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Effect of networking density on the patterning performance of molecular layer deposited alucone electron beam/EUV resists

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Abstract

One of the main barriers to continued device scaling in the era of extreme ultraviolet (EUV) lithography is the need for improved photoresist chemistries to address challenges such as poor EUV sensitivity, inadequate etch resistance, and pattern collapse. Metal-organic photoresists are a promising class of materials that can address many of these challenges, and among them, resists deposited via hybrid molecular layer deposition (MLD) have attracted interest for their unique advantages in thickness control, chemical homogeneity, and compatibility with vacuum processing. However, despite many successful demonstrations of patterning, little is known about how the molecular design of hybrid MLD resists affect their lithographic performance. In this work, we study the effect of the network structure, a common feature of all hybrid MLD resists, via a series of aluminum alkoxide ('alucone') resists with varying networking density. Their patterning mechanism is investigated via electron beam lithography (EBL), a common proxy for EUV, and compared to their EUV-induced reactions studied via flood exposure and *in situ* characterization. We show that the resist with least networking density demonstrates the best sensitivity and resolution, with the ability to resolve dense line/space gratings as small as 14 nm half pitch via EBL.

Keywords

Molecular layer deposition, metal-organic thin films, extreme ultraviolet lithography, photoresist, electron beam lithography

Introduction

One of the main driving forces behind Moore's Law and the continuous shrinking of feature sizes in microelectronics is the constant improvement to the resolution limit of photolithography. Extreme ultraviolet (EUV) lithography is currently employed in leading-edge nodes to pattern the smallest features due to its short wavelength (13.5 nm) relative to the preceding photolithography technology using 193 nm ArF excimer lasers (in the deep ultraviolet, or DUV, range) as the light source. Although EUV lithography, specifically high-NA (numerical aperture) EUV, has the potential to extend the resolution limit of photolithography down to 8 nm,¹ its ultimate patterning resolution is currently limited by the photoresist.² Several new challenges toward photoresist design are introduced in the transition to EUV. First, traditional photoresist materials composed of organic polymers have a smaller absorption cross-section at the EUV wavelength than at wavelengths previously used for photolithography, leading to poor sensitivity and low throughput.³ Furthermore, the low probability of photon-electron interaction also magnifies the importance of stochastic effects, such as photon shot noise⁴ and chemical stochasticity⁵ (i.e. non-uniform distribution of chemical moieties in a multi-component resist), leading to greater line edge roughness (LER) and a higher probability of point defects such as line breaks and bridges.⁶⁻⁹ In addition, the high photon energy/small wavelength (91.8 eV, 13.5 nm) of EUV promotes ionizing interactions over resonant photochemistry with the resist material, complicating the potential reaction pathways for patterning to occur.⁹⁻¹²

Metal-organic resists are a promising new class of resist chemistry that may address these challenges. The inclusion of metal atoms in the resist structure is primarily motivated by the greater absorption cross-section at 13.5 nm of many metals (Al, Zn, In, Sn, Hf etc.) compared to the organic species (C, H and O) composing polymeric photoresists.¹³⁻¹⁵ Furthermore, the inclusion of metals can result in greater etch resistance, enabling thinner resists that can meet the stricter depth-of-focus requirements of future high-NA and hyper-NA EUV.¹⁶ A number of metal-incorporating photoresist systems have been explored in the literature, such as metal oxide-infiltrated polymeric resists¹⁷, metal oxide nanoclusters¹⁸⁻²⁰ and tin oxo-clusters.²¹⁻²³ Efforts from industry include a tin-oxide based resist from Inpria Corporation,^{24,25} and an all-dry metal-incorporating resist system from Lam Research.^{26,27}

Metal-organic resists deposited via hybrid molecular layer deposition (MLD) are a recent addition to the family of EUV resist chemistries being investigated. As a combination of atomic layer deposition (ALD) and molecular layer deposition (MLD), hybrid MLD utilizes alternating exposures of a metalorganic and an organic vapor-phase precursor with tailored chemistries such that they react with the substrate surface in a self-limiting manner, thereby achieving deposition of single molecular layers. Similar to ALD, hybrid MLD films exhibit molecular scale thickness control and uniformity, enabling ultrathin photoresists that may not be achievable with other deposition techniques. In addition, as a dry deposition process, hybrid MLD can theoretically attain greater chemical homogeneity than traditional spin-coating deposition by removing the need for auxiliary components such as adhesion layers, solvents, or surfactants,^{6,27,28} and avoiding solution-induced chemical segregation.⁵

There are now many examples of hybrid MLD resists in the literature that demonstrate nanopatterning via exposure sources that serve as a proxy for EUV, including electron beam lithography (EBL) and DUV lithography. Shi et al. investigated a 'hafnicon' film deposited by tetrakis(dimethylammonium)hafnium and ethylene glycol (EG) and demonstrated patterning via EBL (at 50 kV) by resolving 50 nm isolated lines.²⁹ Several aluminum-based ('alucone') resists have also been deposited via trimethylaluminum (TMA) and different alcohols, including EG,^{30,31} hydroquinone,³²⁻³⁵ and 2-butene-1,4-diol.³⁶ More recently, Zn-

based hybrid MLD films were also shown to demonstrate excellent resolution and capability for dry development.^{28,37–39}

These numerous studies demonstrated that hybrid MLD resists are both feasible and highly tunable. At the same time, the variety of metals and organic ligands used resulted in divergent patterning performance and radiation chemistry. However, correlations between each chemical motif and patterning performance have yet to be identified, due to the differences across the various studies in processing conditions such as resist thickness, exposure source (DUV vs. EBL) and energy, choice of developer, and post-application/post-exposure baking. These processing steps can strongly affect the resist behavior, and therefore inconsistencies across studies complicate any comparisons of resists from these works. To gain a more systematic understanding of how the MLD film chemistry can be tailored to meet EUV resist requirements, MLD films with different chemical motifs should be compared under identical conditions to isolate their structure-property relationships. Findings from such experiments have the potential to lead to rational design rules for MLD photoresist chemistries, accelerating the development of high-performance resists.

In this work, we investigate one such molecular motif, particularly the effect of networking density of the material. We define the networking density (i.e. crosslinking density or connectivity) of hybrid MLD films as the number of connections that each metal atom makes with neighboring metal atoms via a shared organic ligand, which varies with the coordination number of the organic ligand and the metal oxidation state. This structural parameter has been found to impact both the chemical and mechanical stability of metal-organic hybrid materials,^{40,41} and therefore could also affect their patterning outcomes in lithography. Since networking density is a function of the metal atom (e.g. 3 ligands coordinated to Al(III) in alucone vs. 4 ligands coordinated to Hf(IV) in hafnicone), studying its effect in isolation is necessary to deconvolve the impacts of chemistry and structure when comparing different resist chemistries. To this end, we elected to focus on aluminum as the metal atom while varying the counter-reactant. We deposit three alucone films using TMA and three different alcohols: glycerol, EG, and methanol/EG, resulting in Al-GL, Al-EG, and Al-MeOH-EG, respectively. The alcohols were selected for their different coordination numbers – glycerol is tri-coordinated, EG bi-coordinated, and methanol is singly coordinated – resulting in bonding networks that vary structurally but exhibit the same aluminum alkoxide bonding chemistry. Using EBL (at 100 kV) as a proxy for EUV lithography, we probe the exposure mechanism and pattern quality of the three alucone film, demonstrating that the difference in networking density significantly changes their sensitivity, contrast, and achievable resolution. Ultimately, we show that the least networked alucone film, Al-MeOH-EG, exhibits the best patterning performance, with the ability to resolve dense gratings as small as 14 nm half pitch. Furthermore, we also show that Al-MeOH-EG demonstrates similar chemical transformations and negative tone behavior under EUV flood exposure – albeit with notably poor sensitivity, requiring 20–50 times larger EUV dose compared to commercial EUV resists – suggesting that its performance as an e-beam resist could be translated to EUV lithography.

