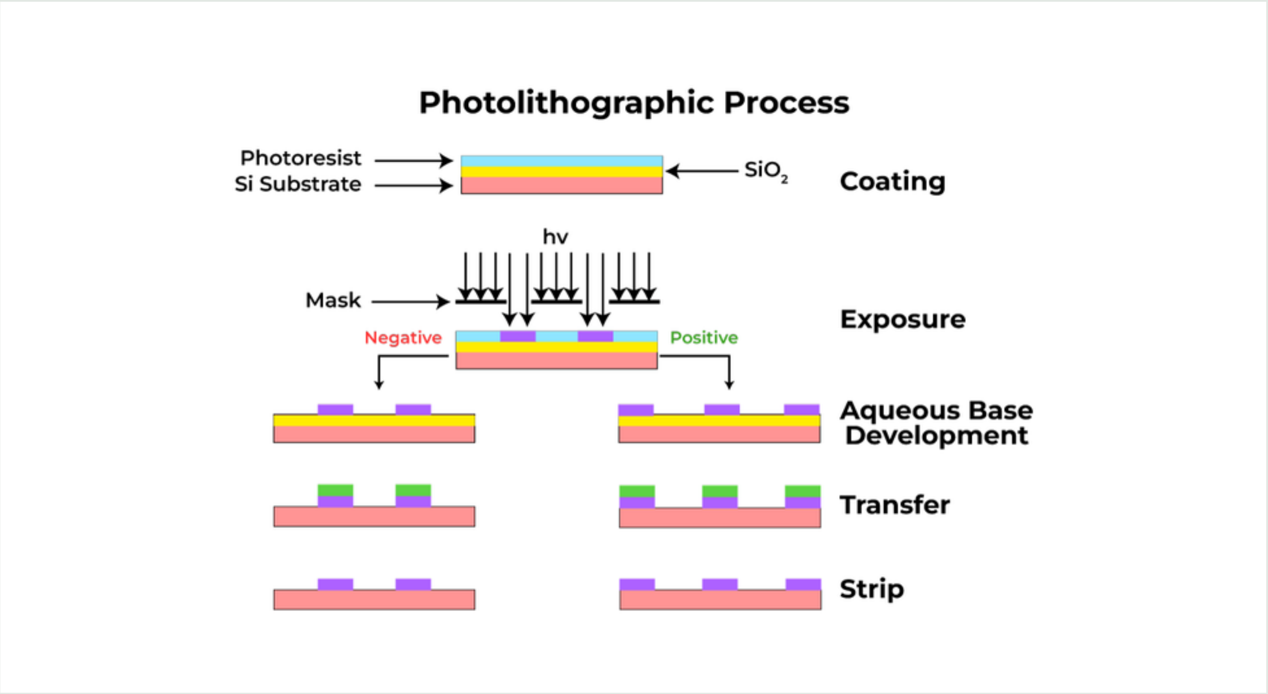
RESIN GREEN

Materials for a greener digital future

Newsletter

Developing greener materials and nanometrology methods for sustainable photolithography



The Resin Green in a nutshell

The challenge: Conventional lithography processes used in semiconductor device manufacturing for pattern definition require excessive usage of resists (usually photosensitive polymer-based materials) and developers (solvents or aqueous bases), which are both containing components toxic to the user and/or environment. Moreover, the synthetic polymeric materials used in resists are mostly derived from non-reusable petroleum-based sources. This indirectly leads to large enhancements in the cost and environmental footprint of the semiconductor manufacturing processes (Fig.1).

