

Lawrence Berkeley National Laboratory

LBL Publications

Title

Ultralow line edge roughness of hybrid multilayer Extreme ultraviolet resist with vertical molecular wire structure

Permalink

<https://escholarship.org/uc/item/59g231qv>

Journal

Materials Today, 87

ISSN

1369-7021

Authors

Lee, Jaehyuk
Ji, Hyeonseok
Koh, Chawon
[et al.](#)

Publication Date

2025-08-01

DOI

10.1016/j.mattod.2025.04.007

Copyright Information

This work is made available under the terms of a Creative Commons Attribution-NonCommercial License, available at <https://creativecommons.org/licenses/by-nc/4.0/>

Peer reviewed



Research

Ultralow line edge roughness of hybrid multilayer Extreme ultraviolet resist with vertical molecular wire structure

Jaehyuk Lee^{a,1}, Hyeonseok Ji^{a,1}, Chawon Koh^{a,g}, Juyeong Lee^a, Ji-Hoo Seok^b, Jinho Ahn^b, Chang Gyoum Kim^c, Jiho Kim^d, Inhui Hwang^d, Hyungju Ahn^d, Kug-Seung Lee^d, Sangsul Lee^d, Dimitrios Kazazis^e, Prajith Karadan^e, Yasin Ekinci^e, Gregory Denbeaux^f, Ji Young Park^g, Won-Joon Son^g, Seungmin Lee^g, Tsunehiro Nishi^g, Bruno La Fontaine^h, Myung Mo Sung^{a,*}

^a Department of Chemistry, Hanyang University, Seoul 04763, Republic of Korea

^b Division of Materials Science and Engineering, Hanyang University, Seoul 04763, Republic of Korea

^c Korea Research Institute of Chemical Technology (KRICT), Daejeon 34114, Republic of Korea

^d Pohang Accelerator Laboratory, POSTECH, Pohang 37673, Republic of Korea

^e Paul Scherrer Institute (PSI), Villigen 5232, Switzerland

^f Department of Nanoscale Science and Engineering, State University of New York at Albany, NY 12203, USA

^g Semiconductor R&D Center, Samsung Electronics Co., Ltd., Gyeonggi-do 18448, Republic of Korea

^h The Center for X-Ray Optics, Lawrence Berkeley National Laboratory, CA 94720, USA

ARTICLE INFO

Keywords:

Molecular layer deposition (MLD)
Hybrid multilayer resist
Extreme Ultraviolet (EUV) lithography
Vertical molecular wire structure
Cross-linking mechanism
Line edge roughness (LER)

ABSTRACT

This study introduces an innovative extreme ultraviolet (EUV) resist featuring a vertically oriented molecular wire architecture, designed to achieve exceptionally low line edge roughness (LER). The resist is synthesized via molecular layer deposition, a gas-phase technique that allows precise monolayer-level control over thickness, ensuring excellent reproducibility, conformality, and uniformity. The hybrid multilayer resist is constructed through controlled ligand-exchange reactions between diethylzinc and 3-mercaptopropanol (3MP), which create vertically oriented molecular wires with widths below 1 nm. This innovative structure achieves an unprecedentedly low LER of 1.37 nm at a dose of 60 mJ/cm². EUV exposure induces unique cross-linking coordination bonds between the zinc atoms and the oxygen and sulfur atoms in 3MP without degassing, thereby enhancing EUV sensitivity. The combination of vertically oriented high-aspect-ratio molecular wires and effective lateral cross-linking significantly improves EUV sensitivity and robustness during etching. This pioneering hybrid multilayer EUV resist may satisfy the stringent requirements of advanced semiconductor manufacturing.

Introduction

The relentless miniaturization of electronic devices, as prescribed by Moore's law, necessitates continual advancements in lithographic techniques to achieve ever-smaller feature sizes and higher device complexity. Extreme ultraviolet (EUV) lithography, which involves a significantly shorter wavelength (13.5 nm) than deep ultraviolet (DUV) lithography (193 nm), presents a substantial resolution advantage for fabricating the sub-10 nm features critical for next-generation devices [1–3]. However, the widespread adoption of EUV lithography faces significant technical challenges, with photon shot noise being a primary concern. This issue arises from the drastically reduced photon density in

EUV, which is only 1/14th of that in DUV at an equivalent exposure dose [4]. This reduced photon density leads to stochastic fluctuations in resist activation that detrimentally affect resolution and exacerbate line edge roughness (LER) [4,5]. To overcome these challenges and fully harness the potential of EUV lithography, the development of high-performance EUV resists is crucial. Ideal resists must possess high sensitivity for efficient manufacturing throughput, excellent resolution, and LER control for precise patterning, along with strong etch resistance to withstand the processing conditions [6–8]. Among these factors, LER control is particularly critical, as it represents the variation in a patterned line's edge profile, which significantly impacts device behavior. The International Roadmap for Devices and Systems has set increasingly stringent

* Corresponding author.

E-mail address: smm@hanyang.ac.kr (M.M. Sung).

¹ These authors contributed equally: Jaehyuk Lee, Hyeonseok Ji.

<https://doi.org/10.1016/j.mattod.2025.04.007>

Received 22 September 2024; Received in revised form 24 March 2025; Accepted 12 April 2025

Available online 24 April 2025

1369-7021/© 2025 Elsevier Ltd. All rights are reserved, including those for text and data mining, AI training, and similar technologies.

targets for pattern sizes and LER, such as achieving a 0.8 nm LER by 2028 [9]. As the semiconductor industry advances toward sub-10 nm half-pitch technology nodes, precise LER control is becoming increasingly critical. In response, extensive research efforts are being devoted to developing strategies to mitigate LER and enhance EUV lithography performance for future technology nodes.

Chemically amplified resists (CARs) were initially used in EUV lithography due to their high sensitivity, achieved through a photoacid generation process. However, this approach suffers from significant limitations in terms of LER, as acid diffusion leads to variations along feature edges, resulting in LERs exceeding 2.5 nm [10–18]. Despite innovations such as quenchers and multi-trigger resist systems [19,20], LER improvements remained insufficient, staying above 1.7 nm, falling below industry targets. In response, non-CAR polymer-based resists were developed [21,22], which bypass the chemical amplification process. These resists offer more uniform reactions and improved LER control (approximately 2.0 nm) due to minimal acid diffusion. However, this benefit is achieved at the cost of lower sensitivity, which necessitates higher exposure doses. As feature sizes shrink and high-numerical aperture exposure tools are used, next-generation EUV lithography demands thinner resists to avoid pattern collapse and satisfy depth of focus requirements. Traditional polymer-based resists, including CARs and non-CARs, often lack sufficient etch resistance for such thinner films due to their inherent low chemical and mechanical stabilities, leaving the underlying layers vulnerable during etching [23]. To overcome these limitations, inorganic resists have emerged as a promising alternative, demonstrating significant potential in EUV lithographic performance [24–31]. Inorganic resists include metal oxide nanoparticles, metal-based nanoclusters, and organometallic compounds. For example, hafnium oxide and zirconium oxide nanoparticles exhibit high etch resistance and reduced LER [32,33]. Inpria Corporation has developed tin-containing metal oxide-based resists that show promising results in terms of lithography pattern fidelity, further underscoring the potential of inorganic materials in advanced lithography [34,35]. Additionally, Lam Research Corporation has introduced organo-metal oxide-containing EUV resists, which are fabricated via vapor phase deposition [36,37]. The dry process reduces the risk of pattern collapse and enables the manufacturing of finer feature sizes, addressing some of the challenges associated with conventional wet-process resists. Inorganic resists offer a path toward lower LER, as their smaller unit components minimize fluctuations during exposure and development processes, thereby helping to reduce LER [23]. However, achieving ultralow LER in advanced chip manufacturing remains difficult, even with efforts to shrink metal oxide and nanocluster resists. To this end, research is also exploring alternative approaches, such as single-molecule-sized organometallic resists [38–42]. While promising, this strategy requires more cross-linking reactions to maintain pattern fidelity after EUV exposure, which potentially hinders fine feature patterning [43]. The transition from CARs to inorganic resists highlights the ongoing struggle to meet the ever-stricter LER requirements in EUV lithography, highlighting the need for continuous innovation in resist materials and processes to advance semiconductor industry.