Experimental methods

Materials: The precursors trimethylaluminum (TMA, 98%, Strem Chemicals), glycerol (99.5%, Sigma-Aldrich), ethylene glycol (anhydrous, Sigma-Aldrich), and methanol (99.9%, Fischer Chemical) were used as received without further purification. Prior to the deposition, n-doped Si(100) substrates (WRS Materials) were cleaned in acetone and isopropyl alcohol, dried with N₂, and exposed to UV-ozone in air for 15 minutes (Novascan PSV-UV4) to remove organic contaminants. The thickness of the native SiO₂ on the Si substrate was measured to be 1.7 nm using ellipsometry.

Hybrid molecular layer deposition: Hybrid MLD of alucone films was performed in two custom-built, hot-wall tubular reactors similar to those described previously.⁴² Both reactors use N₂ as a carrier gas at a working pressure of 300 mTorr.

The first reactor, used to deposit Al-MeOH-EG and Al-EG, was pumped by a Leybold D8A dual stage rotary vane pump with a base pressure of ~5 mTorr measured at the pump inlet. The reactor wall and gas delivery manifold were heated to 110°C. EG was heated to 45°C to increase its vapor pressure. TMA and methanol were held at room temperature (~25°C).

The second reactor was used to deposit Al-GL separately from the other two films, to prevent cross-contamination of the glycerol and EG counter-reactants. It was pumped by an ALCATEL 2012a rotary vane pump with a base pressure of ~5 mTorr measured at the pump inlet. The reactor wall and gas delivery manifold were heated to 150°C and 140°C, respectively, to maintain a positive temperature gradient from the precursors to the reactor chamber to minimize precursor condensation. Glycerol was heated to 90°C to increase its vapor pressure, and TMA was held at room temperature (~25°C).

During each pulse (half-cycle), the following sequence occurred: (1) a 15 s pre-pulse pump step, in which all valves except that to the pump were closed to evacuate the chamber to a base pressure of ~5 mTorr; (2) the precursor pulse step, when the precursor is dosed; and (3) the purge step, when the chamber was purged with 300 mTorr N₂ to remove unreacted vapor phase precursors.

Al-MeOH-EG was deposited by dosing TMA, methanol, and EG separately and sequentially during each cycle, with pulse/purge times of 6/180/6/120/9/180 s. Al-EG was deposited via TMA/EG cycles with pulse/purge times of 6/180/9/180 s, and Al-GL via TMA/glycerol cycles with pulse/purge times of 6/180/9/120 s.

Electron beam lithography: Patterning was performed with the Raith EBPG 5200+ Electron Beam Lithography system at 100 kV accelerating voltage. All exposures were performed on resists with film thickness of 25 ± 3 nm. Line patterns (1:1 line/space with pitches varying between 20 and 60 nm) were exposed with 0.2 nA beam current (200 μ m aperture, spot size ~2.3 nm) to minimize forward scattering and obtain the best possible resolution. Larger features were exposed with large beam currents to minimize write time: 2 μ m squares for atomic force microscopy (AFM) were exposed with 150 nA beam current (400 μ m aperture, ~60 nm spot size), and 80 μ m $\times$ 600 μ m rectangles for x-ray photoelectron spectroscopy (XPS) were exposed with 250 nA beam current (400 μ m aperture, ~105 nm spot size). To develop the resists, samples were dipped in 1.2 M hydrochloric acid for 60 s, rinsed in de-ionized water for 10 s, and blown dried with a N₂ gas stream. The developer conditions were uniform to facilitate performance comparisons, and were chosen by finding the minimum concentration required to dissolve all three alucone films (**SI Table S1**). Alternatively, Al-MeOH-EG was developed with MF-319 (Kayaku Advanced Materials Inc.), a

commercial 2.38 wt% tetramethylammonium hydroxide (TMAH) developer diluted at a 1:200 volume ratio with de-ionized water using the same procedure.

EUV flood exposure: EUV flood exposures were carried out at beamline 12.0.1.2 of the Advanced Light Source (ALS). The beamline delivers tunable radiation in the EUV/soft-X-ray regime; for all experiments the wavelength was fixed at 13.5 nm, the industry-standard EUV lithography wavelength. Square Si coupons (30 mm $\times$ 30 mm) coated with Al-MeOH-EG films were mounted on a motorized stage and irradiated with a rectangular EUV spot measuring 1 mm $\times$ 5 mm, producing a uniformly exposed area of 12 mm $\times$ 5 mm. The incident dose was controlled by translating the sample beneath the beam at velocities between 0.01 mm s⁻¹ and 1.35 mm s⁻¹. The post-exposure development followed the same procedure described for electron beam lithography. Total electron yield (TEY) and outgassing measurements were conducted simultaneously using a recently developed experimental setup.⁴³ Samples were continuously irradiated with a moderate EUV photon flux ($\sim$ 1.3 mJ/cm²/s), with the exposure duration varied to control the total EUV dose. TEY was determined by measuring the drain current generated by electrons emitted from the sample and normalizing it to the incident photon flux, which was detected using a calibrated silicon photodiode. Outgassing was monitored in parallel using a residual gas analyzer (RGA). To isolate the contributions from EUV-induced processes, background signals recorded in the absence of EUV exposure were subtracted from the measured spectra. The resulting outgassing profiles enabled identification of evolved chemical species and their temporal evolution during EUV irradiation.

Characterization: The thicknesses of deposited films were determined by spectroscopic ellipsometry (Alpha SE ellipsometer, J.A. Woollam Co., Inc.) at 70° incident angle. The Cauchy model was used to model the alucone films (A = 1.516, B = 0.00253 for Al-EG and Al-MeOH-EG; A = 1.600, B = 0.00100 for Al-GL).

X-ray reflectivity (XRR) characterization was carried out using a PANalytical Materials Research Diffractometer - X'Pert 2 to determine the density of the alucone films. The instrument was in a Mirror + Parallel Plate Collimator (PPC) configuration, with a 1/32° divergence slit in the mirror optics and a 0.27° PPC receiving slit. Measurements were taken at 45 kV and 40 mA using a Cu K α X-ray source over a 2 θ range of 0 to 4°. XRR data were fitted using the GenX 3 simple reflectivity model with a surface alucone layer, SiO₂ interface layer, and Si substrate.

XPS was performed in PHI VersaProbe 3 and VersaProbe 4 instruments with an AlK α (1486.6 eV) X-ray source at 50 W (200 μ m spot size) for characterization of non-patterned and 4.5 W (20 μ m spot size) for probing exposed features. Pass energies of 224 eV and 55 eV were used for survey and core level scans, respectively, for experimental resolutions of 1.4 eV and 0.8 eV. Dual beam (low energy ion and electron) charge neutralization was used to minimize sample charging. To remove surface contamination, samples were sputtered with an argon gas cluster ion beam (2.5 kV, 5 nA) for 3 minutes. The lack of sample damage was confirmed by taking spectra before and after sputtering (**SI fig. S1**).