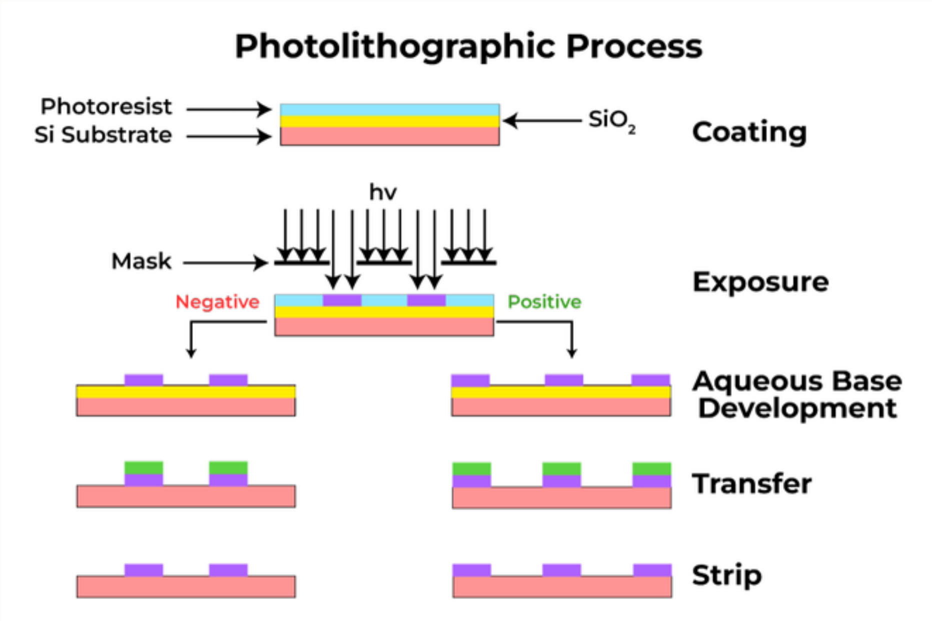


Fig.1

Our proposal: RESIN GREEN aims to develop green and environmentally friendly materials with high efficiency for photolithography. The target is to replace the standard organic solvents and the highly alkaline solutions used in development. Primarily water or greener organic solvents like very dilute basic developers will only be considered, if necessary, for meeting high-performance requirements. In particular, the aim is to investigate both bio-sourced materials and new synthetic polymer-based photoresist platforms suitable for exposure at 193 nm, 248 nm, I-line and EUV lithographies to achieve significant breakthroughs.

In the case of bio sourced materials, chitosan and alginates derived from different biological sources, are promising alternative resists as they are biodegradable, non-toxic and water soluble. Chitosans are linear co-polymers, derived from chitin, the second most abundant biopolymer on earth acquired from food-industry waste. They have been demonstrated earlier as resist for deep-UV and electron-beam lithography, and the patterned structures were successfully used for plasma transfer processes. Alginates are also linear polysaccharides, derived originally from brown algae. Alginates are commonly used as sodium salts, which is not suitable for semiconductor device processing and therefore, ammonium alginates are being synthesized to enhance their usability.

The industrial relevance of the proposed resists will be justified by advanced metrology methods and techniques based on Scanning Electron Microscope and Atomic Force Microscope imaging of patterns empowering with machine learning tools for the enhancement of their analysis results.

The “magical” PAG molecules: first encouraging results

The main limitation of polymer-based photoresists including chitosan and alginate is their negligible absorption in the UV range, which restricts their applicability in highthroughput device fabrication. However, when these resist formulations are endowed with smallmolecule photoacid generators (PAGs), their sensitivity to UV radiation increases significantly, enabling efficient photochemical activation (Fig. 2).

In Resin Green we have designed and developed new PFAS-free PAG molecules to be compatible with water soluble polymeric photoresists selected and/or designed especially for use in hydrophilic matrices and exposure at 248 nm, especially in formulations of chitosan (see Fig. 2).

