N-Heterocycles for inducing high-sensitivity to inorganic resist compositions

Avik Das [a], Neha Thakur [b], Promit Chakraborty [a], Santu Nandi [a], Manvendra Chauhan [c], Gaurav Jayaswal [d], Dipanjan Dutta [c], Ambar Shukla [e], Nilesh Ladani [e], Prashant Verma [e], Santosh Kumar [d], Satinder K. Sharma [c], Subrata Ghosh [a]

Email: d24074@students.iitmandi.ac.in

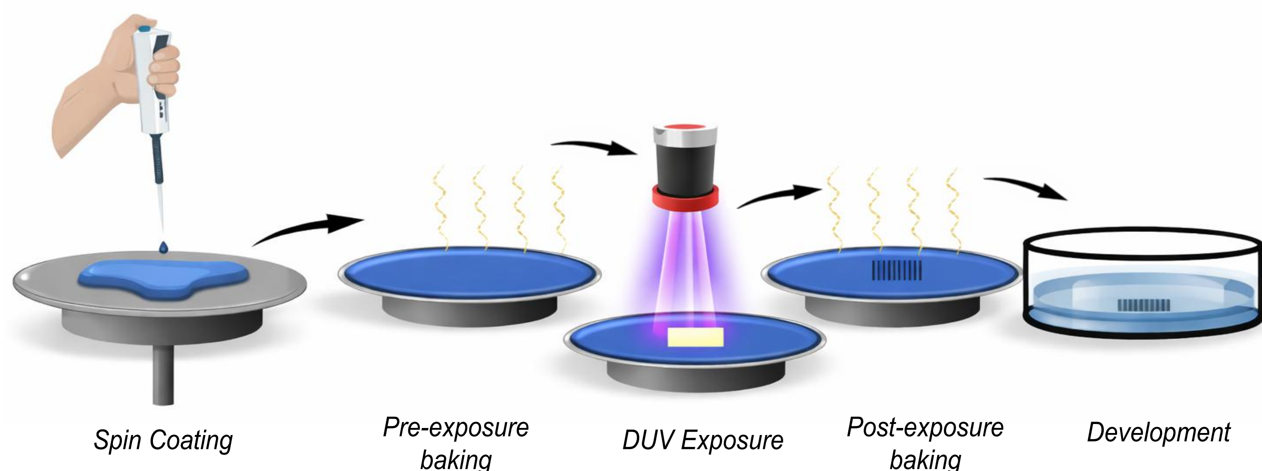
[a] School of Chemical Sciences, Indian Institute of Technology Mandi, Himachal Pradesh-175005

[b] Indian Knowledge System and Mental Health Applications Centre, Indian Institute of Technology Mandi, Himachal Pradesh-175075

[c] School of Computing and Electrical Engineering, Indian Institute of Technology Mandi, Himachal Pradesh-175005

[d] Semiconductor Laboratory, Mohali, Punjab-160071

[e] Space Application Centre-Indian Space Research Organisation, Ahmedabad, Gujarat-380015



Abstract

Although many inorganic salts are readily available in bulk at high purity, they generally show little to no sensitivity towards electron-beam (e-beam) or photon exposure, limiting their applicability as photoresist materials. Zinc (II) acetate, a well-known salt, is a representative example, showing negligible sensitivity. In our ongoing work to develop inorganic-organic hybrid resist materials, we hypothesize that introducing heterocyclic compounds with suitable metal-chelating functionality could enhance the sensitivity of such inorganic salts through potential complexation and interaction with exposure radiation. To validate our hypothesis, we designed and developed substituted pyrazole-based carboxylic acids and investigated their role as small-molecule sensitizers for zinc acetate dihydrate. The resulting zinc metal-based resist composition, (ZnNH), exhibited remarkable improvements in the sensitivity. Results show efficient responses to both deep-

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ultraviolet (DUV) photon and e-beam exposure. In e-beam lithography, the resist composition shows an onset of response in e-beam at a dose as low as 19 μC cm^{-2} and achieves a complete polarity switching, as supported by the normalized remaining thickness (NRT) curve, at doses 111 μC cm^{-2} under a 17.0 kV electron acceleration voltage and a beam current of 56.3 pA. Importantly, the composition of the resist system is well-suited to practical scalability for high-volume manufacturing. The current findings highlight a promising pathway to scalable, highly sensitive zinc-based resist systems for nanopatterning applications, with further potential as an extreme ultraviolet lithography (EUV) hybrid resist platform.