This study introduces an innovative EUV resist designed to minimize LER through a novel vertically oriented molecular wire architecture. This resist features a hybrid multilayer structure, with molecular wires aligned vertically and synthesized via molecular layer deposition. This gas-phase, layer-by-layer growth methodology, akin to atomic layer deposition, involves using sequential saturated surface reactions to construct each hybrid monolayer. The resulting multilayer exhibits a unique hybrid structure with vertically oriented molecular wires less than 1 nm wide, achieving an unprecedentedly low LER of 1.37 nm at a moderate exposure dose of 60 mJ/cm². The EUV exposure induces unique cross-linking reactions through coordination bonds between zinc atoms and the oxygen and sulfur atoms in the organic molecules, with no degassing. This distinctive cross-linking mechanism, combined with the vertically aligned molecular wire structure, enhances the EUV

sensitivity of the resist. Lateral cross-linking between adjacent wires greatly reduces their solubility in the developing solution, providing excellent EUV sensitivity and robustness during subsequent etching processes. This novel hybrid multilayer EUV resist represents a significant breakthrough, overcoming the limitations of previous generations and satisfying the stringent demands of advanced semiconductor manufacturing.

Result & Discussion

Fabrication of hybrid multilayer EUV resist via MLD

The construction of hybrid multilayers requires the terminal groups of the hybrid monolayer to be sufficiently reactive to adsorb the next monolayer. This is achieved using a bifunctional organic molecule. Fig. 1a illustrates the layer-by-layer synthesis of hybrid multilayers via molecular layer deposition (MLD). Diethylzinc (DEZ) serves as the inorganic precursor, while 3-mercaptopropanol (3MP) acts as the bifunctional organic precursor. A Si substrate, rich in hydroxyl (OH) groups, is exposed to DEZ within the MLD chamber. This induces a ligand-exchange reaction, whereby DEZ molecules are chemisorbed onto the substrate surface, generating a monolayer of ethyl zinc oxide (C₂H₅ZnO) species. As the chemisorbed DEZ molecules possess ethyl groups, the 3MP, with its two functional groups (hydroxyl and thiol) at opposite ends of the propyl chain, reacts with these ethyl groups. The hydroxyl group of 3MP reacts preferentially, replacing the ethyl group and forming a zinc 3-mercaptopropoxide (ZnOC₃H₆SH) monolayer (Fig. S1 and Table S1). The propyl chains of 3MP facilitate the close packing of the monolayer via self-assembly, ensuring structural integrity and uniformity of the hybrid multilayer. The remaining thiol group in the self-assembled 3MP molecules serves as the active site for the next DEZ molecule in the subsequent MLD cycle, leading to the formation of a zinc thiolate species. Fig. 1b depicts a theoretical model of the hybrid multilayer comprising vertically aligned molecular wires. This idealized configuration assumes all *trans*-propyl chains within the structure to be perfectly perpendicular to the substrate surface. Specifically, the hydroxyl group of 3MP establishes a covalent bond with the underlying zinc atom, while the thiol group forms a covalent bond with the zinc atom above. Assuming this ideal configuration with fully extended and completely perpendicular propyl chains, the anticipated thickness of the zinc 3-mercaptopropoxide hybrid monolayer is approximately 7.72 Å.

In a true MLD process, the surface reactions must be self-terminating and complementary to achieve uniform, conformal, and high-quality zinc 3-mercaptopropanol (Zn-3MP) hybrid multilayers. To confirm the self-terminating nature of the reaction between 3MP and DEZ, an experiment was conducted by varying the 3MP dosing time between 1 s and 20 s (Fig. S2a). The growth rate of the Zn-3MP hybrid multilayer was measured using an ellipsometer at deposition temperatures of 80°C – 120°C (Fig. S2b). Based on the results, the hybrid multilayer thickness per cycle became saturated when the 3MP dosing time exceeded 10 s, confirming a self-terminating reaction between 3MP and DEZ on the Si substrate. Similarly, rapid saturation of the growth rate was observed when the DEZ dosing time surpassed 1 s, suggesting a fast, self-terminating reaction between the DEZ and the pre-adsorbed 3MP on the substrates (Fig. S2c). All experiments investigating self-terminating growth involved 150 cycles. The saturation data implies that both DEZ and 3MP fully react with the available active sites on the substrate surface. Atomic force microscopy (AFM) was employed to characterize the patterned Zn-3MP as a function of the number of MLD cycles (Fig. 1c–e). The AFM images confirm the anticipated hybrid monolayer thickness and MLD growth rate for Zn-3MP. The measured hybrid monolayer thickness was approximately 7.5 Å per cycle. The images also reveal exceptionally smooth and uniform surfaces for the Zn-3MP monolayer and multilayers, with a root mean square (RMS) roughness of only 2.5 Å. This is comparable to the RMS roughness of the initial clean Si substrate (2.1 Å). The Zn-3MP multilayers maintained this

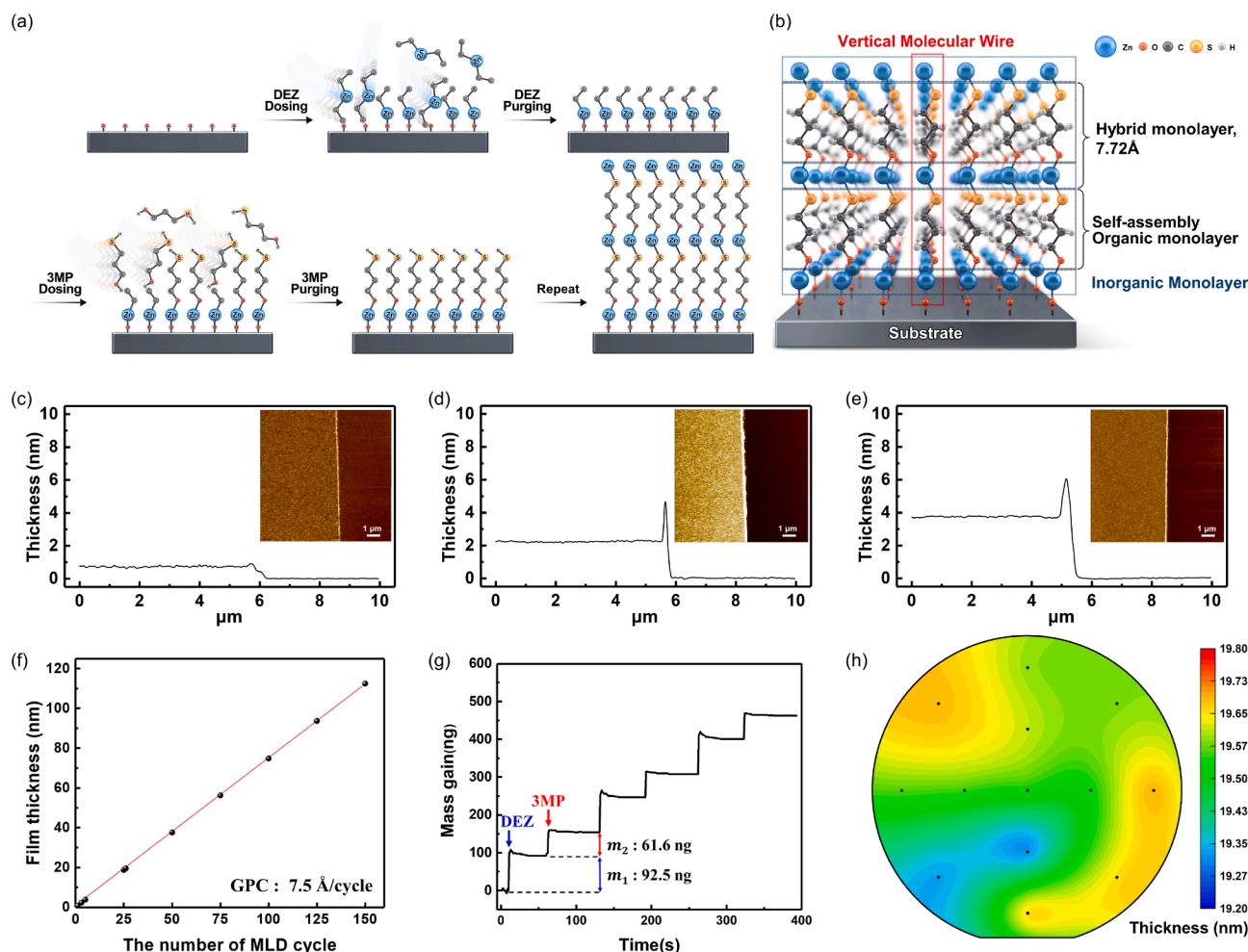


Fig. 1. Fabrication of hybrid multilayer EUV resist via MLD. a, Schematic of the MLD process. b, Illustration of the ideal vertical molecular wire structured hybrid multilayer. c–e, Variation in line profile and surface roughness with the number of deposition cycles: c, 1 cycle, d, 3 cycles, e, 5 cycles (Inset: AFM image depicting the deposited Zn-3MP and the substrate). f, Film thickness as a function of the number of MLD cycles. g, Mass gain calculated via QCM analysis of Zn-3MP MLD. h, Ellipsometry mapping measurements showing thickness uniformity.

surface smoothness regardless of the number of MLD cycles, suggesting a two-dimensional growth mode in which Zn-3MP monolayers are deposited one on top of another. Fig. 1f demonstrates a near-linear increase in Zn-3MP thickness with the number of MLD cycles, reflecting a growth rate of approximately 7.5 Å per cycle, which is consistent with the AFM results. This indicates that the surface reactions involved in the MLD process are complete and complementary, leading to uniform layer-by-layer growth.

