Dual-Component Functionalized Allylated Calix[4]arene-Dibutyltin Diacrylate Blends as Organic-Inorganic Hybrid Resist Compositions for Nanolithography

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Abstract

The present work reports a novel organic-inorganic hybrid resist system based on an allylated calixarene matrix chemically blended with organometallic tin diacrylate (**CAlMe-DBTAc**), designed to enhance lithographic performance. The unique architecture of the calixarene core provides a rigid, low-molecular-weight framework that facilitate high-resolution patterning, while the incorporation of tin acrylate introduces an organometallic entity that potentially boost the lithographic performance of the developed composition for nanopatterning applications. A systematic optimisation of material composition and processing conditions, including thin-film optimisation with respect to solid loading and spin-coating parameters to achieve low film thickness are presented. The synergistic interaction between the organotin species and the calixarene network, likely mediated through terminal cross-polymerisation enables negative-tone resist behaviour. Moreover, the organic matrix is expected to assist in addressing the resist film shrinkage typically associated with the inorganic resist systems. Additionally, owing to the strong EUV absorption of Sn containing species, the presented resist system represents a potential framework for the next-generation EUV lithography nanopatterning applications.

1. Introduction

Continued scaling of semiconductor devices has pushed conventional organic photoresists toward fundamental limits in resolution, sensitivity, and stochastic variability, particularly for next-gen extreme ultraviolet (EUV) lithography applications.[1] While inorganic and metal-oxide resists offer high EUV absorption and etch resistance, they often suffer from significant film shrinkage, cracking, and limited process latitude.[2,3] Organic-inorganic hybrid resist platforms have therefore emerged as a promising strategy to balance sensitivity, etch resistance, resolution, and film stability for next-generation nanopatterning.[4]

Molecular resists based on rigid, low-molecular-weight architectures are particularly attractive due to their reduced line-edge roughness and improved pattern fidelity.[5] Calixarene derivatives, with their well-defined aromatic cores and high structural rigidity, enable high-resolution imaging at ultra-thin film thicknesses.[6] However, their practical application in EUV lithography is limited by inherently low absorption of EUV photons. Incorporation of elements that have high EUV absorption coefficient provides an effective route to

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enhance resist sensitivity through increased EUV photon absorption and subsequent secondary electrons generation.[7]

Among the metals explored for EUV lithographic applications, tin (Sn) exhibits one of the highest EUV atomic absorption coefficients, offering substantial sensitivity advantages.[8] Early demonstrations of dodecameric Sn-oxo cluster resists stimulated extensive investigation into multinuclear Sn-oxo systems,[9,10,11] followed by the development of Sn-carboxylate platforms capable of sub-10-nm half-pitch patterning.[12] Thus, this presents with significant scope for the development of furthermore efficient tin-based resists with improved performance, as fully inorganic Sn-based resists may encounter challenges related to film integrity, shrinkage, and processing robustness.

Organic-inorganic hybrid approaches provide an alternative pathway by integrating metal-based absorption centres within structurally rigid organic matrices, thereby mitigating mechanical instability while maintaining the ease of processing and lithographic performance.[13] In this context, calixarene-based frameworks present an attractive scaffold due to their molecular rigidity, low molecular weight, and demonstrated high-resolution capability.

In this work, we report an organic-inorganic hybrid resist composed of an allylated calixarene matrix blended with organometallic tin diacrylate, schematic represented in Fig 1. The formulation leverages synergistic interactions between the calixarene framework and organotin acrylate, potentially via terminal cross-polymerisation, yielding negative-tone patterning with enhanced sensitivity compared to analogous systems. Systematic optimisation of resist composition and processing parameters enables formation of uniform ultra-thin films at low solid loading. At preliminary stages, the resist demonstrates micron-scale patterning using optical lithography, highlighting its potential compatibility with higher-resolution techniques such as electron-beam and EUV lithography. The combination of strong EUV-absorbing organotin species with a rigid organic matrix presents this hybrid system as a promising candidate for next-generation lithography, offering good sensitivity, resolution, and reduced film shrinkage.[14]