1. Introduction

Lithography is a cornerstone of microfabrication, enabling the precise transfer of patterns onto semiconductor wafers to define intricate features with high accuracy. Its importance lies in controlling the size, shape, and alignment of device components, which directly affect chip performance, speed, and power efficiency. Novel photoresists[1,2] with increased sensitivity, improved line-edge roughness, and enhanced etch resistance, achieving sub-10 nm features will be crucial. Hybrid organic-inorganic resists[3] and chemically amplified systems (CARs)[4,5] are also focused on improved resolution and performance. These developments collectively push the limits of Moore's Law[6] further forward, making denser, faster, and more energy-efficient electronic devices possible while maintaining manufacturability and cost-effectiveness for next-generation semiconductor manufacturing. Researchers have advanced technology and materials to overcome the lithographic challenges encountered, such as diffraction limits, line-edge roughness, and pattern collapse.[7] The shift from ArF immersion (ArFi, 193 nm) to extreme-ultraviolet lithography (EUVL, 13.5 nm) enables a fundamental improvement in the resolution through the use of shorter exposure wavelength.[8] Prior to EUV adoption, multiple patterning techniques and immersion lithography have been the most widely explored lithography tools to extend capabilities and resolution limits.[9] Improvements in photoresist chemistry, such as CARs and hybrid organic-inorganic formulations, enabled finer features and enhanced etch resistance. More sensitive resists reduce required exposure doses to increase throughput. In concert, these resists should maintain low stochastic defects and high critical dimension control. Thus, the development of next-generation high-sensitivity resists is crucial for achieving finer patterning while maintaining an optimal balance between throughput, resolution, and reliability in advanced semiconductor fabrication.

Metal-based hybrid molecular systems show great potential as resist platforms for advanced lithography applications. By carefully selecting the metal component, these materials can be tailored to achieve the desired optical absorption and properties such as high etch resistance required for high-resolution patterning.[10] Over the past decade, zinc-based inorganic photoresists have emerged as a compelling alternative to traditional organic systems due to their high absorption coefficient for EUV photons and etch resistance.[7] Ober's group[11]

presented metal-organic framework (MOF)-based zinc clusters like Zn-BA and Zn-mTA, designed specifically for EUV lithography, and presented 14–16 nm line/space features with better edge roughness compared to zirconia or hafnia-based resists. Additionally, hybrid zinc-containing films deposited by molecular layer deposition[12,13] exhibit superior patterning via electron-beam exposure and good etch resistance, highlighting the potential of Zn in next-generation lithography materials.

Our current work focuses on triggering high sensitivity to an insensitive zinc salt, $Zn(OAc)_2.2H_2O$. We hypothesized that heterocyclic compounds with suitable metal-chelating functionality may enhance the sensitivity of such inorganic salts through potential complexation and interaction with exposure radiation. To validate our hypothesis, we report herein the exploration of substituted pyrazole-based carboxylic acids as small-molecule sensitizers for zinc acetate dihydrate. The resulting resist compositions exhibited improved sensitivity and excellent film-forming ability. Importantly, the resist system we developed can be scaled up for large-scale manufacturing. These findings point to a promising direction for developing zinc-based resists that are both highly sensitive and suitable for nanopatterning. In addition, this approach could also be useful for developing hybrid resists for extreme ultraviolet (EUV) lithography applications.