All XPS spectra were analyzed using CasaXPS.⁴⁴ Binding energy correction was performed by fitting the Al 2p region with a doublet to account for spin-orbit splitting, and calibrating the Al 2p_{3/2} peak to 74.1 eV (**SI note S1**). Atomic compositions were calculated from peak intensities by estimating sensitivity factors via a method described previously.⁴⁵ Core level spectra were fitted with a Shirley background and SGL peak functions (Gaussian-Lorentzian sum with 10% Lorentzian contribution).

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy was performed with a Nicolet iS50 FTIR spectrometer with a Ge ATR attachment (Harrick VariGATR) and HgCdTe detector.

FTIR spectra were taken with 64 scans at 0.482 cm^{-1} resolution and background subtracted with a spectrum of the bare Ge crystal.

AFM was performed with a Bruker Dimension Icon using an NSC-15 standard tapping mode AFM probe. 512-pixel scans were performed with a scan rate of 0.25 Hz. AFM data were processed and analyzed using Gwyddion 2.65 software. Data leveling was performed with the flatten base tool to remove bow and tilt, and row alignment was performed by selecting only areas unexposed to the electron beam.

Scanning electron microscopy (SEM) was performed with a FEI Magellan 400 XHR SEM using the in-lens secondary electron detector. Images were taken using 1 kV landing voltage, 300 V beam deceleration, and 6.3 pA beam current.

Results and discussion

Hybrid MLD of alucone is achieved by alternating pulses of the TMA precursor and an organic precursor. By varying the organic precursor, different variants of alucone can be deposited. To vary the crosslinking density of alucone films, we select a series of simple alcohol organic precursors – methanol, EG, and glycerol – all of which form aluminum alkoxide bonds when reacting with TMA, but differ in the number of reactions available per molecule (**fig. 1a**).

Because EG and glycerol are bifunctional and trifunctional ligands, respectively, they can be cycled with TMA in a traditional two-precursor MLD scheme, as reported previously,^{40,46} to form Al-EG and Al-GL. All three precursors used for these two deposition processes exhibit the typical saturation behavior for MLD processes (**SI fig. S2**). On the other hand, growth of Al-MeOH-EG requires a three-precursor scheme, since methanol alone cannot promote MLD growth: its single reactive group is consumed when reacting with chemisorbed TMA, forming terminal Al-O-CH₃ surface groups. Therefore, EG is pulsed after methanol in a three-precursor scheme (Al-MeOH-EG) to introduce new hydroxyl groups for TMA adsorption. Because methanol competes for the same reaction sites as EG, the growth of Al-MeOH-EG is likely dominated by non-ideal adsorption mechanisms such as surface physisorption and absorption of EG in the porous MLD film.⁴⁷ Chemisorption may also occur via ligand exchange, since Al-O-CH₃ surface groups may be displaced by EG to form Al-O-(CH₂)₂-OH. Thus, methanol is effectively a growth inhibitor that partially blocks the adsorption of EG, yielding an inverted saturation curve in which the growth per cycle (GPC) decreases with increasing methanol exposure (**Figure 1b**). The GPC for all three processes is constant with cycle number, which is expected for a typical MLD process (**Figure 1c**). The GPC saturates at $\sim 2.5\text{ Å/cycle}$ for Al-EG and $\sim 5.1\text{ Å/cycle}$ for Al-GL. The larger GPC of Al-GL may be due to the larger molecular size of glycerol and the availability of reaction sites after a double reaction in which two hydroxyl groups react with the surface. For EG, such double reactions would result in the loss of active surface hydroxyl groups, reducing the GPC.⁴⁸ Another explanation for the difference in GPC may be excess precursor absorption within the film which occurs due to the low volatility of glycerol. Al-MeOH-EG has a GPC of 2.1 Å/cycle , slightly lower than that of Al-EG, which we attribute to methanol terminations partially blocking growth. Using XRR, we determine that all three alucone films exhibit similar densities – $1.6\text{--}1.7\text{ g/cm}^3$ – consistent with densities reported in the literature for alucone grown with either EG or glycerol (**SI fig. S3**).^{40,46,49}

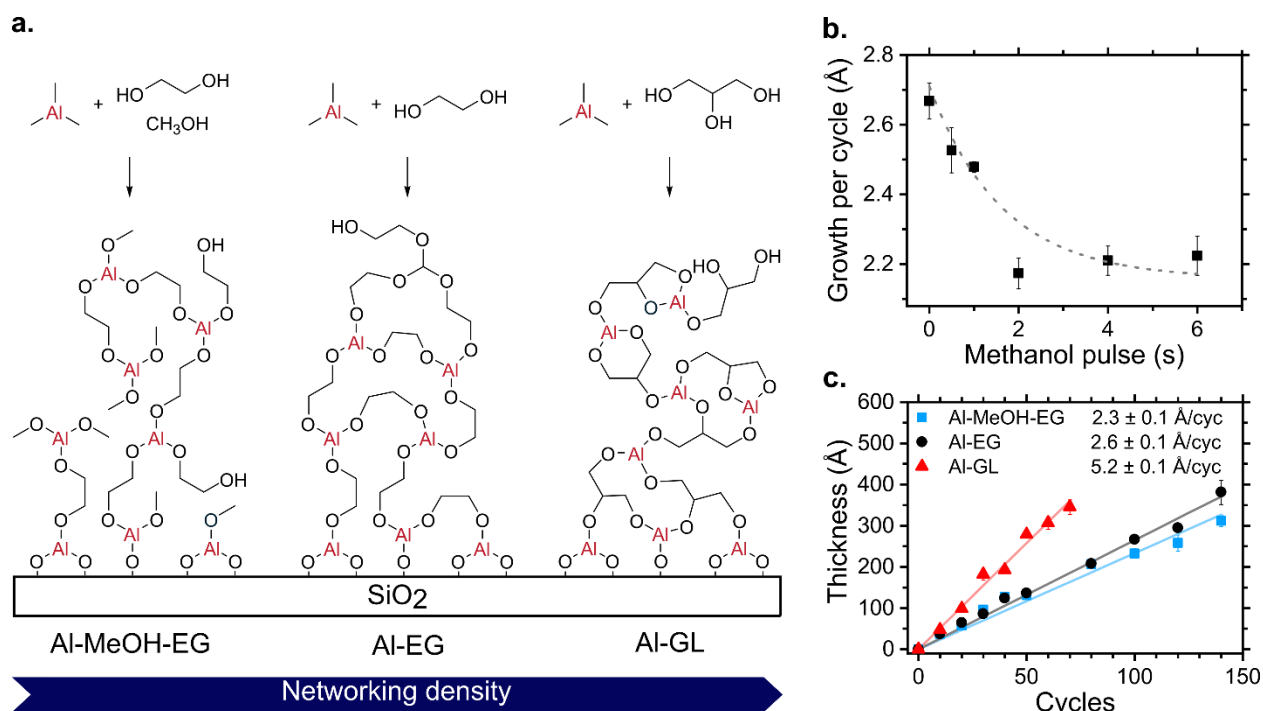


Figure 1. (a) Growth precursors and idealized molecular structures of deposited alucone films; (b) Saturation curve of methanol in Al-MeOH-EG at 100 cycles; (c) Film thickness measured via ellipsometry as a function of cycles for the three alucone films. Error bars represent the standard deviation in thickness from multiple samples in the same deposition.