A quartz crystal microbalance (QCM) was utilized to quantify the MLD process of Zn-3MP because the high sensitivity of this device to mass changes enables accurate analysis of thin film deposition (Fig. 1g). During the MLD process, the QCM crystal was alternately exposed to the DEZ and 3MP precursors. In the DEZ dosing step, the mass gain (Δm_1) reflects the net change due to ligand exchange, where the DEZ molecules replace the surface hydroxyl or thiol groups, releasing ethane as a byproduct. Consequently, Δm_1 represents the net mass of the added DEZ molecule and the removed ethane. Similarly, during the 3MP dosing step, Δm_2 accounts for both the added 3MP molecule and the removed ethane. The QCM analysis revealed mass gains of $\Delta m_1 = 92.5$ ng for DEZ and $\Delta m_2 = 61.6$ ng for 3MP. Using these values and the molecular weights of the precursors, the coverages per cycle were calculated to be 3.87 Zn/nm²-cycle and 3.70 3MP/nm²-cycle, indicating a near-1:1 ratio between Zn atoms and 3MP molecules. This ratio substantiates the self-limiting and complementary nature of the MLD process, ensuring stoichiometric control and preventing uncontrolled multilayer growth. The

calculated coverages also suggest the formation of highly dense Zn-3MP molecular layers with a vertically oriented structure, comparable in density to close-packed self-assembled monolayers (Fig. S3) [44,45]. Fig. 1h presents the thickness variation map of a Zn-3MP multilayer deposited on a 4-inch Si wafer via MLD. After 26 MLD cycles, an average thickness of 19.5 nm was achieved, corresponding to a deposition rate of approximately 7.5 Å per cycle. Moreover, the measured thicknesses exhibited a remarkably low standard deviation of 0.12 nm, highlighting the excellent thickness uniformity of the Zn-3MP multilayer across the entire 4-inch wafer.

Structure characterization

Fig. 2a illustrates a Zn-3MP multilayer featuring a vertically oriented molecular wire structure. This configuration was confirmed through X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), and extended X-ray absorption fine structure (EXAFS) analysis. These analyses confirm the vertical orientation of the Zn-3MP molecules, facilitated by van der Waals interactions among the 3MP organic molecules that form the self-assembled Zn-3MP multilayers. We anticipate that the close packing of these molecular wires, with sub-nanometer distances, contributes to the ultralow line edge roughness (LER). XPS analysis of the Zn-3MP multilayer (Fig. 2b) revealed the presence of Zn, O, C, and S in a measured atomic ratio of Zn:O:C:S = 1:1.1:3.1:1, which closely matches the ideal ratio of 1:1:3:1 expected for

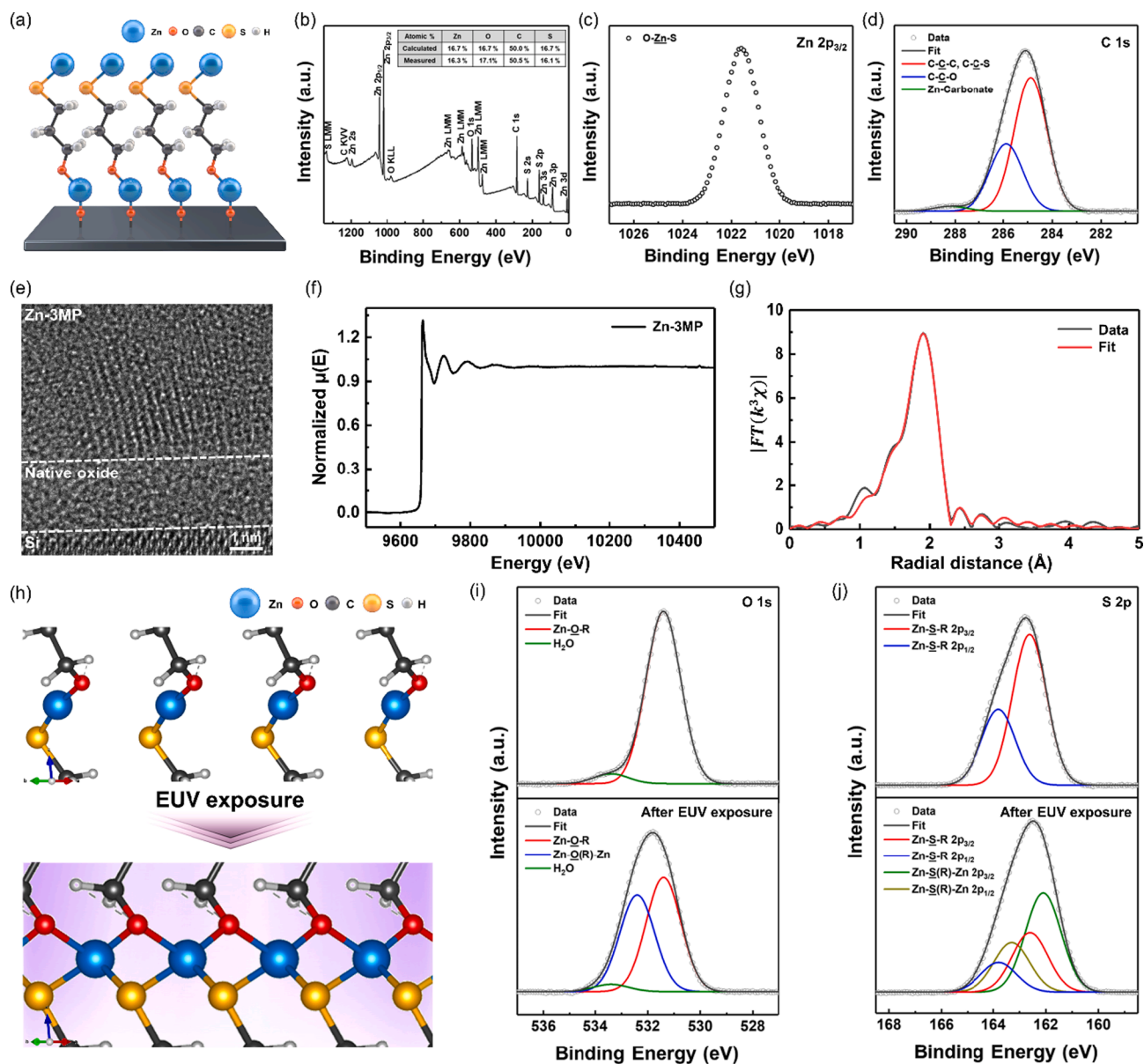


Fig. 2. Structure characterization and cross-linking mechanism under EUV exposure. a, Illustration of the expected vertical molecular-wire-structured Zn-3MP hybrid multilayer. b, XPS survey spectrum (Inset: elemental ratio of Zn, O, C, and S). c, XPS Zn 2p_{3/2} high-resolution spectrum. d, XPS C 1s high-resolution spectrum. e, Cross-sectional TEM image of the Zn-3MP hybrid multilayer. f, Normalized XAFS spectrum of the Zn-3MP hybrid multilayer. g, k³-weighted Fourier-transform representation of the data shown in Fig. 2f and fitting results between the Zn-3MP hybrid multilayer and the structural model. h, Schematic of the cross-linking reaction during EUV exposure of the Zn-3MP hybrid multilayer. i, XPS O 1s and j, XPS S 2p high-resolution spectrum before(top) and after(bottom) EUV exposure.