2. Materials & Methods

2.1 Materials

Zinc acetate dihydrate (crystalline) was purchased from Sigma Aldrich. Propylene glycol methyl ether acetate (PGMEA) was purchased from TCI. Methacrylic acid was purchased from CDH (India). All other chemicals to synthesize the N-heterocycle were purchased from local sources and used as received.

2.2 Synthesis

Pyrazole-based N-heterocycles were synthesized following literature procedures **Figure 1**.

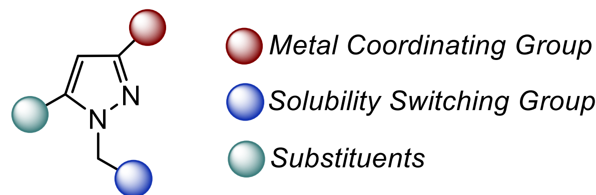

Figure 1: Representative Chemical Structure of N-Heterocycle based organic sensitizer.

2.3 Formulation

13.5 mg of organic sensitizer and 6.5 mg of $Zn(OAc)_2.2H_2O$ were added to a 2 ml sample preparation vial. To it, 1 ml of propylene glycol methyl ether acetate (PGMEA) was added as the lithographic solvent (making a 2% w/v concentration). The mixture was then vortexed for an hour to obtain a clear solution. To this solution,

10 μL of methacrylic acid was added, and the mixture was vortexed for 1 minute. The solution was then filtered through a 0.22 μm PTFE filter to remove particles of micrometer size. The solution was further used for thin film deposition using spin coater.

2.4 Preparation of the Thin Film

A single-sided, polished p-type (100) silicon wafer was cut to approximately 2 cm × 2 cm pieces and cleaned using a standard protocol consisting of 15 minutes of consecutive sonication in DI water, acetone, and IPA. Then, the ZnNH formulation was drop-cast onto the wafer and spin-coated at 5000 rpm for 50 seconds at 500 rpm/sec to get a smooth film with an average thickness of ~15 nm. Pre-exposure baking was applied at 110 ℃ for 90 seconds to remove the residual solvent. All experiments were conducted using the same film conditions and substrate.

3. Result & Discussion

3.1 Thin Film Formation & Characterization

Spin coating is a popular method for preparing thin films with high uniformity on flat Si wafers because of its simplicity, ease of control, and applicability to solution-processed materials. The thickness of the resulting films is mainly determined by solution properties (viscosity, concentration, and solvent evaporation rate) and by spin-coating conditions (spin speed, acceleration, and spin time).[14] Generally, the thickness of the resulting films is inversely proportional to the spin speed. Increasing the solution concentration and viscosity results in thicker films, whereas faster solvent evaporation and longer spin times produce thinner films. Spin coating enables controlled thickness variation, making it highly useful for lithographic and functional thin-film applications. However, surface roughness is a very important parameter that determines the quality of pattern transfer, optical, and interfacial properties. Surface roughness depends on solution homogeneity, particle agglomeration, solvent evaporation rate, and subsequent soft baking or annealing. Optimized spin-coating conditions, baking conditions and adequate filtration of the solution generally produce films that are smooth, pinhole-free, and have low root-mean-square (RMS) roughness values, often in the sub-nanometer to a few-nanometer range. Film roughness is usually measured by AFM, while film thickness is determined by ellipsometry. In summary, optimizing spin-coating conditions is necessary to produce thin films with good uniformity and low surface roughness.

Film roughness, as discussed previously, is an important parameter for lithographic applications. To obtain a smooth, thin film with photoresist properties, spin-coating parameters, including rotation speed, time, and acceleration, need to be optimized. Line-RMS roughness of photoresist-coated thin film at different rotational

speeds were determined and found to be within a nanometer region. At a rotation speed of 5000 rpm, the film roughness was observed to be 0.131 nm. Surface roughness contributes to linewidth variation, increased line-edge roughness, and loss of pattern fidelity. A smooth film (**Figure 2 (a)**) provides the correct focus within the depth-of-focus limits, which is essential for high-resolution patterning. Low surface roughness also provides uniform development and pattern transfer.[15] We determine the film thickness as a function of different spin rotational speeds (**Figure 2 (b)**) and we chose 5000 rpm for further studies, and the thickness at this speed was measured to be ~15 nm. After optimizing the film-forming conditions, we checked the thermal stability of the films (pre-exposure baking temperature). From 80 °C to 130 °C (90 seconds), the film remained quite stable, but the AFM image (**Figure 2 (c)**) shows a significant microscopic deformation at 130 °C. At 110 °C, we optimized the pre-exposure baking time to 90 seconds to achieve uniform films.