X-ray photoelectron survey spectra (**fig. 2a**) reveal the chemical composition of the deposited alucone films. The films consist entirely of C, O and Al. These elements are present at C, O, and Al ratios, normalized by the Al content, of 1.0:1.6:1, 1.7:1.9:1, and 2.2:2.2:1 for Al-MeOH-EG, Al-EG, and Al-GL respectively. All three alucones can ideally be described as network polymers with Al(OCH₂)₃ repeating units, and have the same theoretical atomic composition of 3:3:1 C:O:Al. The experimentally-measured carbon and oxygen deficiency relative to aluminum may be attributed to the presence of aluminum oxide (Al-O-Al), hydroxide (Al-OH), or oxyhydroxide (Al-OOH), which are difficult to distinguish by XPS due their small binding energy differences in the Al 2p and O 1s core levels.⁵⁰ These inorganic species can be formed during deposition from an undesired reaction between TMA and the Al-O-C group to form Al-O-Al bonds, moisture contamination reacting with surface TMA groups, or by post-deposition decomposition in ambient environment.⁴⁶ Additionally, alcohol precursors can function as an oxidant for metal oxide ALD; chemisorbed alkoxides can react to form Al-OH groups, enabling TMA to react and form inorganic alumina in the subsequent half-cycle.^{46,51} The presence of inorganic aluminum species may increase the resist sensitivity, as they contribute to the formation of inorganic clusters that are responsible for solubility switch during patterning.³⁰

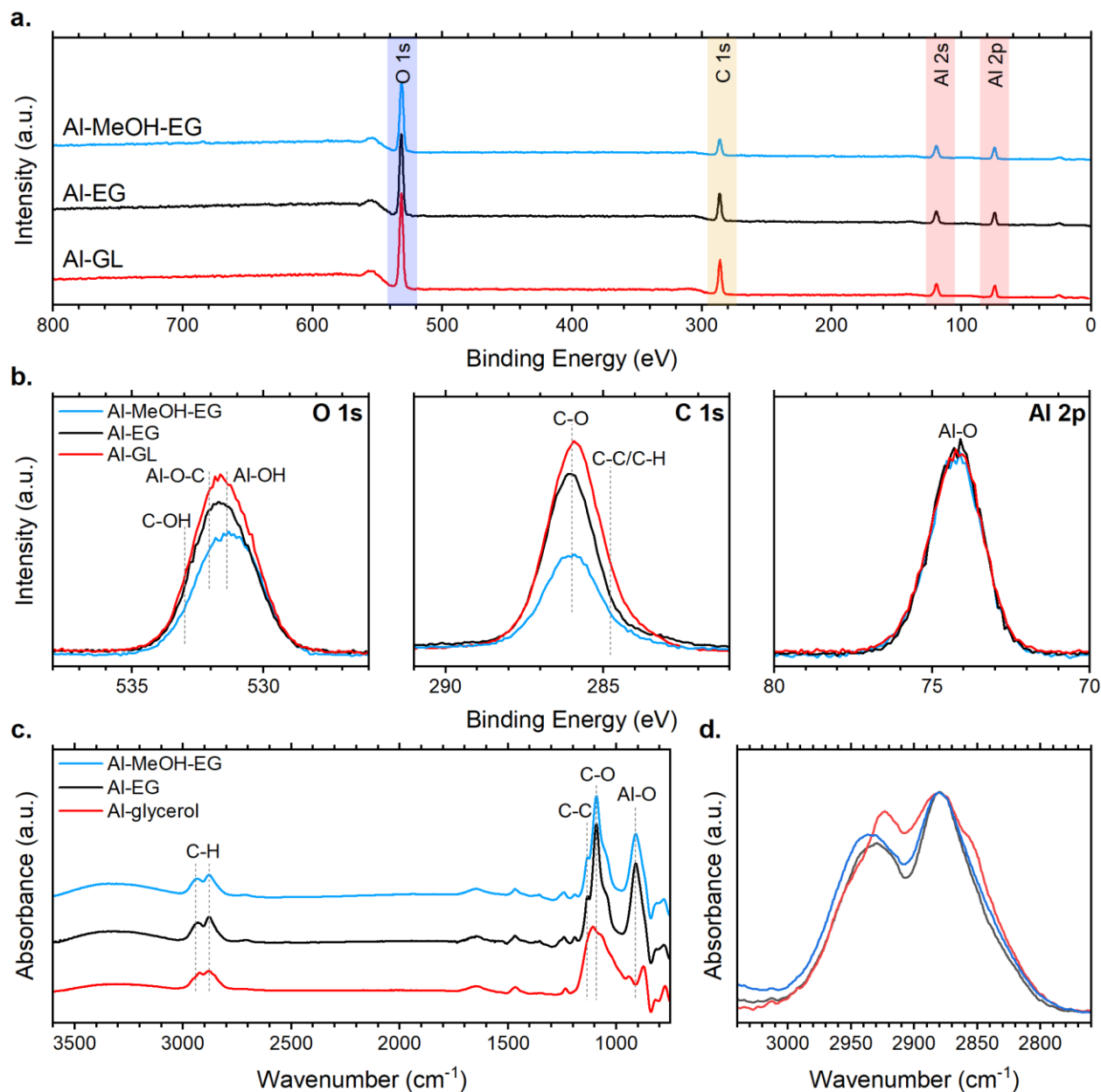


Figure 2. (a) XPS survey spectra of the alucone films. (b) High resolution XPS spectra of core levels in the alucone films with intensities normalized to the Al 2p peak area of each film. (c) ATR-FTIR spectra of alucone films with dashed lines indicating major peak assignments. (d) C-H stretching region of ATR-FTIR spectra normalized to the maximum absorbance at $\sim 2880\text{ cm}^{-1}$ (symmetric C-H stretch).

Despite the non-ideal atomic ratios, the alkoxide groups of the organic precursors are preserved (**fig. 2b**). All three alucone films exhibit the same binding energy shifts in their C 1s core level, including a primary peak attributed to C-O⁵² ($\sim 286.0\text{ eV}$), and a shoulder attributed to adventitious carbon⁵³ ($\sim 284.8\text{ eV}$). Similar O 1s peak positions ($531.4 \pm 0.1\text{ eV}$) are also observed between the different alucone films. Although this peak is primarily attributed to the metal-organic Al-O-C bond,⁴⁶ the presence of uncoordinated hydroxyl groups⁵⁴ ($\sim 533\text{ eV}$) and aluminum hydroxide⁵⁰ ($\sim 531.5\text{ eV}$) likely contributes to the slight differences in the O 1s peak position between the alucone films.