Zn-3MP ($-\text{ZnOCH}_2\text{CH}_2\text{CH}_2\text{S}-$). Slight deviations in the ratio are attributable to air exposure before XPS measurement. The high-resolution Zn 2p_{3/2} peak in Fig. 2c indicates the presence of Zn-O and Zn-S species at 1021.6 eV [46]. This is consistent with the O 1s high-resolution peak at 531.4 eV in Fig. 2i, indicating Zn-O-R species [47]. The high binding energy peak at 533.4 eV is associated with adsorbed water molecules [48]. The S 2p region in Fig. 2j shows a spin-splitting doublet with S 2p_{1/2} and 2p_{3/2} peaks separated by 1.2 eV, where the S 2p_{3/2} peak at 162.6 eV corresponds to Zn-S-R species [46]. These molecular layers are formed through a surface reaction between the reactive zinc-ethyl group of DEZ and the hydroxyl and thiol groups of 3MP. The detailed C 1s spectrum in Fig. 2d shows peaks at 284.9 eV and 285.9 eV, corresponding to the $(-\text{CH}_2-)/(-\text{CH}_2\text{S}-)$ and $(-\text{CH}_2\text{O}-)$ species in Zn-3MP, respectively [47,49]. The minor peak at 288.2 eV is attributed to adventitious organic materials from air exposure [50]. Notably, the peak area at 285.9 eV is approximately half of that at 284.9 eV. This peak

ratio (about 2:1 between 284.9 eV and 285.9 eV) is consistent with the Zn-3MP structure ($-\text{ZnOCH}_2\text{CH}_2\text{CH}_2\text{S}-$). Air stability is a crucial factor for practical applications; therefore, XPS measurements were conducted following exposure to air for up to 72 h post-deposition. The results showed no significant changes in the O 1s peak positions (531.4 eV, 533.4 eV), confirming the air stability of Zn-3MP during this period (Fig. S4a-c). Typically, XPS characterization of Zn-3MP resists was performed within 12 h of MLD deposition.

Grazing-incidence wide-angle X-ray diffraction (GI-WAXD) analysis was performed to evaluate the crystallinity of the Zn-3MP multilayers, as shown in Fig. S5a. The two-dimensional GI-WAXD patterns from the 19.5 nm Zn-3MP revealed no distinct diffraction features, indicating an amorphous polymeric structure with a lack of long-range order. Interestingly, the cross-sectional TEM image (Fig. 2e) shows vertically oriented Zn-3MP molecular wires within the hybrid multilayer deposited on the Si(100) substrates. These wires exhibit sub-nanometer

intermolecular spacing and a tilt angle of less than 15° relative to the substrate surface normal, indicating short-range order confined to these vertically aligned structures. The random in-plane arrangement of Zn-3MP molecules within the XY plane likely prevents the establishment of long-range order (Fig. S6), resulting in the amorphous characteristics observed through GI-WAXD. The formation of these vertically oriented molecular wires is attributed to the preferential alignment of Zn-3MP molecules perpendicular to the substrate surface during MLD, primarily driven by van der Waals interactions among the 3MP organic molecules. To further elucidate the local atomic arrangement within the Zn-3MP multilayer, Extended X-ray absorption fine structure (EXAFS) analysis was conducted. Fig. 2f shows the background-removed X-ray absorption fine structure (XAFS) spectrum of the multilayer. The EXAFS oscillation, observed above the Zn absorption edge ($E_0 = 9,660$ eV), were extracted and Fourier-transformed into real space for subsequent analysis. The EXAFS data was fitted to theoretical calculations to quantitatively determine the distances between the Zn atom and its nearest neighboring atoms. The fitting procedure was centered on the Fourier-transformed EXAFS data within the 1.0 – 3.0 Å range, considering the Zn-O and Zn-S pairs in Zn-3MP. The entire EXAFS signal was well-fitted with the Zn-3MP structure (Fig. 2a), as shown in Fig. 2g, and the results are listed in Table S2. All parameters were within acceptable ranges, indicating that this structural model provided a good agreement with the experimental data.

Cross-linking mechanism under EUV exposure

XPS analysis was performed to examine the effects of EUV exposure on the Zn-3MP multilayer. The analysis revealed significant cross-linking reactions within the multilayer after EUV exposure at a dose of 100 mJ/cm^2 , attributed to the formation of coordination bonds between the zinc and the oxygen/sulfur functional groups. This exposure led to conformation changes in the multilayer, as evidenced by a 7.8 % reduction in thickness (Fig. S7). These cross-linking reactions reduced solubility in the development solution, transforming the multilayer into a negative-tone resist. XPS survey scans of the resist after EUV exposure revealed the presence of Zn, O, C, and S in a near-stoichiometric ratio of Zn:O:C:S = 1:1.1:3.2:1 (Fig. S8), which aligns with the pre-exposure composition of 1:1.1:3.1:1. The high-resolution O 1s spectra highlighted significant changes upon exposure (Fig. 2i). The initial peak at 531.4 eV indicated the presence of Zn-O-R species. Post-exposure, a new peak emerged at 532.4 eV, corresponding to Zn-O(R)-Zn cross-linking via coordination-bonding, as shown in Fig. 2h [51]. The high-resolution S 2p spectra also exhibited significant changes after EUV exposure (Fig. 2j). Before exposure, doublet peaks at 162.6 eV (S 2p_{3/2}) and 163.8 eV (S 2p_{1/2}), associated with Zn-S-R species, were observed. These peaks shifted to lower binding energies of 162.1 eV (S 2p_{3/2}) and 163.3 eV (S 2p_{1/2}), respectively, after exposure, indicating the formation of Zn-S(R)-Zn species [52]. These observations suggest that EUV exposure induces significant structural changes within the Zn-3MP multilayer, accompanied by unique cross-linking reactions. Specifically, the oxygen in Zn-O-R species and the sulfur in Zn-S-R species form additional coordination bonds with adjacent zinc atoms, producing Zn-O(R)-Zn and Zn-S(R)-Zn cross-linking bonds. Analysis of the peak areas indicates a significant cross-linking reaction following EUV exposure. The high-resolution O 1s spectra exhibited two prominent peaks at 531.4 eV and 532.4 eV, corresponding to Zn-O-R and Zn-O(R)-Zn species, respectively. The relative peak areas indicated that approximately 46 % of oxygen atoms participated in cross-linking between adjacent Zn-3MP units. Similarly, the S 2p_{3/2} spectra revealed peaks at 162.6 eV (Zn-S-R) and 162.1 eV (Zn-S(R)-Zn), with an area ratio suggesting that approximately 63 % of sulfur atoms participated in cross-linking.

During deposition, the Zn-3MP multilayers primarily formed vertical bonds (along the Z-axis). The vertical molecular wire structure likely prevents additional coordination bonds between oxygen in Zn-O-R species (or sulfur in Zn-S-R species) and adjacent zinc atoms during

deposition due to the steric hindrance of close-packed self-assembled 3MP chains. Only weak long-distance interactions are expected. However, EUV exposure caused structural conformational changes in the Zn-3MP multilayer, transitioning the zinc coordination from a linear to a tetrahedral arrangement. This shift facilitated cross-linking through coordination bonds in the lateral direction (XY-plane), significantly increasing the molecular weight of the Zn-3MP units. This resulted in a substantial change in the solubility of the multilayer during development, consequently enhancing its EUV sensitivity. The proposed cross-linking mechanism did not produce by-products, as evidenced by the absence of outgassing during exposure to 2000 eV electrons. The feasibility of inducing cross-linking reactions within the Zn-3MP multilayer via EUV exposure was confirmed through *ab-initio* simulations (Fig. S9a-f). The optimized Zn-3MP multilayer, with an interchain distance of 5 Å, revealed vertically aligned chains with an 11.7° tilt (Fig. S9b). Weak sulfur-zinc interactions (2.39 Å) indicate a natural tendency for alignment between adjacent chains (Fig. S9c). Upon EUV exposure, the Zn-3MP chains showed increased packing density, leading to the formation of Zn-centered tetragonal O-Zn-S cross-links (Fig. S9d-f). These cross-links, associated with a free energy reduction of 2.19 eV, are facilitated by the activation of oxygen and sulfur atoms through EUV-induced electrons. This process enhances interchain interactions and structural integrity, resulting in a 9.3 % reduction in unit-cell thickness, consistent with experimental observations (Table S3).