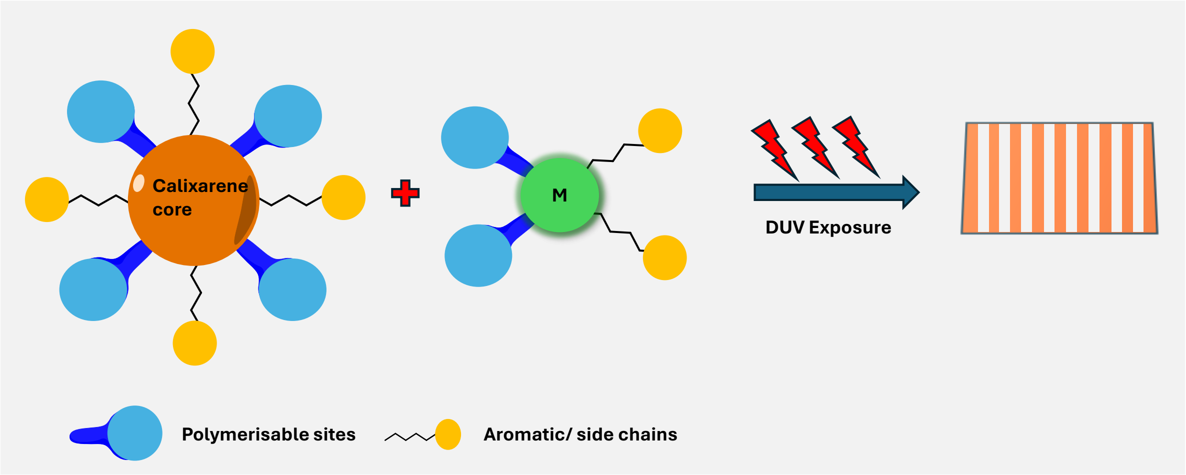

Fig 1: Schematic showing the Organic-Inorganic hybrid resist composition for Lithography applications

2. Experimental Section

2.1 Materials

Allylated calixarene and organometallic tin diacrylate were synthesised following established procedures.[15] All chemicals were purchased from commercial sources and were directly used without further purification.

2.2 Resist Formulation

10 mg of functionalised calixarene (CALMe) and 10 mg of tin diacrylate (DBTAc) were dissolved in 1 ml propylene glycol methyl ether acetate (PGMEA) to obtain a 2 wt% solution. The mixture was vortexed until visually clear, followed by filtration through a 0.22 μm PTFE filter to remove particulates. The resulting formulation was used directly for thin-film deposition.

2.3 Thin Film Preparation

Single-side polished p-type Si (100) substrates were cleaned by sequential sonication in DI water, acetone, and IPA. Films were spin-coated at optimised conditions (6000 rpm for 50 s) to achieve ~35 nm thickness. Post-application baking was carried out at 90 °C for 60 s on a hot plate to remove residual solvent in the thin film after spin coating.

3. Results and Discussion

3.1 Thin Film Optimization

Spin coating parameters were systematically optimized to achieve smooth, defect-free films. Film thickness decreased monotonically with increasing spin speed, while the minimum surface roughness (Rq ~0.3 nm) was obtained at 6000 rpm, measured by AFM.

3.2 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed on resist thin films before and after exposure to elucidate photon (~250 nm light source) induced chemical transformations associated with polarity switching. The C 1s spectra show a relative decrease in total carbon content after exposure (Fig. 2d), accompanied by a relative increase in the carbonyl (–C=O) component at 288.5 eV. Consistently, the O 1s spectra exhibit an enhanced O–Sn contribution at 530.5 eV following exposure (Fig. 2e), possibly suggesting the formation of tin–oxygen coordination within the cross-linked network. In addition, the increase in area under the Sn 3d peak (Fig 2f) indicate an overall enrichment of tin species in the exposed regions. These results collectively support an exposure-induced chemical restructuring that eventually leads to negative-tone resist behaviour.