ATR-FTIR corroborates the XPS peak assignments, with major peaks assigned to C-C, C-O, and Al-O stretching (**fig. 2c**); their positions are 1131 cm^{-1} , 1092 cm^{-1} , and 910 cm^{-1} respectively for both Al-MeOH-EG and Al-EG, but are red-shifted to 1107 cm^{-1} , 1072 cm^{-1} , and 875 cm^{-1} for Al-glycerol. The three films also show small differences in the C-H stretch region ($\sim 2800\text{-}3000\text{ cm}^{-1}$, **fig. 2d**) that highlight their networking differences. Al-EG is expected to have only CH_2 groups and exhibits the corresponding symmetric (2879 cm^{-1}) and anti-symmetric (2929 cm^{-1}) CH_2 stretches. Al-MeOH-EG exhibits a blue-shifted anti-symmetric stretch (2937 cm^{-1}) attributed to CH_3 from methoxide (methanol ligand), and a shoulder towards lower wavenumber attributed to CH_2 antisymmetric stretching from EG. Al-glycerol shows at least four distinct peaks, which we assign to a pair of CH_2 (anti)symmetric stretches and a pair of CH stretches

red

Since the chemical bonding is similar between the different alucone films, we expect their chemistries during e-beam exposure to be similar, thus allowing differences resulting from networking density to be probed.

EBL is used in this study as a proxy to EUV lithography, because it mimics the generation of secondary electrons that is the primary interaction between EUV photons and photoresists.^{28,55} In this work, we utilized a 100 kV electron beam which is at a much higher energy than that of the EUV photons (91.8 eV) and their secondary photoelectrons ($< 80\text{ eV}$).^{10,56} However, due to the generation of secondary electrons with energies on the order of $\sim 100\text{ eV}$ during high-energy EBL and greater interaction cross-section for electrons with $< 100\text{ eV}$, the majority of electron-induced reactions occur via low-energy electrons.^{11,57} Although the moderate differences in the secondary electron energy distribution between EUV and EBL theoretically results in possible differences in the dominant electron-matter interaction,¹¹ a direct comparison of EUV and EBL exposures with organic resists has shown that EUV sensitivity can be correlated with EBL sensitivity, suggesting that, for certain resists, similar reaction channels can be replicated.⁵⁸ Thus, EBL is expected to provide insights into the resist chemistry and image quality that can be expected for EUV lithography; indeed, several studies of MLD resists have demonstrated similar behavior between EBL and EUV lithography.^{32,39}

To investigate the chemistry occurring during resist exposure and development, XPS is performed on exposed and developed alucone resist features (see **SI note S2 and fig. S4** for experimental details). **Figure 3a-b** show representative XPS spectra of Al-MeOH-EG after exposure and development. All three resists show similar chemical changes, and survey spectra of Al-EG and Al-GL are included in **SI fig. S5**.

The XPS survey spectra of Al-MeOH-EG after exposure (200 mC/cm^2 electron dose) and development (1 minute in 1.2 M HCl) compared to an unexposed region after development is shown in **fig. 3a**. In the unexposed region, the alucone film is completely dissolved, evidenced by the complete loss of the Al 2p peak and near-complete loss of the C 1s peak. In addition, Si 2p and Si 2s peaks originating from the underlying Si/SiO₂ substrate are now detected. On the other hand, the substrate is not detected in the exposed region. Instead, the Al 2p peak is retained, and new peaks are detected the C 1s core level, assigned to the formation of alkyl/alkenyl (285 eV) and carbonyl (290 eV) groups^{40,46} and the loss of alkoxide (286 eV) groups (**fig. 3b**, represented by the arrows). A slight shift towards lower binding energy is also observed in the O 1s region, indicative of the conversion of organic oxygen species to inorganic AlO_x species (**SI fig. S6**).⁵⁰

Figure 3c summarizes the atomic ratios for all three alucone variants after each step in patterning process (deposition, exposure, and development). Both Al-EG and Al-MeOH-EG lose a significant fraction of organic ligands after exposure, as evident from the decrease of the C/Al ratio. Meanwhile, Al-GL retains most of its carbon content after exposure, which indicates a relative lack of sensitivity. We also note that all the observed changes (change in C 1s BE shifts and reduction in C/Al ratio) occur after exposure, and no chemical changes occur after development. This result indicates that the resist is reacting upon electron exposure, and that the e-beam reaction product is stable in the developer.

All the aforementioned chemical changes observed via XPS are consistent with those from previous reports focused only on alucone with EG (Al-EG).^{30,31} Therefore, the proposed patterning mechanism from those reports for Al-EG is likely applicable to all three alucone variants: (1) cleavage of the Al-O-C bond, (2) desorption of volatile reaction products (i.e. outgassing of organic ligands), and (3) densification via formation of metal oxide nanoclusters that results in resistance to solvation, resulting in negative tone patterning. This mechanism has also been proposed for several other metalcone resists exhibiting similar exposure-induced chemical changes.^{29,37}

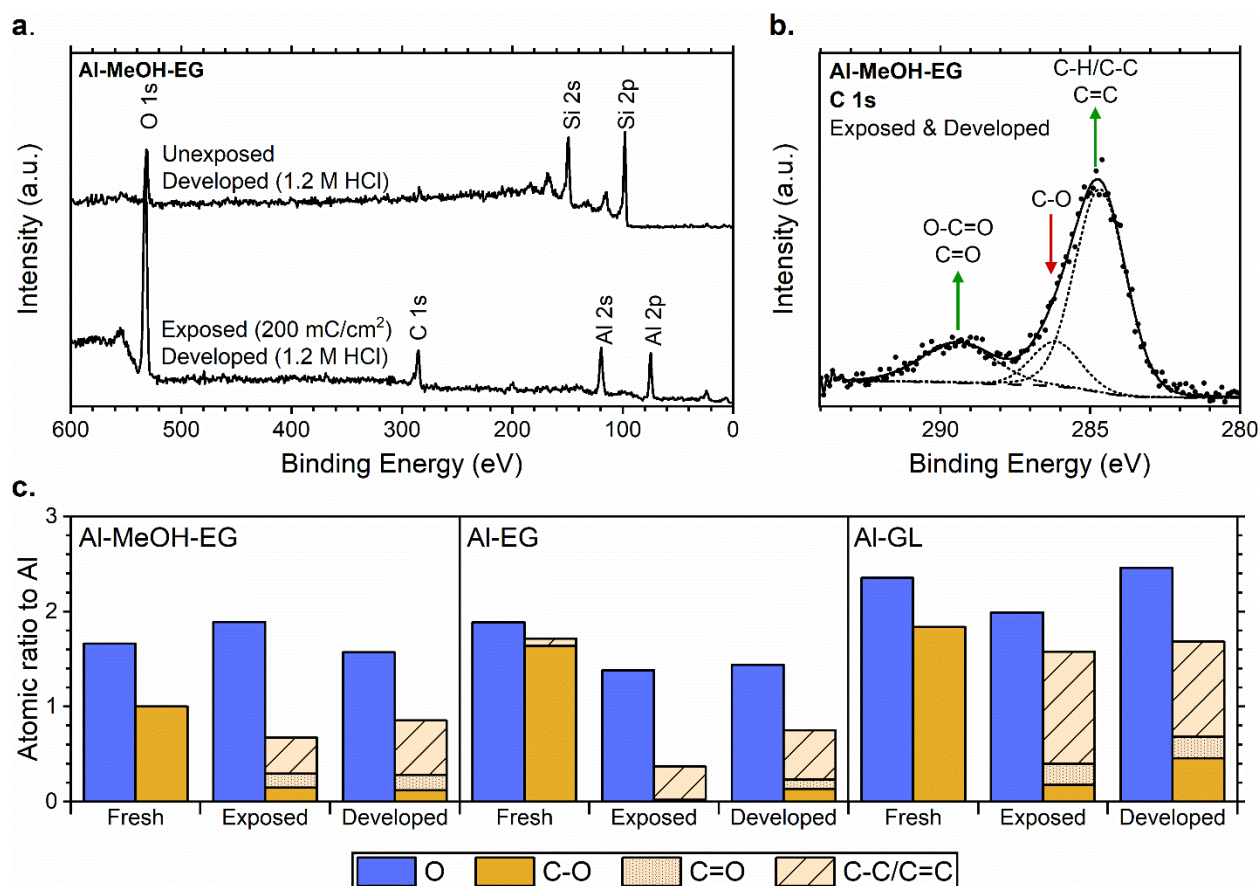


Figure 3. (a) XPS survey spectrum of developed Al-MeOH-EG without exposure and after 200 mC/cm² electron beam exposure. (b) XPS C 1s core level of Al-MeOH-EG after 200 mC/cm² electron beam exposure and development, showing chemical changes to the organic ligand; green and red arrows indicate the formation and loss, respectively, of species relative to the as-deposited film. (c) Changes in XPS atomic concentrations of oxygen and carbon species of each alucone film as a result of electron beam exposure and development.