Lithographic performance

Zn-3MP multilayer resists, 19.5 nm thick, were deposited on silicon wafers using 26 MLD cycles. Electron-beam lithography was performed at the Paul Scherrer Institute (PSI) to evaluate the patterning performance at various doses and pitches. The resists were developed in a 0.35 wt% solution of tetramethylammonium hydroxide (TMAH) for 10 s. Field-emission scanning electron microscopy (FE-SEM) analysis revealed high-quality line/space (L/S) patterns with pitches of 36 nm and 28 nm (Fig. 3a, 3b) at an acceleration voltage of 100 keV. Analysis on the 36 nm pitch pattern ($2,052 \text{ } \mu\text{C/cm}^2$ dose) showed an unbiased LER of 2.17 nm and a critical dimension (CD) of 13.4 nm. Similarly, the 28 nm pitch pattern ($2,175 \text{ } \mu\text{C/cm}^2$ dose) exhibited an unbiased LER of 2.39 nm and a CD of 10.8 nm. These high resolutions and low LER values demonstrate the potential of Zn-3MP for EUV lithography. To assess the pattern fidelity further, a dose and focus matrix was generated using Microfield Exposure Tool 5 (MET-5) at Lawrence Berkeley National Laboratory (Fig. 3c). The matrix covered doses from 40 mJ/cm^2 to 80 mJ/cm^2 in 10 mJ/cm^2 increments, with focus steps of 15 nm. The FE-SEM images confirmed successful pattern transfer across all doses and focuses. Magnified FE-SEM images (Fig. 3d, 3e) showcased a wide range of half-pitch sizes, from 8 nm to 45 nm. The performance of a photoresist is critically evaluated by its sensitivity (D_{50}), defined as the exposure dose required to retain 50 % of the initial film thickness. A lower D_{50} indicates higher sensitivity, reducing exposure times and increasing throughput. As seen in Fig. 3f, the Zn-3MP multilayer functions as a negative-tone resist, with its sensitivity varying based on the developer concentration. For a fixed development time of 10 s, the D_{50} values for TMAH concentrations of 0.30, 0.33, and 0.35 wt% were determined to be 23.6, 32.6, and 41.3 mJ/cm^2 , respectively. The EUV contrast curve, according to comparative analysis from 4A to 1 (PAL), EUV-IL (PSI), and MET-5 (LBNL), shows high consistency and reliability (Fig. S10). The excellent EUV sensitivity of this multilayer resist is attributed to its unique cross-linking mechanism and vertically aligned molecular wire structure. The molecular wires, with sub-nanometer widths and considerable heights, undergo lateral cross-linking during exposure, which significantly reduces their solubility in the developing solution. Lithographic contrast (γ), which quantifies the sharpness of the interface between exposed and unexposed areas, is calculated as the slope of the resist contrast curve, which plots the resist thickness against the logarithm of the exposure dose. From the sensitivity curves, the resist

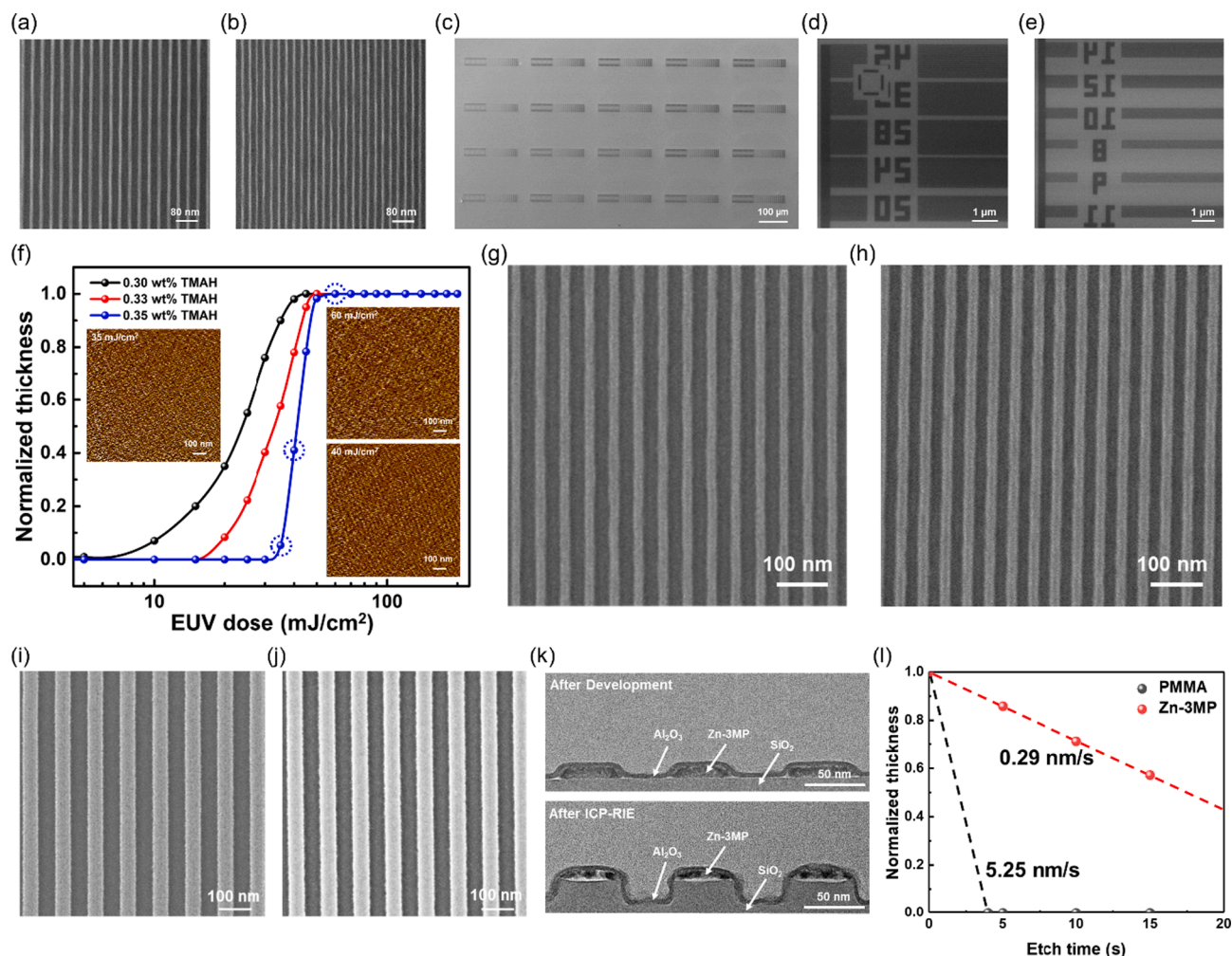


Fig. 3. Lithographic performances and plasma etch resistance. a, b, line/space (L/S) patterns created by electron beam lithography (EBL) with pitches of 36 nm and 28 nm at doses of 2,052 $\mu\text{C}/\text{cm}^2$ and 2,175 $\mu\text{C}/\text{cm}^2$, respectively. c, FE-SEM images of dose and focus matrix generated using Microfield Exposure Tool 5 (MET-5). The center dose is 60 mJ/cm^2 , with a dose step of 10 mJ/cm^2 and a focus step of 15 nm. d, e, Magnified FE-SEM images of L/S patterns generated using MET-5 with half-pitch sizes ranging from 8 nm to 45 nm at a dose of 60 mJ/cm^2 . f, EUV contrast curves for Zn-3MP multilayer resist developed with 0.30, 0.33, and 0.35 wt% TMAH solutions. g, FE-SEM image of a 36 nm pitch L/S pattern created by EUV lithography at a dose of 45 mJ/cm^2 . h, FE-SEM image of a 32 nm pitch L/S pattern achieved at a dose of 60 mJ/cm^2 . i, j, FE-SEM images of L/S patterns i, before and j, after ICP-RIE. k, Cross-sectional TEM images of the resist before and after ICP-RIE of L/S patterns. l, Etch resistance of the resist L/S pattern, demonstrating the resist's durability.