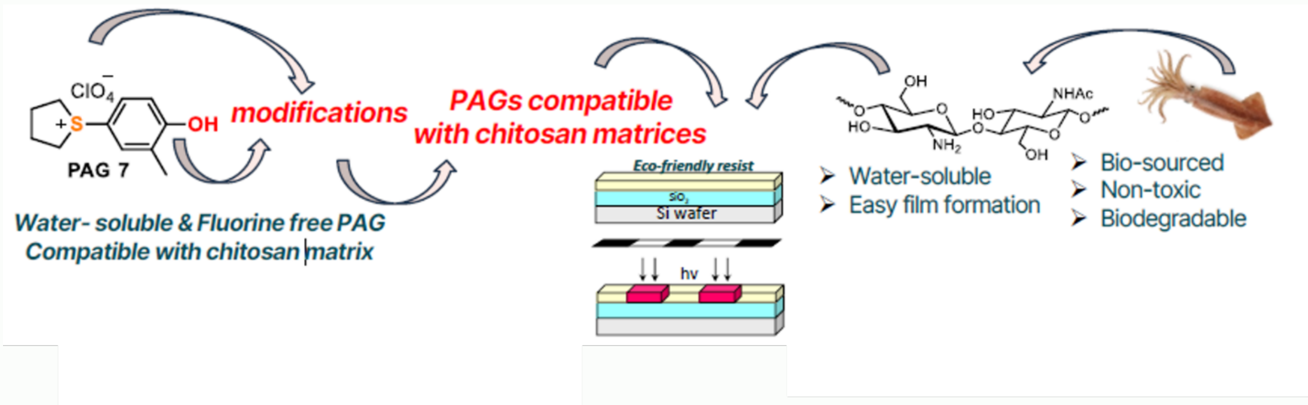


Fig. 2. A schematic illustrating the basic concept of using water soluble & fluorine free PAG chitosan compatible matrix

Within such molecules in chitosan composition, a very small percentage of bio-sourced organic acid in chitosan formulations Is able to assist in chitosan dissolution, while the photo-resist development is performed directly in pure water, thus avoiding the use of highly toxic bases.

Initially, the patterning response is assessed via thickness retention/contrast curves (Fig 3),

while for the most promising chitosan formulations hard-contact imaging is performed and optical microscopy is used to assess imaging capabilities.

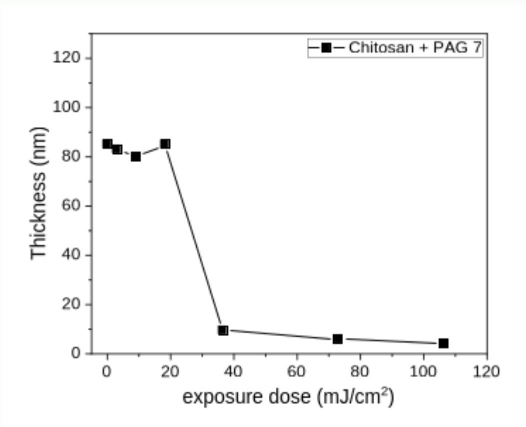


Fig. 3. Positive tone contrast curves of chitosan-based photoresists, employing a novel water-soluble and fluorine free PAG

Notably, a negative-tone response is observed in chitosan, for the first time, in addition to the positive-tone behavior reported in the literature so far, under DUV exposure at different conditions. Positive tone imaging is also achieved, in the context of this work, at 248 nm with selected PAGs and certain processing modifications (Fig.4 and Fig.5).