To characterize the lithographic performance of the alucone films, we measure the film thickness as a function of electron dose using a dose matrix pattern (see **SI note S3** and **fig. S7**) to construct lithographic contrast curves (**fig. 4a**). All three alucone films demonstrate negative tone patterning behavior as evident by the increase in post-development resist thickness (normalized to the maximum post-development thickness) with dose. However, after the maximum thickness has been reached, further exposure results in a gradual decrease in resist thickness. This behavior is most likely due to film shrinkage during exposure from the continued loss of organic ligands and film densification, rather than a tone inversion (reversed solubility trend with further exposure). To confirm this hypothesis, we measure the same square pattern before development, now with the unexposed resist as the baseline (**fig. 4b**). As expected, exposure causes the film to shrink, and the thickness decrease scales with electron dose far beyond the saturating dose for solubility switch to occur. However, although Al-EG and Al-GL shrink monotonically with dose, Al-GL expands by 1 nm at lower doses before shrinking. We speculate that as the metal-organic bonds in the highly crosslinked polymer network are cleaved and rearranged, relaxation and disentanglement could occur, resulting in volume expansion. Thickness expansion at low doses does not occur for Al-EG and Al-MeOH-EG, likely because there are fewer strained bonds in less crosslinked films, resulting in less relaxation.

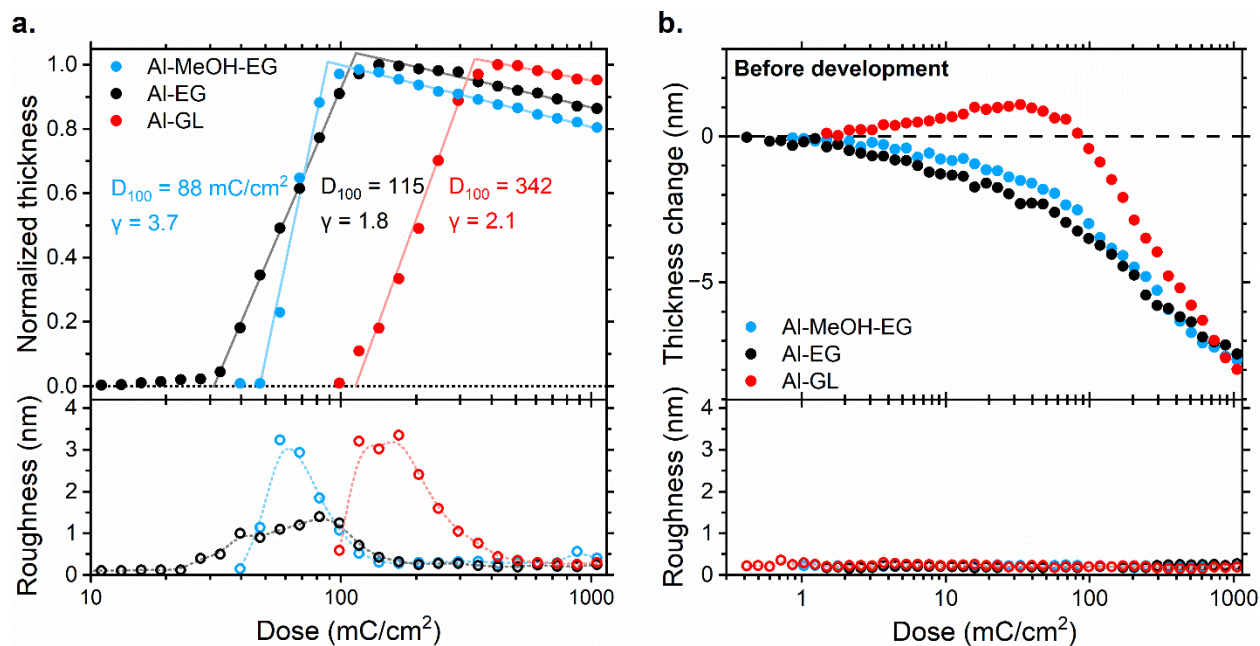


Figure 4. (a) [Top] Electron beam contrast curve of ~ 25 nm alucone resists normalized by the maximum post-development resist thickness $t_{\max}$, and [Bottom] root mean square (RMS) surface roughness at corresponding doses. (b) Thickness change and RMS surface roughness of ~ 25 nm alucone resists as a function of electron dose, before development. The D_{100} dose and contrast γ determined from the measurement for each resist are shown in (a).

Although all three films exhibit negative tone patterning and overexposure-induced shrinkage, their contrast curves are clearly different. We fit the logarithmic contrast curve to quantify these differences (see **SI note S4** and **fig. S8**), defining sensitivity as the dose D_{100} at which the maximum post-development thickness $t_{\max}$ is achieved and log contrast (γ) as the thickness change per logarithmic increase in dose when the film

is partially exposed ($0 < \text{thickness} < t_{\text{max}}$), normalized by t_{max} . For good resist performance, lower D_{100} indicates better resist sensitivity, and higher γ indicates better contrast.

The calculated D_{100} and γ of each resist are shown in **fig. 4a**. Al-MeOH-EG exhibits the best sensitivity, with Al-EG performing only slightly poorer. Al-GL demonstrates significantly worse sensitivity than both Al-MeOH-EG and Al-EG, as predicted by its relative lack of post-exposure chemical transformation observed via XPS. We attribute the sensitivity difference for Al-GL to several possible factors affecting the conversion efficiency during exposure. The increased coordination of glycerol ligands and crosslinking in the surrounding environment may decrease the yield of secondary electron-induced reactions via a cage effect, i.e. by limiting the degree of freedom for ligands undergoing bond cleavage and increasing the probability of recombination (see schematic illustration in **fig. 5a**).⁵⁹ Alternatively, since each glycerol ligand contains more hydroxyl groups than does EG or methanol, more cleavage events may need to occur at each ligand to completely liberate the ligand and allow outgassing. Since it is unlikely for multiple excitation events to occur at the same ligand instead of a few excitation events spread out over multiple ligands (see **SI note S5**), increasing the number of coordinating groups per ligand would decrease the fraction of completely liberated ligands at any given electron dose (**fig. 5b**). Finally, liberated ligands may face a diffusion barrier which is affected by networking density, such that increasing networking density decreases the rate of outgassing (**fig. 5c**). All these effects of increased networking would favor preservation of the organic-rich network, obstructing the formation of inorganic nanoclusters during exposure and thus decrease the resist sensitivity.