contrast (γ) is defined as $\gamma = 1/\log_{10}(D_2/D_1)$, where D_1 is the dose at which the resist film starts to remain and D_2 is the dose at which 100 % of a negative-tone resist remains after exposure and development. High γ values correspond to shaper features with minimal edge blurring. The Zn-3MP multilayer achieved γ values of 1.66, 2.51, and 6.46 at different TMAH concentrations (Fig. 3f), which surpass those of other EUV resists, such as polymethyl methacrylate (PMMA) polymer, hydrogen silsesquioxane and Zn-based clusters [30,31,53,54]. Atomic force microscopy (AFM) analysis of the developed resist surface at a TMAH concentration of 0.35 wt% revealed exceptionally low RMS roughness values of 0.66 nm, 0.38 nm, and 0.40 nm at exposure doses of 35, 40, and 60 mJ/cm^2 , respectively. This indicates that the multilayer resist was uniformly developed from the top down. The high-resolution patterning capabilities of the Zn-3MP resist were investigated using an EUV interference lithography (EUV-IL) system at PSI considering development under a 0.35 wt% TMAH concentration. FE-SEM images (Fig. 3g, 3h) reveal L/S patterns with 36 nm and 32 nm pitch, achieved with doses of 45 and 60 mJ/cm^2 , respectively. At the 45 mJ/cm^2 dose, the unbiased LER was measured to be 1.42 nm, with a CD of 13.78 nm. Notably, at the moderate dose of 60 mJ/cm^2 , the LER was measured to be a world-record low of 1.37 nm. Furthermore, no residue or scum was observed in the

unexposed regions of the resist. The EUV patterning data strongly suggests that the vertically oriented molecular wire structure of the multilayer is crucial in achieving these ultralow LER values. This structure facilitates efficient lateral cross-linking during exposure, which reduces solubility and enhances pattern fidelity.

Etch resistance

In the pursuit of electronic miniaturization, ever-thinner resists are required for creating smaller features. This necessitates superior etch resistance to ensure successful pattern transfer. To evaluate the etch resistance of the Zn-3MP resist, it was patterned via electron-beam lithography (dose: 2,000 $\mu\text{C}/\text{cm}^2$, half-pitch: 50 nm) (Fig. 3i). Subsequently, inductively coupled plasma-reactive ion etching (ICP-RIE) with SF_6/O_2 gas successfully transferred the pattern without defects (Fig. 3j) and improved the LER further from 3.81 nm to 3.30 nm. The cross-sectional TEM image (Fig. 3k) confirms a high etching selectivity between Zn-3MP and SiO_2 (1:15.0). To quantify the etch resistance, the etch rate of the Zn-3MP was compared with that of a commercial PMMA resist (Fig. 3l). Under identical etching conditions, the Zn-3MP resist exhibited a significantly lower etch rate (0.29 nm/s) than the PMMA

resist (5.25 nm/s), indicating an approximately 18-fold increase in etch resistance. This excellent etch resistance is attributed to the presence of inorganic zinc species and the unique cross-linking mechanism within the Zn-3MP multilayer resist, which enable the formation of robust ultrafine patterns. These findings collectively highlight Zn-3MP as a promising EUV resist material for future electronic device fabrication, offering exceptional patterning LER and robust etch resistance.

Conclusion

In this study, we have developed an advanced EUV resist that achieves exceptionally low LER by virtue of a vertically oriented molecular wire architecture. The Zn-3MP hybrid multilayer, synthesized via MLD, features molecular wires narrower than 1 nm, aligned vertically. This unique architecture achieves an unprecedentedly low LER of 1.37 nm at a moderate EUV dose. EUV exposure induces unique cross-linking reactions between adjacent molecular wires without degassing, thereby enhancing the resist's sensitivity. The combination of high-aspect-ratio molecular wires, their vertical orientation, and unique cross-linking reactions significantly improves both the EUV sensitivity and etch resistance of the hybrid multilayer resist. Furthermore, MLD technology enables the precise construction of hybrid multilayers with monolayer accuracy, allowing each layer to be tailored for specific functions such as EUV absorption, electron-induced cross-linking, or etch resistance. This tunable approach also facilitated the creation of a taper shape within the hybrid multilayer resist, further enhancing its lithographic performance. This innovative design effectively addresses the limitations of previous generations, offering a significant potential to meet the stringent demands of advanced semiconductor manufacturing. Consequently, this procedure presents an ideal fabrication technique for the future development of vertically tailored hybrid multilayer resists.

Methods

Substrate preparation. We purchased 4-inch p-type Si (100) wafers (resistivity of $> 1 \Omega \text{ cm}$, 500 μm thickness) and 4-inch oxidized Si wafers with a 300 nm-thick thermally grown SiO_2 layer (resistivity of $< 0.005 \Omega \text{ cm}$, 500 μm thickness) from Namkang Hi-Tech. These wafers were initially treated with a chemical cleaning process that involved degreasing, NH_4OH boiling (alkali treatment), HCl boiling (acid treatment), rinsing in deionized water, and blow-drying with nitrogen to remove contaminants and grow a thin protective oxide layer on the surface.

Deposition of Zn-3MP hybrid multilayer. All chemicals used in this study were purchased from commercial sources and used as-received. For the Zn-3MP hybrid-multilayer, MLD was performed within a custom-built MLD chamber. To determine the MLD process temperature window, we measured the growth rate of the Zn-3MP hybrid multilayer across substrate temperatures ranging from 80°C to 120°C. The optimal temperature window for MLD, characterized by growth saturation, was identified between 90°C and 110°C. A consistent growth rate of $\sim 7.5 \text{ \AA}$ per cycle was achieved within this range. Below 90°C, higher growth rates were observed, likely due to the precursor condensation. Conversely, temperatures above 110°C resulted in a rapid decrease in the growth rate, potentially due to the disruption of self-assembly process. For this study, Zn-3MP multilayer resist samples were deposited at 100°C using Ar at a flow rate of 100 standard cubic centimeters per minute (sccm) as a carrier/purging gas. The Zn-3MP hybrid multilayer was deposited using DEZ (Lake Materials, 97 %) and 3MP (TCI, 97 %) as the MLD precursors. Each MLD cycle consisted of 1 s of DEZ exposure, 60 s of Ar purging, 10 s of 3MP exposure, and 60 s of Ar purging. DEZ and 3MP were evaporated at 20°C and 60°C, respectively, and were introduced into the chamber to achieve a high pressure of 1 Torr.

Characterization of hybrid multilayer deposition. The Zn-3MP thickness was confirmed via ex-situ ellipsometry (FS-1, FilmSense) and non-contact-mode AFM (XE-100, Park Systems). In Fig. 1c-e, Zn-3MP

patterns were fabricated via a liftoff process [55]. Sacrificial ink patterns were drawn on Si substrates with a commercial permanent marker pen (Namepen-T, MONAMI Co., Ltd.). Following Zn-3MP deposition via MLD, the ink patterns were selectively removed with an organic solvent, such as isopropanol or ethanol, leaving the Zn-3MP intact on the non-ink-coated regions, resulting in well-defined patterns. To assess the uniformity of Zn-3MP film thickness, thickness mapping was performed on a 4-inch Si wafer using an AIM AE-86 Automatic Ellipsometer. The measurements were taken at 13 evenly distributed points across the wafer, excluding a 10 mm edge margin. The morphology of the thin films was determined through non-contact-mode AFM (XE-100, Park Systems).

The QCM measurement was conducted in the MLD chamber using 6 MHz gold-coated quartz crystals (Inficon) before and after the deposition of Zn-3MP. To prepare a reproducible crystal surface, ZnO was deposited on the quartz crystal for at least 300 cycles using DEZ and H_2O as the precursors. The QCM sensor was equilibrated at 100°C for 30 min, and the baseline frequency (f_0) was recorded. During the deposition, DEZ was exposed for 1 s at a pressure of 1 Torr, followed by the exposure of 3MP for 10 s at the same pressure. Sequential introduction of the precursor gases into the reaction chamber enabled layer-by-layer surface reactions characteristic of the MLD process. The frequency changes of the QCM crystal were monitored and recorded in real-time using a thin film monitor (Wiz QCM-1200 Premium, WizMAC), an MLD QCM sensor (Front Load single Sensor, Inficon), and a software program (QCM Control & Acquisition V 2.3, WizMAC). The measured shifts in the frequency of the sensors were converted into changes in mass (Δm) using the Sauerbrey equation.