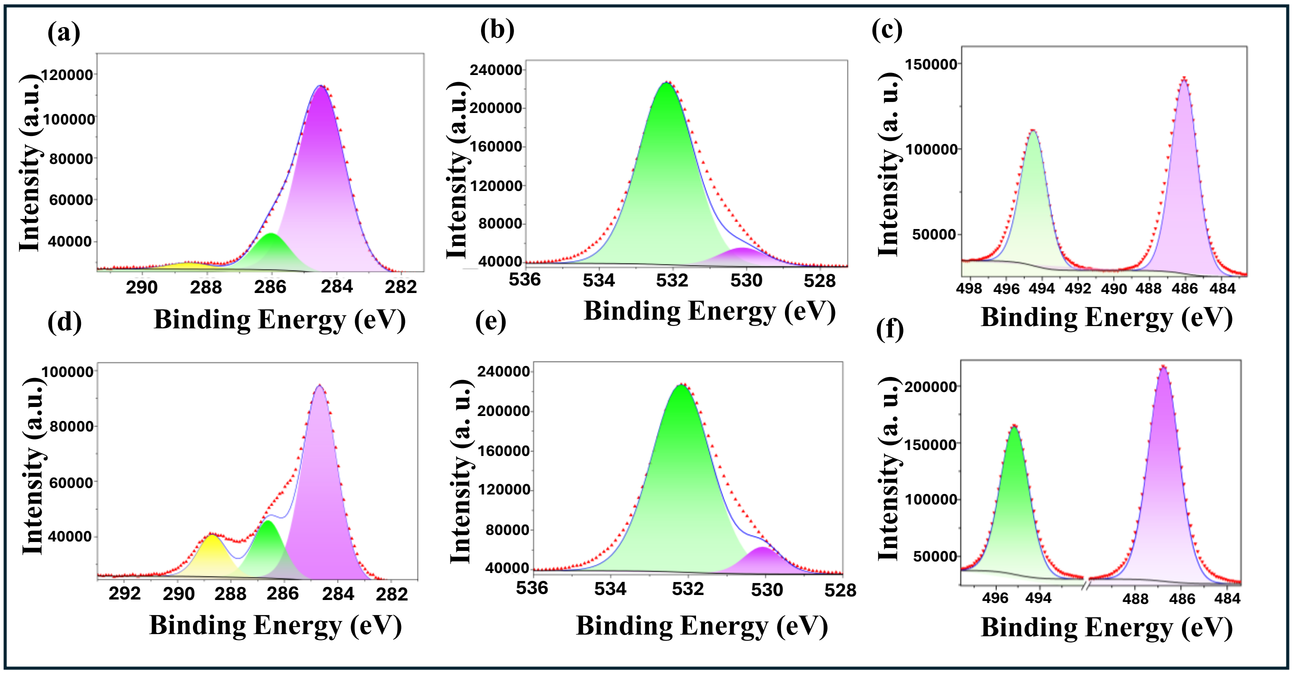

Fig 2: High Resolution XPS Spectra of CAlMe-DBTAc Films for C 1s, O 1s, and Sn 3d (a,b,c, respectively) before exposure and (d,e,f, respectively) after ~ 254 nm DUV exposure.

3.3 DUV Exposure and Patterning

DUV lithography was performed using an in-house ~254 nm exposure system. The resist shows resolved micron size features at doses of ~350-420 mJ cm^{-2} using a bright-field mask. The post-application bake (PAB) and Post-exposure bake (PEB) were applied to be 90 °C and 125 °C, respectively. High-contrast negative-tone patterns were obtained using 2-heptanone as the developer. Optical microscopy and AFM imaging reveal uniform micron-size patterns, with preliminary resolution approaching ~5 µm, as shown in Fig 3(c). Dose-response measurements indicate significantly enhanced sensitivity relative to analogous calixarene-based blended systems,[14] attributed to potential efficient radiation absorption by the Sn centres and subsequent crosslinking reactions.