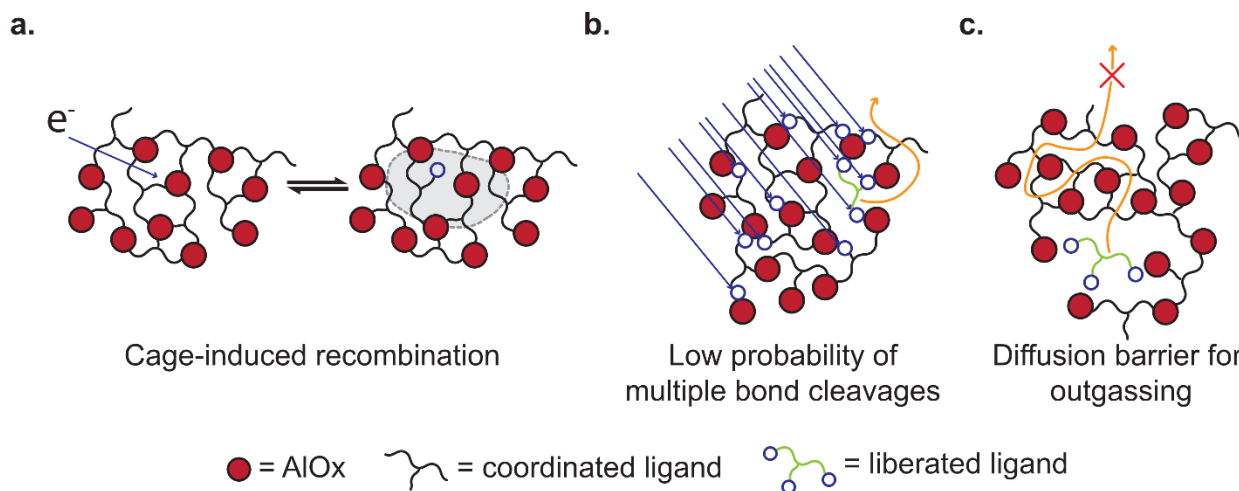


Figure 5. Possible mechanisms for increased networking density affecting resist sensitivity: (a) increase in cage-induced recombination; (b) decreased probability of ligand liberation due to low probability of multiple bond cleavages; (c) increased diffusion barrier.

Other than the difference in sensitivity, the alucone films also show a difference in contrast: Al-MeOH-EG has significantly better contrast ($\gamma = 3.7$) than both Al-EG ($\gamma = 1.8$) and Al-GL ($\gamma = 2.1$), indicating that the solubility switch is occurring over a relatively small dose range for the least networked film. However, **Figure 4b** shows that chemical changes are occurring across a much larger dose range for all three alucone films. Therefore, the difference in contrast likely originates from the development process. We hypothesize that there exists a critical concentration of organic ligands that governs the solubility of the resist material.

At low doses (see schematic illustration in **fig. 6a**), the ligand concentration is higher than the critical point, and the film contains individual metal centers and AlO_x nanoclusters formed during exposure that are still soluble in the developer. With increasing dose, the inorganic concentration increases, impeding solvent diffusion and reducing the development rate until the film is not fully dissolved, resulting in partial solubility switch (**fig. 6b**). Differences in the development rate in this partially exposed regime can occur due to differences in networking density, which could also affect solvent diffusion. This would lead to a difference in contrast, resulting in the improved contrast for Al-MeOH-EG as shown above. Once the ligand concentration drops below the critical point (**fig. 6c**), the nanoclusters coalesce into inorganic domains with a much lower dissolution rate. Differences in networking density become negligible, due to the low organic content. However, ligand desorption can continue to occur with additional exposure, resulting in further film shrinkage.

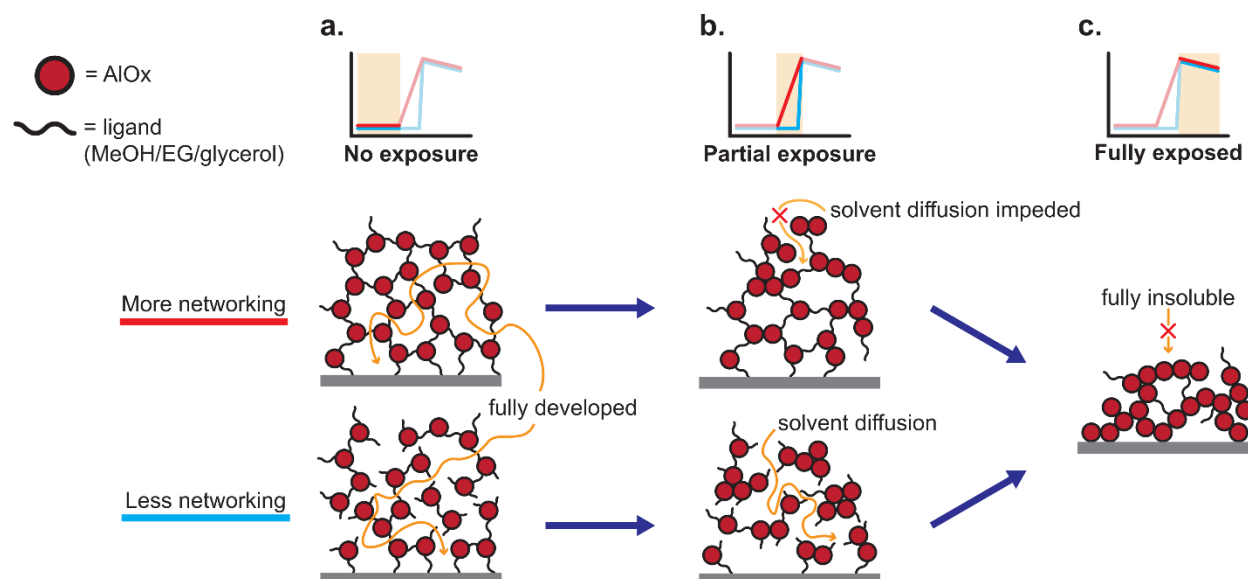


Figure 6. Effect of networking density on contrast. (a) Unexposed resists are fully soluble. (b) Partial exposure results in nanoclusters that impede solvent diffusion, reducing development rate. Increased networking also impedes diffusion, worsening contrast. (c) Fully exposed films contain coalesced inorganic domains with a negligible development rate.

Although D_{100} provides an estimate of the dose required for complete solubility switching, the dose for patterning nanoscale features accurately – the dose-to-size – typically varies depending on the feature size and geometry. Therefore, to test the nanopatterning capabilities of the alucone resists, we patterned 24 nm half pitch (hp) 1:1 line/space gratings with a range of doses above D_{100} (**fig. 7**). Dense gratings are chosen because they are relatively difficult to resolve compared to isolated features, and are also most relevant to industrial lithographic processes.⁶⁰ Among the three resists, only Al-MeOH-EG exhibits well-defined line patterns across the dose range shown, with only variations in linewidth observed. Al-EG patterns contain bridging defects at all three doses; we hypothesize that these patterns were overexposed for the targeted feature size, leading to significant partial exposure in the trench region. During development, phase separation of such partially exposed regions can lead to bridge defects.^{61–63} Phase separation would also explain the increased surface roughness of partially exposed features (**fig. 4a**, bottom). Similar to Al-EG,

Al-GL forms similar bridge defects at the two higher doses; at the lowest dose (423 mC/cm²), pattern collapse occurs. We attribute this critical failure to underexposure, resulting in partial dissolution/gelation of the exposed pattern during the development step that leads to the loss of mechanical strength. These results show that the optimal dose window for patterning at this resolution is widest for Al-MeOH-EG and decreases with increasing networking density.