Structural characterization of hybrid multilayer. XPS measurements were conducted using a Thermo Fisher Scientific K-Alpha + instrument. High-resolution spectra were acquired with a monochromatic Al K α X-ray source (1486.6 eV) at a 0° emission angle relative to the surface normal. The X-ray flux was approximately 1×10^{12} photons/s $\bullet$ cm^2 , with an exposure duration of ~ 30 min per sample. The spectra were calibrated on a binding energy scale to the position of the C 1s C–C bond at 284.9 eV. The TEM observations were performed using a JEOL JEM-ARM200F microscope operating at 200 kV, installed at the National Center for Inter-university Research Facilities at Seoul National University. The cross-sectional TEM specimens were prepared with a focused ion beam (FIB) using a FEI Helios G5 UC system. Al_2O_3 , epoxy and platinum were deposited on the sample surface to protect the Zn-3MP thin film from ion beam bombardment during the FIB process.

The XAFS measurements were recorded at the 8C nano-probe XAFS beamline (BL8C) at the Pohang Light Source-II (PLS-II) in the 3.0 GeV storage ring, with a ring current of 300 mA. To eliminate higher-order harmonics, the X-ray beam was monochromated using a Si (111) double crystal, which reduced the beam intensity by 30%. The X-ray beam was then delivered to a secondary source aperture, where the beam size was adjusted to 0.3 mm (v) $\times$ 1 mm (h). A high voltage (3,000 V) was applied to ionization chambers filled with N_2/Ar gas mixtures to detect the X-ray intensity. For the XAFS measurements, the samples were exposed to X-rays with a photon flux of $\sim 2 \times 10^{14}$ photons/s $\bullet$ cm^2 for 1 h to ensure comprehensive data acquisition. The XAFS spectra were recorded in fluorescence mode and analyzed using the Athena module of the Demeter package [56]. A structural model, consistent with the proposed vertically oriented molecular wire configuration, was constructed by editing the FEFF card. During the fitting process, parameters such as the distance (d), the Debye-Waller factor (σ^2), which includes thermal vibration and structural disorder, and ΔE_0 were varied for each single scattering signal, while multiple scattering signals were ignored.

GI-WAXD measurements were performed at the Pohang Accelerator Laboratory (PAL). The X-ray beam was monochromated using a Si (111) crystal, with a wavelength of 1.12 Å ($E = 11.06 \text{ keV}$) and a sample-to-detector distance (SDD) of 222 mm. The diffraction angle was calibrated using pre-calibrated sucrose (Monoclinic, P21, $a = 10.8631 \text{ \AA}$, $b = 8.7044 \text{ \AA}$, $c = 7.7624 \text{ \AA}$, $\beta = 102.938^\circ$). 2D GI-WAXD images were

acquired with a 2D charge-coupled detector (Rayonix Ltd., MX117-HS). Zn-3MP samples were exposed for 10 s with an incidence angle of 0.12° in a vacuum chamber, with a photon flux of approximately 5×10^{15} photons/s • cm².

Ab-initio structure optimizations of hybrid multilayer. All optimizations were performed using the Vienna Ab Initio Simulation Package [57,58]. The Perdew-Burke-Ernzerhof functional within Grimme's DFT-D3 method with the zero-damping function and the projector-augmented wave method were used to describe the exchange-correlation energy, van der Waals interaction, and electron-ion interactions [59–61]. A $2 \times 2 \times 1$ Monkhorst-Pack mesh was used for the Brillouin zone sampling. An energy cutoff of 400 eV and a smearing parameter of 0.2 eV were used for the plane waves. Cell optimizations were performed to create the structural model of the cross-linked hybrid multilayer.

Outgassing measurement of hybrid multilayer. The outgassing measurement of the hybrid multilayer resist was conducted by cleaving a resist-coated wafer and placing it in a vacuum chamber for electron exposures using a Kimball Physics EFG-7 electron gun at 2,000 eV. The electron current was set to 155 nA, as measured by a Faraday plate detector, with the spot size of approximately a 1 cm-diameter circle on the resist. Exposures ranged from less than 1 s to 500 s, with the highest dose reaching approximately 80 $\mu\text{C}/\text{cm}^2$. The background chamber pressure was maintained at less than 10^{-7} Torr and outgassing during exposure was monitored using an Extrel MAX300 quadrupole mass spectrometer. Across the measured masses up to 200 AMU, no outgassing signal from the resist was detected above the chamber's background levels.

Lithographic performance of hybrid multilayer. EUV sensitivity and contrast tests were performed at the 4A-1 beamline at PLS-II, operated with an electron energy of 3 GeV, a current of 250 mA, and a repetition rate of 500 MHz, using an elliptically polarizing undulator to generate photon energies of 30–1000 eV. Precise irradiation was achieved using pinholes with diameters of 200 μm to define the exposed areas, and 100–300 nm thick silicon nitride (Si_3N_4) membranes were employed to control the photon flux precisely within 5–50 %, enabling doses of 5–200 mJ/cm^2 , which could not be achieved with a shutter alone. The transmitted beam signal was digitized using an EUV photodiode (Optodiode, AXUV 100G) and an electrometer (Keithley, model 6514), and the post-exposure pattern thickness was measured using a KLA Tencor AS500.

EUV lithography was conducted using the MET-5 at the Lawrence Berkeley National Laboratory, which utilizes a 13.5 nm synchrotron light source and a numerical aperture (NA) of 0.5, and an EUV-IL system at PSI for nanopatterning periodic L/S features. The L/S patterns were imaged using field-emission scanning electron microscopes (ZEISS Gemini SEM 560 and Hitachi Regulus 8220). The LER and CD were evaluated using image analysis software, Line and Contact Edge Roughness Meter (Lacerm), SEM-Measured Image Lines Estimator (SMILE), and Fractilia MetroLER (Fig. S11).

Electron beam lithography on the silicon wafer substrates was performed at PSI using a Vistec EBPG 5000PlusES and at the Korea Advanced Nano Fab Center (KANC) using a Jeol JBX9300FS, both operating at an acceleration voltage of 100 kV and a current of 200 pA. The pattern files, prepared as GDS files, included half-pitch features ranging from 100 nm to 18 nm.

Etch resistance of hybrid multilayer. An ICP-RIE system was used to evaluate the etch resistance of the Zn-3MP EUV resist. The L/S pattern created via e-beam lithography was transferred onto the SiO_2 substrate at 20°C under a chamber pressure of 7 mTorr, using sulfur hexafluoride (SF_6) and oxygen (O_2) gases in a ratio of 45 sccm to 5 sccm, and at an ICP power of 2000 W. Subsequently, the depth and shape of the patterns formed on the SiO_2 wafer were measured through TEM and AFM. Additionally, a PMMA thin film was spin-coated on the SiO_2 wafer to compare the etch rates. PMMA 950 K A6 in anisole, purchased from EM Resist Ltd., was diluted in chlorobenzene at a 1:5 vol ratio. The solution

was spin-coated at 4000 rpm for 75 s (with a ramp time of 1 s). To evaporate the solvent, the coated samples were baked in an oven at 170°C for 15 min. After exposure to an electron beam, a positive tone pattern was developed using a solution of methyl isobutyl ketone and isopropyl alcohol at a 1:3 ratio. The samples were dipped in this developer solution for 30 s, before being rinsed in IPA for 30 s to form the electron beam pattern on the PMMA.

Author contributions

J.L. and H.J. contributed equally to this work. J.L. and H.J. conceived the idea and carried out sample fabrication and characterization. J.Y.L. assisted with QCM measurements. I.H. and K.-S.L. performed EXAFS analysis, with I.H. contributing to the writing of the corresponding section of the manuscript. H.A. conducted GI-WAXD analysis. J.Y.P. conducted the mechanism simulations and wrote the corresponding section of the manuscript. G.D. performed out-gassing measurements and data analysis. J.K. and S.L. performed the EUV sensitivity test and data analysis. D.K., P.K., and Y.E. executed EUV lithography and contributed to data analysis. C.K., J.-H.S., J.A., C.G.K., W.-J.S., S. L., T.N. and B.L.F. provided valuable discussions. J.L., H.J. and M.M.S. wrote the manuscript with input from all authors. This work was directed and supervised by M.M.S. All authors discussed the results, read the manuscript, and approved its content.