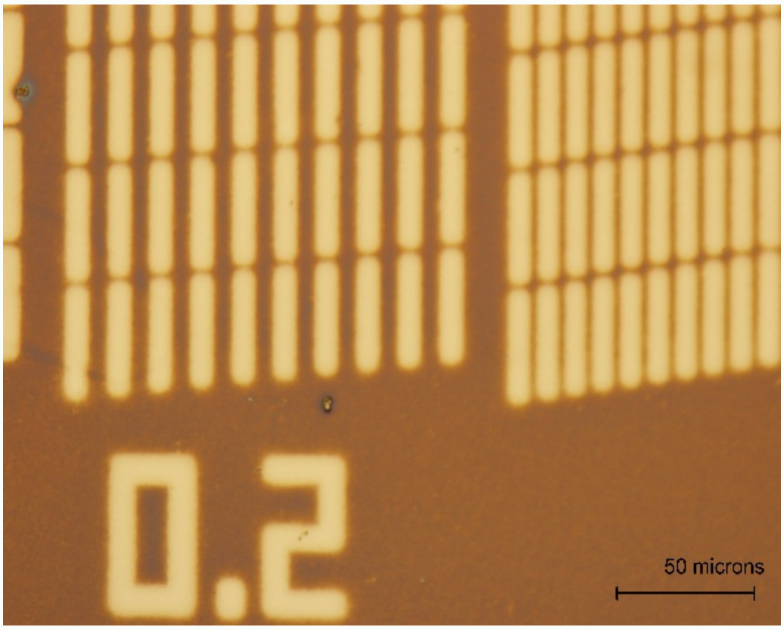


Fig. 4. Left image) Negative tone lithography at 248nm of chitosan-based photoresist formulations. Right image) Positive tone lithography at 248nm of chitosan-based photoresist formulations

These findings highlight the decisive role of both polymer–PAG interactions and exposure wavelength in governing solubility switching. Overall, these early results demonstrate the feasibility of PAG-enabled patterning at 193 nm,248 nm and i-line, in chitosan and provide structure–property guidance for extending this approach to other eco-friendly solvent-compatible polymers. Ongoing work broadens the PAG set, with emphasis on non-fluorinated counter-anion variations, further contributing to sustainable lithography.

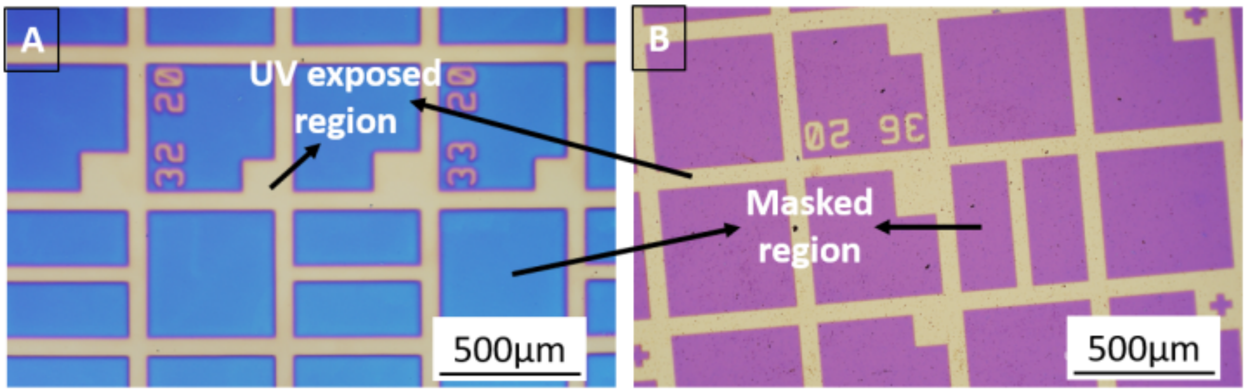


Fig 5. Optical microscopic images of near-UV exposed pattern on chitosan (A) and alginate (B) resists . Coloured area (blue or violet) are the non-exposed (masked) regions.

Do not forget to measure the patterns you create: Hybridizing the giants of nanometrology (SEM and AFM)

Evaluation of the compliance of the produced lithographies, with the industrial standards is a necessary step. In order to perform this, we first need to be able to see what we have constructed. Therefore, we have to “penetrate the nanometer barrier” to be able to see deviations from ideally designed patterns. And the most widely used way to do this is by analysing SEM and AFM microscopy images and data. After imaging the pattern structures, we will have to be able to measure them and quantify pattern dimensions and roughness, employing a nano-metrology software that specializes in microscopy analysis images for characterization at the nano-scale (see Fig. 7).

