Systematic Investigation of Tin-Based Metal-Organic Cluster Resists for High-Resolution Next Generation Lithography

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Abstract

Scaling of integrated circuits pushes resist technology into a new regime of higher sensitivity and resolution, which is limited by stochastic effects. Hybrid resists, particularly Sn-based metal-organic clusters (Sn-MOCs), have emerged as promising candidates due to higher EUV absorption cross-sections, robust inorganic frameworks, and potential for low-line-edge roughness (LER) and line width-roughness (LWR). Here, we developed a solution-phase cluster assembly, Sn-MOCs based resists featuring aromatic ligands systematically attached to the Sn-core, where alkyl substitutions fine-tune both electronic and steric properties, enabling precise control over solubility, sensitivity, and pattern development. High-resolution patterning was screened using helium ion beam lithography (HIBL), and the optimised formulation resolved down to ~16 nm half-pitch (*HP*) line patterns. The measured LER/LWR value for *HP* line patterns are; 2.04 ± 0.04 nm / 3.11 ± 0.06 nm (45nm), 1.98 ± 0.04 / 2.92 ± 0.03 (38nm), 1.70 ± 0.09 nm / 2.69 ± 0.17 (20nm), 1.53 ± 0.06 /2.10 ± 0.06 (16nm), demonstrating improved roughness control with insistent scaling.The development process was accomplished using an optimized developer for 45s, which provided optimized sensitivity resolution and process compatibility in Sn-MOCs. It demonstrates that rational ligand selection provides a powerful handle for optimising sensitivity, resolution, and process compatibility in Sn-MOCs resist formulations, paving the way for high-NA, EUVL.

Introduction

For decades, semiconductor technology has continued to make great strides through advances in reducing transistor size, resulting in higher integration density, better device performance, and a greater reduction in the cost per function[1]. However, as critical dimensions approach their intrinsic physical and reliability limits, further advances will not be possible through dimensional scaling alone. As a result, there has been increased attention paid to both advanced lithographic techniques and the development of noble resists technology that can provide high resolution, lower line-edge roughness (LER), and increased sensitivity simultaneously [2]. Metal-organic-based resist platforms represent one avenue for overcoming the traditional scaling limit due to their excellent radiation absorption and superior etch resistance[3,4].

Among next-generation fabrication technologies, extreme ultraviolet (EUV) lithography stands out as a key enabler for high-volume manufacturing (HVM) of semiconductor chips at ~10 nm or below nodes. This has led to intensified research into how photoresists interact with EUV photons and exposure tools, which are critical to advancing the scaling of logic and memory devices. Over and above, the EUVL transition to high-NA (numerical aperture = 0.55) has placed even greater necessities for noble photoresist technology, underscoring the prerequisite for high sensitivity, *HP* patterning, critical CD control, and higher etch resistance [5].

Nonetheless, developing and validating EUV photoresists remains a major challenge, partly due to limited access to high-power EUV exposure sources and tools. Despite the different primary exposure mechanisms, both rely on the generation of secondary electrons to trigger resist chemical kinetics. Notably, a single helium ion at~30 keV has been shown to produce an effect similar to that of ~150, EUV photons, as an EUV photon typically interacts only once with the resist molecular formulations and resulting secondary electrons (SEs), whereas a helium ion undergoes multiple inelastic collisions along the path, generating SEs throughout its trajectory [6]. So, the energy profile in both HIBL and EUV next-generation technologies is highly localised, leading to a short proximity limit and minimal scattering effects, in contrast to electron beam lithography (EBL), where extensive electron scattering results in significant long-range proximity effects, making it less comparable [7]. Although electron beam lithography is widely employed as a stand-in for extreme ultraviolet lithography (EUVL), it is limited by significant proximity effects. In contrast, HIBL offers a more challenging exposure environment due to its smaller interaction volume, higher energy density, and reduced forward scattering, thereby providing a more stringent and EUVL-relevant assessment of resist performance, prelude to EUVL technology [8].