CRediT authorship contribution statement

Jaehyuk Lee: Writing – original draft, Investigation, Formal analysis, Data curation. **Hyeonseok Ji:** Writing – original draft, Investigation, Formal analysis, Data curation. **Chawon Koh:** Writing – review & editing, Formal analysis. **Juyeong Lee:** Formal analysis, Data curation. **Ji-Hoo Seok:** Formal analysis. **Jinho Ahn:** Writing – review & editing, Formal analysis. **Chang Gyoung Kim:** Writing – review & editing, Formal analysis. **Jiho Kim:** Formal analysis. **Inhui Hwang:** Writing – review & editing, Writing – original draft, Formal analysis. **Hyungju Ahn:** Writing – review & editing, Writing – original draft, Formal analysis. **Kug-Seung Lee:** Writing – review & editing, Formal analysis. **Sangsul Lee:** Writing – review & editing, Formal analysis. **Dimitrios Kazazis:** Formal analysis. **Prajith Karadan:** Formal analysis. **Yasin Ekinici:** Writing – review & editing, Formal analysis. **Gregory Denbeaux:** Writing – review & editing, Formal analysis. **Ji Young Park:** Writing – review & editing, Writing – original draft, Formal analysis. **Won-Joon Son:** Formal analysis. **Seungmin Lee:** Formal analysis. **Tsunehiro Nishi:** Formal analysis. **Bruno La Fontaine:** Writing – review & editing, Formal analysis. **Myung Mo Sung:** Writing – review & editing, Writing – original draft, Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (No. RS-2022-NR068260 and No. RS-2023-00260527). This work was supported by the National NanoFab Center (NNFC) grant funded by the Korea government (MSIT) (RS-2024-00440910). This project has received funding from the European Horizon 2020 research and innovation programme under grant agreement No 101007417 having benefitted from the access provided by the Paul Scherrer Institute in Villigen, Switzerland within the framework of the NFFA-Europe Pilot Transnational Access Activity, proposal ID416.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mattod.2025.04.007>.

Data availability

Data will be made available on request.

References

- [1] J. Miyazaki, et al., *J. Photopolym. Sci. Technol.* 32 (2) (2019) 195.
- [2] R.F. Pease, et al., *Proc. IEEE* 96 (2) (2008) 248.
- [3] N. Mojarad, et al., *Nanoscale* 7 (9) (2015) 4031.
- [4] J.J. Biafore, et al., *Proc. SPIE* 7273 (2009) 727343.
- [5] P. Kruit, et al., *J. Vac. Sci. Technol. B* 23 (6) (2005) 3033.
- [6] N. Mojarad, et al., *Sci. Rep.* 5 (1) (2015) 9235.
- [7] L. Li, et al., *Chem Soc. Rev.* 46 (16) (2017) 4855.
- [8] E.S. Putna, et al., *Proc. SPIE* 7636 (2010) 76360P.
- [9] The International Roadmap for Devices and Systems (IRDS), *Lithography*, IEEE (2022).
- [10] T. Kozawa, S. Tagawa, *Jpn. J. Appl. Phys.* 49 (3R) (2010) 030001.
- [11] J. Thackeray, et al., *Proc. SPIE* 8682 (2013) 868213.
- [12] R. Brainard, et al., *J. Photopolym. Sci. Technol.* 22 (1) (2009) 43.
- [13] S. Masuda, et al., *Proc. SPIE* 6153 (2006) 615342.
- [14] S. Tarutani, et al., *J. Photopolym. Sci. Technol.* 24 (2) (2011) 185.
- [15] R.A. Lawson, et al., *Proc. SPIE* 6923 (2008) 69230K.
- [16] C.-T. Lee, et al., *Proc. SPIE* 6519 (2007) 65191E.
- [17] S. Zhang, et al., *ACS Omega* 8 (30) (2023) 26739.
- [18] T. Kimura, et al., *J. Photopolym. Sci. Technol.* 23 (5) (2010) 643.
- [19] Y. Vesters, et al., *Proc. SPIE* 10143 (2017) 1014324.
- [20] C. Popescu, et al., *Proc. SPIE* 11612 (2021) 116120K.
- [21] A. Rathore, et al., *J. Mater. Chem. C* 8 (17) (2020) 5958.
- [22] R. Gronheid, et al., *Microelectron Eng.* 83 (2006 1103.) 4–9.
- [23] X. Wang, et al., *Mater. Today* 67 (2023) 299.
- [24] S. Chakrabarty, et al., *Proc. SPIE* 9048 (2014) 90481C.
- [25] R.P. Oleksak, et al., *ACS Appl. Nano Mater.* 1 (9) (2018) 4548.
- [26] J. Stowers, D. A. Keszler, *Microelectron Eng.* 86 (4-6) (2009) 730.
- [27] K. Kasahara, et al., *Proc. SPIE* 10143 (2017) 1014308.
- [28] L. Wu, et al., *Eur. J. Inorg. Chem.* 2019 (38) (2019) 4136.
- [29] B. Cardineau, et al., *Microelectron Eng.* 127 (2014) 44.
- [30] H. Xu, et al., *Chem. Mater.* 30 (12) (2018) 4124.
- [31] M.S.M. Saifullah, et al., *ACS Nano* 18 (35) (2024) 24076.
- [32] M. Trikeriotis, et al., *Proc. SPIE* 7639 (2010) 76390E.
- [33] M. Trikeriotis, et al., *Proc. SPIE* 8322 (2012) 83220U.
- [34] J. Stowers, et al., *Proc. SPIE* 9779 (2016) 977904.
- [35] A. Grenville, et al., *Proc. SPIE* 9425 (2015) 94250S.
- [36] R.S. Wise, *Proc. SPIE* 11612 (2021) 1161203.
- [37] H.S. Suh, et al., *Proc. SPIE* 12498 (2023) 1249803.
- [38] J. Passarelli, et al., *J. Micro/nanolith. MEMS MOEMS* 14 (4) (2015) 043503.
- [39] S. Hasan, et al., *Proc. SPIE* 10960 (2019) 109601Q.
- [40] M. Sortland, et al., *J. Micro/nanolith. MEMS MOEMS* 14 (4) (2015) 043511.
- [41] J. Passarelli, et al., *Proc. SPIE* 9051 (2014) 90512A.
- [42] M. Wilklow-Marnell, et al., *J. Micro/nanolith. MEMS MOEMS* 17 (4) (2018) 043507.
- [43] G. Lim et al., *ACS Mater. Au* (2024).
- [44] F. Schreiber, *Prog. in Surf. Sci.* 65 (5-8) (2000) 151.
- [45] R.A. Wind, S.M. George, *J. Phys. Chem. A* 114 (3) (2010) 1281.
- [46] C. Yang, et al., *Sep. Purif. Technol.* 307 (2023) 122860.
- [47] N.E. Richey, et al., *Dalton Trans.* 50 (13) (2021) 4577.
- [48] D.L.T. Nguyen, et al., *ACS Sustain. Chem. Eng.* 5 (12) (2017) 11377.
- [49] U. Bexell, et al., *Surf. Interface Anal.* 36 (7) (2004) 624.
- [50] A. Waldner, et al., *Phys. Chem. Chem. Phys.* 20 (37) (2018) 24408.
- [51] D.S. Bergsman, et al., *Adv. Funct. Mater.* 29 (43) (2019) 1904129.
- [52] P. Atanasova, et al., *RSC Adv.* 11 (10) (2021) 5466.
- [53] R. Fallica, et al., *J. Vac. Sci. Technol. B* 34 (6) (2016) 06K702.
- [54] N. Thakur, et al., *ACS Mater. Au* 2 (3) (2022) 343.
- [55] Q. Jiang, et al., *Adv. Funct. Mater.* 25 (31) (2015) 4976.
- [56] B. Ravel, M. Newville, *J. Synchrotron Rad.* 12 (4) (2005) 537.
- [57] G. Kresse, J. Furthmüller, *Phys. Rev. B* 54 (16) (1996) 11169.
- [58] G. Kresse, J. Furthmüller, *Comput. Mater. Sci.* 6 (1) (1996) 15.
- [59] S. Grimme, et al., *J. Chem. Phys.* 132 (15) (2010) 154104.
- [60] G. Kresse, D. Joubert, *Phys. Rev. B* 59 (3) (1999) 1758.
- [61] J.P. Perdew, et al., *Phys. Rev. B* 54 (23) (1996) 16533.