-cleaning surfaces)
- Silicon photonics (photonic crystals, waveguides, ring resonators, metasurfaces)
- Nano- and Micro-electromechanical Systems (MEMS)

Benefits and Advantages:

- Pore diameter as low as 5 nm contributes to improved diffusion, large-area imprinting uniformity, and minimized roughness if desired by application
- Scalable
- Low cost