Advances in Patterning Materials and Processes XLIII, edited by Ryan Callahan, Anuja De Silva, Proc. of SPIE Vol. 13983, 1398339 · 2026 Published by SPIE
0277-786X · doi: 10.1117/12.3091826

In this study, we synthesised a Sn-MOCs resist formulation aimed at enhancing sensitivity, resolution, and development performance; subsequently, the resist formulation for high-resolution patterns was pre-screened using HIBL[9]. A systematic evaluation of lithographic performance was carried out, including sensitivity, contrast analysis, line-edge roughness (LER) measurements, and demonstrating sub-20 nm high-solution patterning under HIBL exposure[10]. Furthermore, the role of mTA in modifying resist solubility and exposure response was investigated, confirming its effectiveness in improving contrast, resolution and critical dimensions for advanced nanolithography applications[11].

2. Experimental Section

2.1 Materials

Tin (IV) acetate, m-toluic acid, Triethylamine, Ethyl Lactate and Alcohol were procured from Sigma-Aldrich and used without further purification.

2.2 Resist Synthesis and thin film prepration

The Sn–mTA MOC resist was synthesized via a controlled coordination reaction.The resulting product was purified through multiple solvent washing steps and isolated in solid powder form.

To prepare thin films from the synthesised resists, Sn-mTA 2.5 wt.% solutions were first formulated in suitable solvent using vortex mixing to accomplish full dissolution. The resulting solutions were then filtered through a 0.22 µm pore-size syringe filter to remove large particulate impurities, after which they were immediately spin-coated onto RCA-cleaned silicon substrates at ~2500 rpm for 60 s. The deposited films were subsequently soft-baked at 100 °C for 90 s to remove residual solvent, producing uniform films with an average thickness of ~ 29 nm for the resist formulations. Post-exposure baking was carried out at 100 °C for 90 s to facilitate resist cross-linking and ensure compatibility with the development process.

2.3 Helium Ion Beam Lithography (HIBL)

HIBL system (Zeiss ORION NanoFab) was used at ~30 kV, with a He+ beam on a ~ 29 nm resist film, at a current of ~ 0.25 pA, using a ~10 µm numerical aperture. After exposure to a He+ beam, the negative-tone patterns were developed in an optimized developer for 45 sec

2.4 Material and Lithography Characterisation

Fourier transform infrared (FTIR) spectroscopy was performed using an attenuated total reflectance (ATR) accessory on a PerkinElmer Spectrum Two spectrometer to identify surface functional groups and assess chemical bonding within the resist films. ^{1}H NMR spectra were recorded using a JEOL ECX500 MHz spectrometer with TMS as the internal standard for chemical shift referencing. Resist high-resolution patterns were characterised using field-emission scanning electron microscopy (FESEM) from the Zeiss Gemini SEM 500, Germany, to measure pattern features, critical dimension (CD) and large area film surface uniformity. Film thickness analysis was performed using an atomic force microscope (AFM); from Bruker Dimension Icon to evaluate thickness uniformity across the coated substrates. Line-edge roughness (LER) and line-width roughness (LWR) of the exposed line patterns were quantified using SuMMIT® metrology software, an industry-standard tool for nanoscale roughness analysis in lithographic patterning.

3. Results and Discussion

The lithographic performance of the Sn-mTA resist formulation was evaluated using HIBL as a preliminary assessment for EUVL technology.