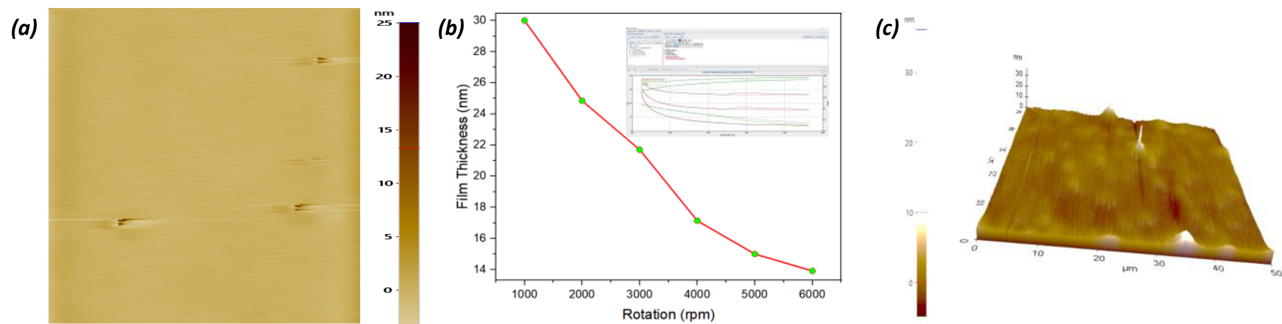

Figure 2: (a) AFM image of thin film coated with Zn-NH at 5000 rpm for 50 seconds; (b) Film thickness measurement at different rotational speeds; inset ellipsometry fitting curve of thin film at 5000 rpm; (c) Film at a prebaking temperature of 130 °C.

3.2 Exposure & Determination of Sensitivity

Electron-beam lithography was performed using a Raith eLine Plus system. Arrays consisting of 12 × 25 blocks, each with a feature size of 500 nm, were exposed to generate the contrast curve. The exposures were performed at an acceleration voltage of 17.0 kV and a beam current of 56.3 pA. A dose range from 1 to 150.5 μC/cm² was employed with an incremental step of 0.5 μC/cm². Following exposure, the films underwent post-exposure baking at 120 °C for 120 s, followed by development for 60 s in a 1:1 (v/v) decalin and toluene mixture with subsequent nitrogen drying. Individual exposed blocks were then scanned and imaged using a Bruker Dimension Icon atomic force microscope. The remaining resist thickness was plotted as a function of the applied electron-beam dose to extract the sensitivity parameters D_0, D_{50}, and D_{100} of the resist system. **Figure 3 (a)** shows the D_0, D_{50}, and D_{100} values at ~19 μC/cm^2, ~36.7 μC/cm^2 and ~111 μC/cm^2 respectively. Contrast(γ) = $1 / \log_{10}(D_{100} / D_0)$ equation was used to determine the contrast to be 1.3045. The photoresist contrast, γ, quantifies how sharply the material differentiates between exposed and unexposed regions. A higher contrast

results in a more abrupt dissolution threshold during development, leading to steeper sidewall profiles and enabling the formation of patterns with higher aspect ratios.[16]

FESEM imaging was conducted using CarlZeiss Gemini 500 instrument. **Figure 3 (b)** is the contrast pad, which was subjected to gradient exposure.