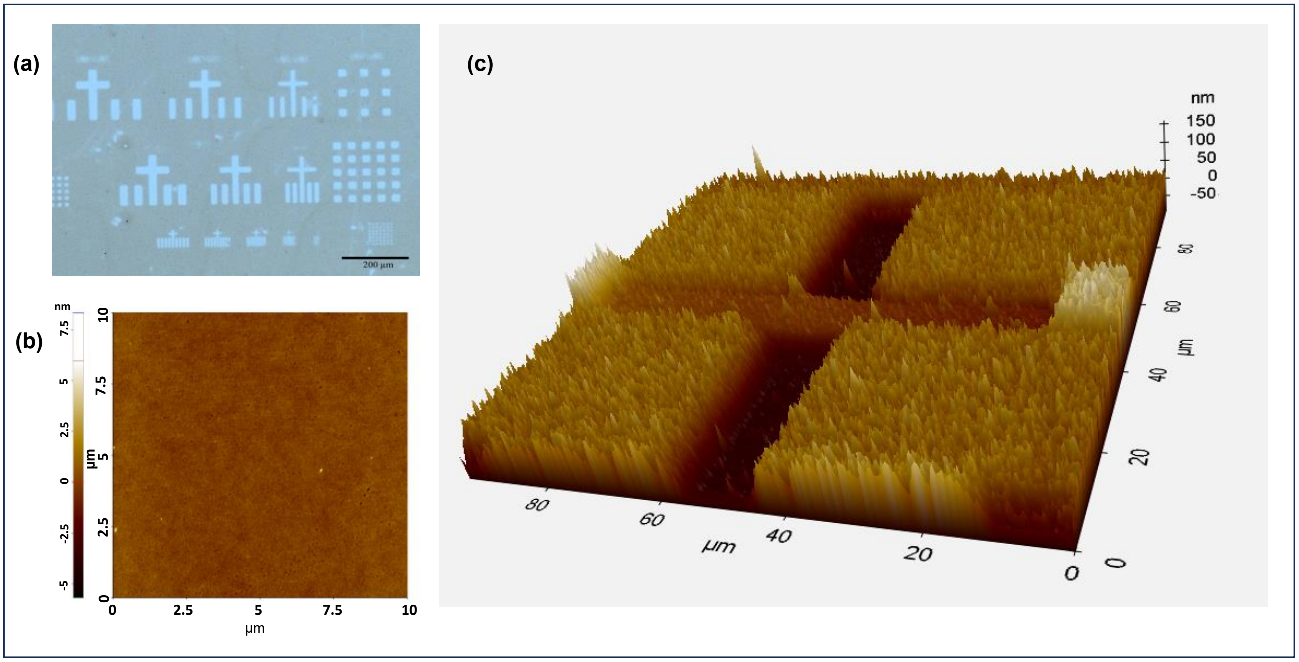

Fig 3: a) Optical microscope image of micron-size features, patterned using DUVL; (b) AFM-image of 10*10 μm^2 of photoresist film (c) AFM images of micron-size cross patterns.

3.4 Proposed Mechanism

Based on the XPS analysis, a schematic mechanism is proposed wherein exposure possibly cleaves Sn-C bonds and also generates radicals on both allyl groups of calixarene and acrylate ligands of tin diacrylate. Terminal cross-polymerisation between the alkenyl moieties of functionalised calixarenes and tin diacrylates leads to the formation of a three-dimensional hybrid network, rendering exposed regions insoluble and producing negative-tone patterns, as shown in Fig 4. The rigid calixarene core limits volumetric shrinkage, while organotin species act as efficient sensitisers.

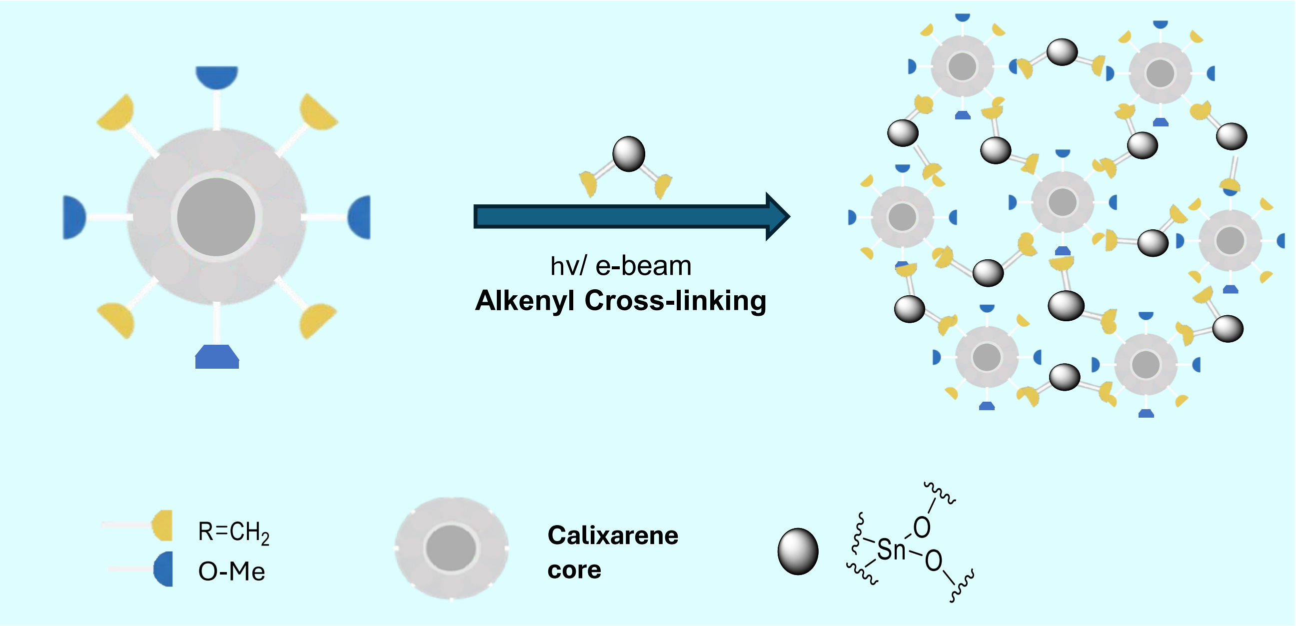

Fig 4: Schematic showing the proposed mechanism of solubility switching through alkenyl crosslinking

4. Conclusion

This work presents a hybrid molecular photoresist combining allylated calixarene with organometallic tin diacrylate to achieve enhanced sensitivity. The resist forms smooth ~35 nm films with sub-nm roughness and exhibits negative-tone behaviour through photon-induced crosslinking. DUV lithography demonstrates well resolved micron-level patterning capability with improved sensitivity over similar analogous systems. The preliminary studies in this work presents this hybrid system as a potential resist composition for advanced nanopatterning lithographic techniques, such as EBL and EUVL, which will be explored in our further studies.

5. Acknowledgement

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