3.1 Lithographic Performance of Resist (Sn-mTA, MOCs)

The lithographic performance of Sn-mTA was evaluated using HIBL. The resulting patterns obtained after developing the Sn-mTA, MOCs resist in optimized developer, as shown in Figure 1(a–d). Half pitch (*HP)* line patterns with critical dimensions of ~ 45 nm, ~ 38 nm, ~20 nm, and ~16 nm were successfully patterned at an He^+ ion exposure dose of ~ 24.8 $\mu C/cm^2$. The measured LER/LWR values for *HP* patterns are ~ 2.04 ± 0.04 nm / 3.11 ± 0.06 nm (45 nm), 1.98 ± 0.04 / 2.92 ± 0.03 (38 nm), 1.70 ± 0.09 nm / 2.69 ± 0.17 (20 nm), 1.53 ± 0.06 /2.10 ± 0.06 (16 nm). The FESEM micrograph

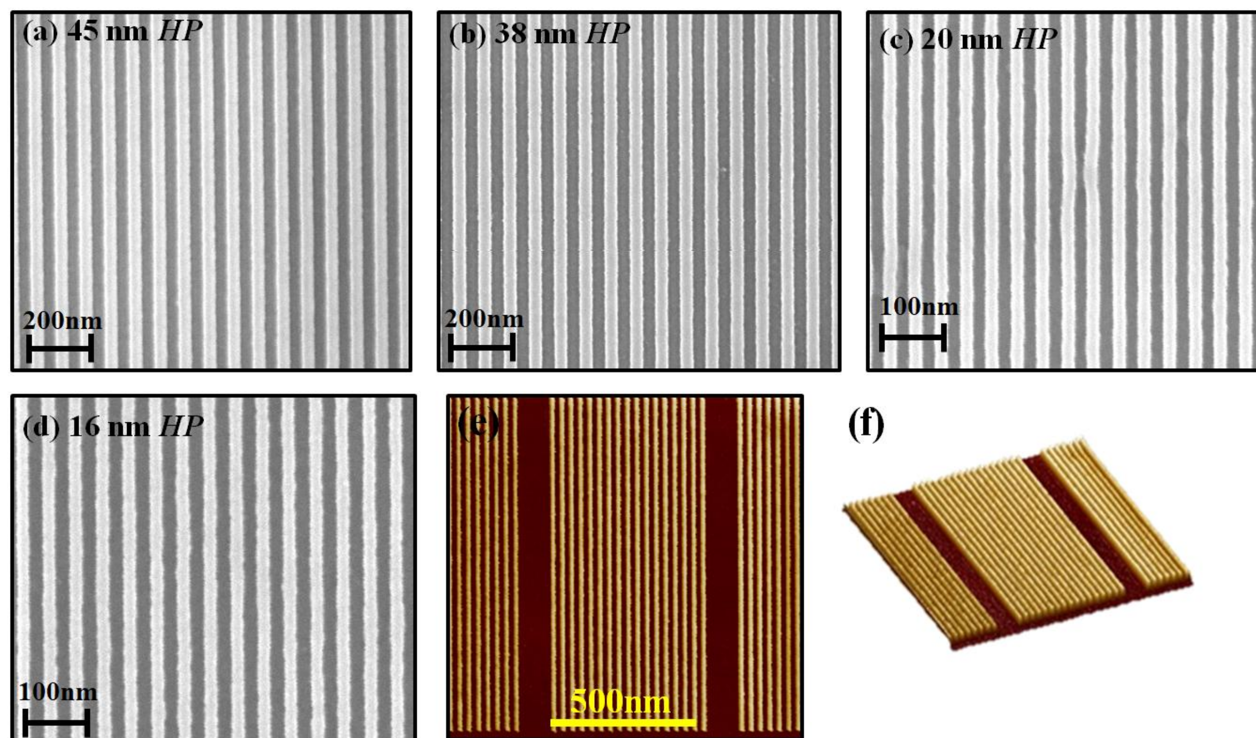

Figure 1. FESEM micrographs of Sn-mTA resist patterns generated using HIBL, showing (a) ~ 45 nm, *HP* (b) ~38 nm, *HP* , and (c) ~20 nm, *HP* (d) ~16 nm, *HP* , line patterns. AFM micrographs of ~16 nm HP line patterns of Sn-mTA: (e) planar view and (f) 3D topographical representation, illustrating surface morphology and pattern fidelity.

clearly demonstrates the *HP* line patterns down to 16 nm developed in optimized developer. AFM images of high-resolution *HP* patterns down to 16nm are shown in Figure 1 (e-f), revealing uniformly developed line patterns and consistent pattern fidelity across the patterned area without any kind of resist residue on the substrate surface.