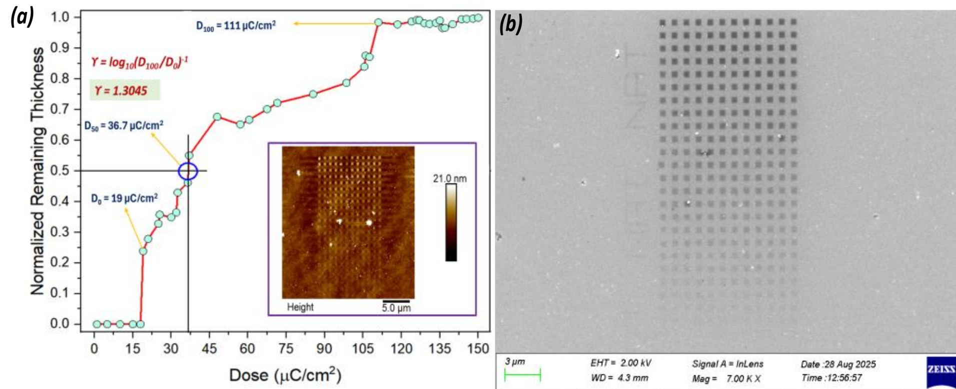

Figure 3: (a) Contrast curve of the photoresist system; inset: AFM image of the pad patterned using EBL for evaluating sensitivity and contrast; (b) FESEM image of the pad.

For establishing patterning potential, initially the present resist composition was subjected to DUV lithography, which was performed using a MIDAS MDA-80FA mask aligner. A 2 wt% photoresist solution was first spin-coated onto a 6-inch silicon wafer, resulting in uniform film. The coated film was then subjected to a pre-exposure baking step to remove residual solvent. DUV exposure was performed using fully automated robotic arms at a light intensity of 2.8 mW/cm² for 30 s. Following exposure, the samples underwent post-exposure baking and subsequent development to obtain the desired patterns on the silicon wafer. **Figure 4** shows optical microscopic images of the DUV-patterned surface. The resist patterned various types of features including line, dot and complex features (Figure 3). All these preliminary studies indicated that the current resist composition has potential to be used as advanced resist system for lithography patterning.

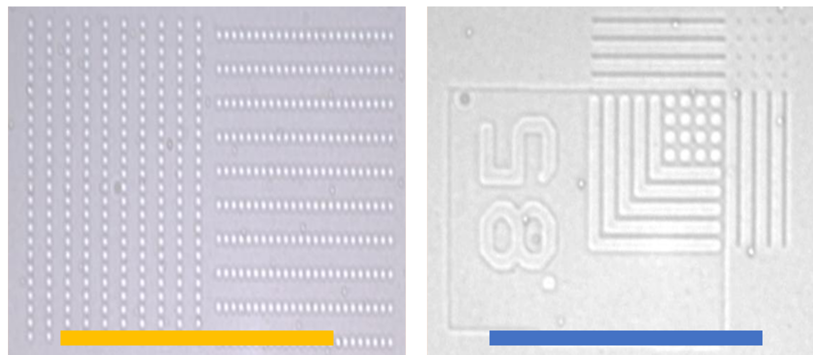

Figure 4: Optical Microscopy images of different patterns and features obtained at a DUV dose of 84 mJ/cm². (Scale bar: Yellow – 75 μm, Blue – 25 μm)

4. Conclusion

In conclusion, this study demonstrates an efficient methodology to enhance the photo-sensitivity of the cost-effective, inherently insensitive inorganic salt, $Zn(OAc)_2 \cdot 2H_2O$, through strategic formulation design. The newly created hybrid resist system requires less exposure dose, suggesting it could be a cheaper alternative to traditional photoresists. The optimized formulation produced uniform patterns over large-area substrates indicates that it is robust and compatible with a wide range of processes. The current study provides a good proof of concept; however, additional research into the fundamental chemical mechanisms is required to fully establish the solubility transition as well as nanopatterning potential, which is ongoing. This current study paves the way for the development of low-cost, high-performance inorganic-organic hybrid photoresists for next-generation nanofabrication.

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