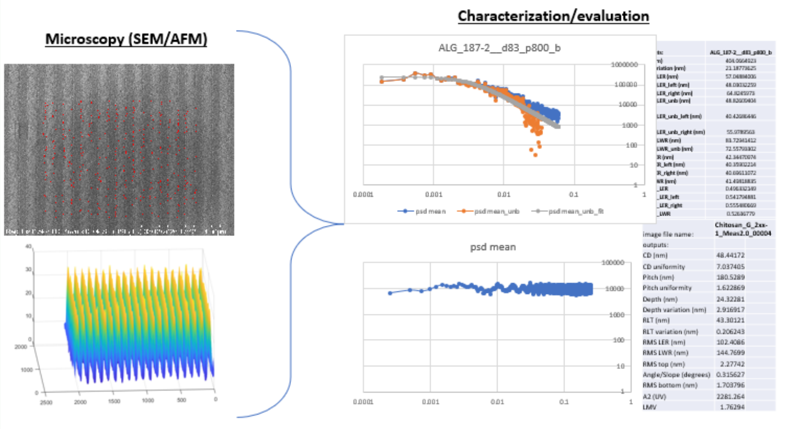


Fig7. Nanometrological characterization and evaluation

Metrological characterization at the nanoscale (nanometrology), allows us to evaluate the produced structures in order to ensure that they meet industrial standards. It is the mean to get to know our research results (nano-patterns) better by unlocking all valuable information contained in the microscopy data. Engaging the state-of-the-art methods, such as the Power Spectral Density, also known as the PSD method and the correlation function, we analyze and compare SEM and AFM data, thus performing a hybrid metrology approach, which provides us with the necessary metrics (RMS, correlation length, roughness exponent, critical dimension, CD uniformity etc), acquiring this way, a complete and accurate characterization of the produced lithographic patterns (fig7).

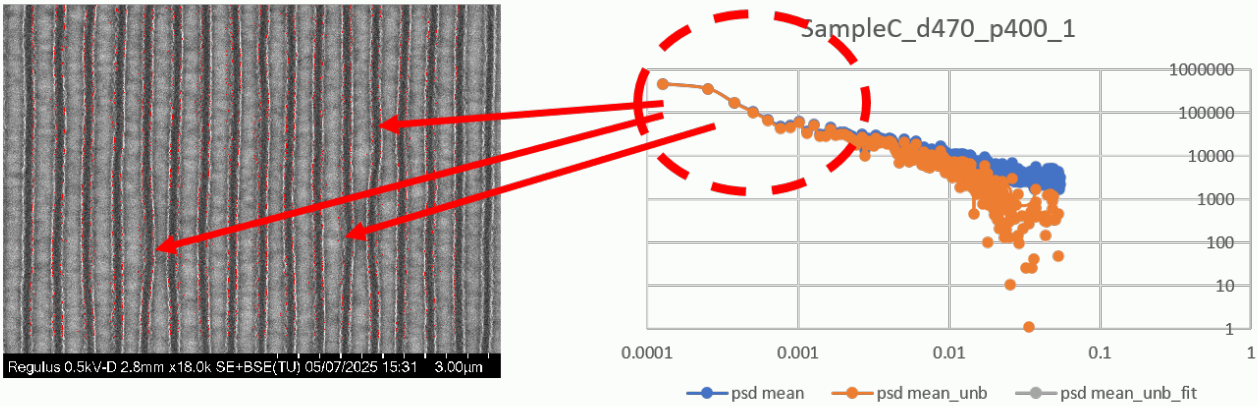


Fig8. Nanometrology characterization enables the detection of errors and defects

Analyzing, comparing and reevaluating will help us detect errors, recognize defects (Fig. 8) and eventually choose/ pinpoint the most promising of the produced resist materials.