The contrast curve is essential for providing insight into lithography functionality and performance. A higher contrast value is generally associated with sharper dissolution profiles in developer and improved line-edge definition; however, the achievable contrast strongly depends on the resist chemistry, interaction with developers and the exposure mechanism.

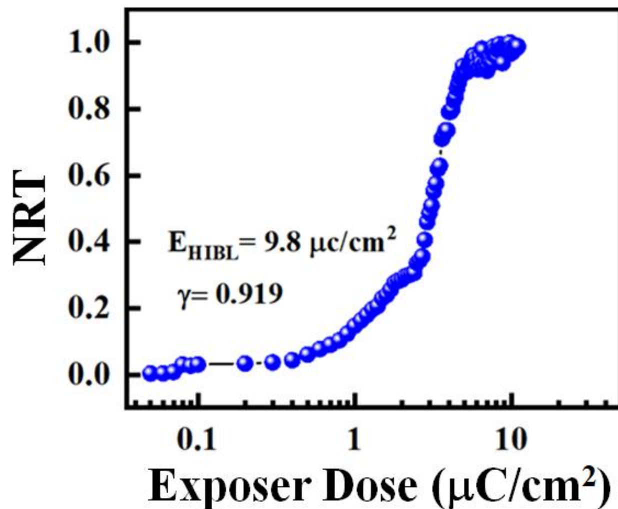

Figure 2 Normalized Remaining Thickness (NRT) vs. exposure dose for contrast measurement of Sn-mTA resist formulations

For the Sn–mTA MOCs resist formulations, contrast curve measurements were performed by exposing ~ 500 nm × 500 nm area blocks with a ~30 keV He^+ beam at doses ranging from 0.05 to 12 μC/cm², and the corresponding contrast curve is shown in Figure 2. Under HIBL exposure, the Sn-mTA resist formulation exhibited an effective contrast value of γ ~ 0.92, indicating a gradual change in resist solubility rather than an abrupt transition.

3.2 FTIR and NMR of Sn-mTA MOCs resist formulations

The FTIR spectrum of the Sn–mTA resist reveals distinct vibrational features corresponding to coordinated carboxylate groups and tin–oxygen bonding. The IR spectrum of the Sn-mTA complex, as shown in Figure 3(a), indicates a strong band at 1578 cm^{-1}, corresponding to the asymmetric COO^- stretch. A band at 1378 cm^{-1} was assigned to the symmetric COO^- stretch. The Sn-O vibration at 488 cm^{-1}, served as a clear fingerprint of metal-ligand bond formation. The reduced broadness in the 2500-3300 cm^{-1} region, relative to free meta-toluic acid, indicates ligand deprotonation[12,13]. The ^{1}H NMR spectrum of the synthesised Sn-mTA complex, as displayed in Figure 3(b), shows characteristic signals at δ 7.8-7.66 (m,

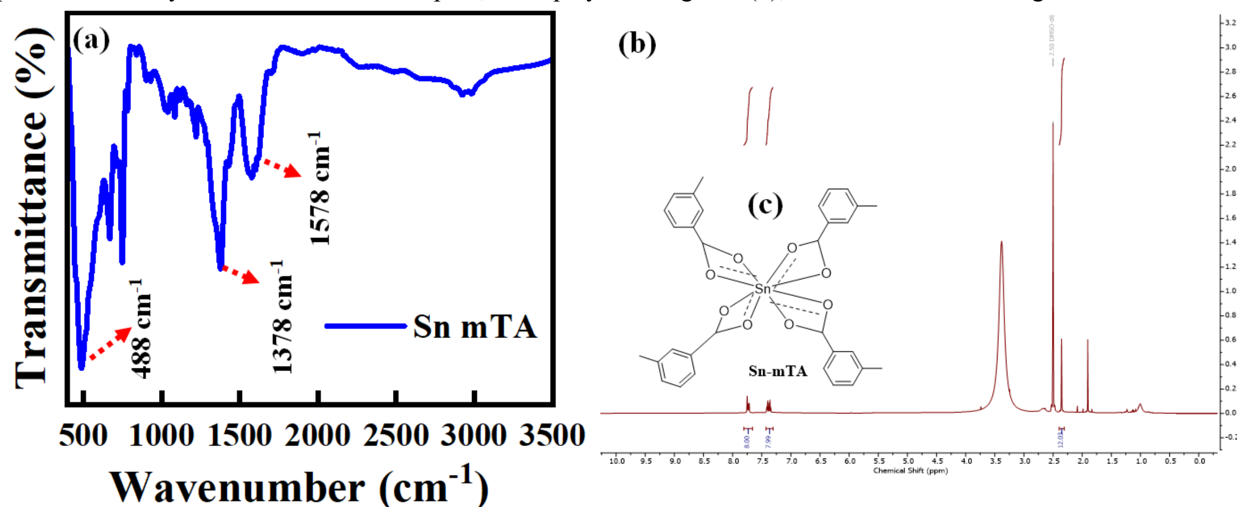

Figure 3. (a) FTIR spectra of the formulated Sn-mTA resist (b) NMR of formulated Sn-mTA resists with proposed structure inset (c)

8H) and δ 7.43-7.31 (m, 8H), corresponding to aromatic protons. A singlet at δ 2.35 (s, 12H) was observed, attributed to the methyl substituent of the meta-toluic acid ligands with a resonance at δ 1.90 ppm attributable to either residual acetate, acetic acid as a byproduct left after cleaning or acetone as an impurity[14]. Whereas the integration values were consistent with the proposed stoichiometry of the complex.

4. Conclusion

In summary, incorporating metatoluic acid (mTA) into Sn-based MOC resist formulations yields well-resolved ~16 nm *HP* line patterns at a considerable He^+ dose of ~24.8 µC/cm^2. LER/LWR for achieved minimum *HP* features were 1.53 ± 0.06 /2.10 ± 0.06. The effective contrast value of γ ~ 0.92, calculated from the NRT curve, demonstrates a considerably sharp dissolution profile for the patterned high-resolution features. In addition, the formation of Sn MOCs was confirmed through FTIR and NMR characterisation. The newly synthesised resist also had acceptable LER/LWR values for ~ 45 nm, ~38 nm and ~20 nm, L/S patterns as 2.04 ± 0.04 nm / 3.11 ± 0.06 nm, 1.98 ± 0.04 / 2.92 ± 0.03, 1.70 ± 0.09 nm / 2.69 ± 0.17, respectively, under exposure doses of ~ 24.8 µC/cm^2. These outcomes underscore the potential for Sn-based MOCs resist formulation to serve as an alternative to EUV lithography at advanced technology nodes.

Acknowledgment

The authors gratefully acknowledge EMD Electronics (70 Meister Ave, Somerville, NJ 08876, USA) for financial support. They also thank the Centre for Design and Fabrication of Electronic Devices (C4DFED) at the Indian Institute of Technology (IIT) Mandi, India, for providing access to the Class 100 cleanroom facilities and advanced characterisation and fabrication tools used in this work. The authors further acknowledge the use of the Zeiss Orion NanoFab system for He^+ beam lithography (HIBL), and the Zeiss Gemini SEM 500 field-emission scanning electron microscope (FESEM), all housed at the C4DFED facility, IIT Mandi.

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