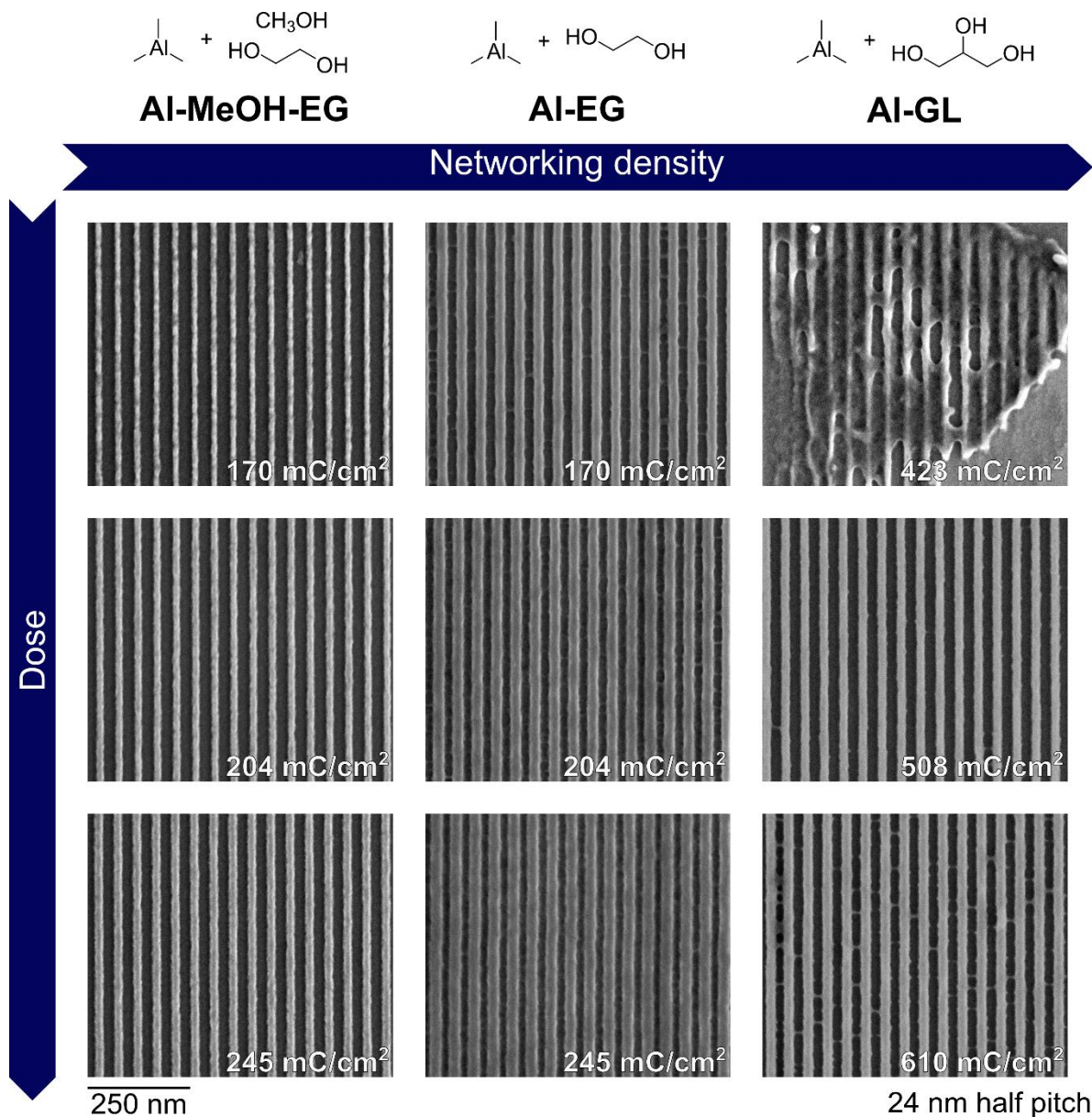


Figure 7. SEM images of 1:1 lines/space gratings (24 nm half pitch) patterned on Al-MeOH-EG (left), Al-EG (center) and Al-GL (right) at varying e-beam doses.

Next, we attempt to define the intrinsic resolution limit of each alucone resist by patterning gratings at increasingly small pitches. All three resists show a dependence of linewidth on exposure dose, highlighting the need to optimize the dose for each resist to determine the smallest resolvable linewidth. By patterning gratings across a range of doses, the smallest achievable pitch for each alucone resist at the dose-to-size can

be determined. **Figure 8a** shows the best resolution achieved for each alucone at any dose: Al-MeOH-EG is patternable down to 18 nm hp, Al-EG to 24 nm hp, and Al-GL to 28 nm hp, showing a clear correlation between resolution and networking density.

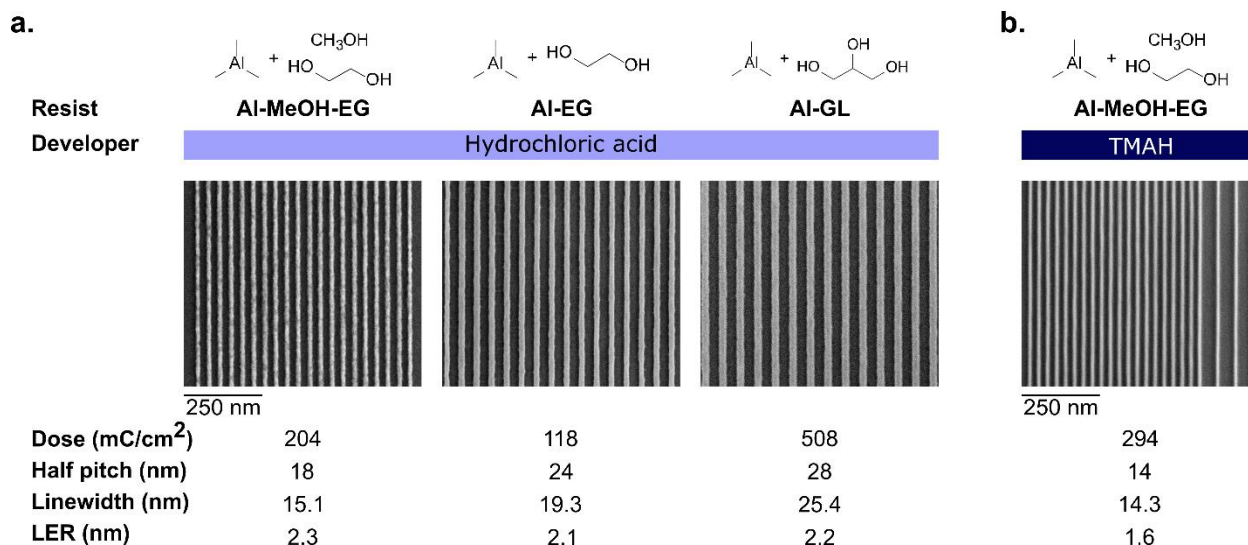


Figure 8. Smallest gratings patternable on each alucone resist when the e-beam exposure dose is optimized, with (a) hydrochloric acid or (b) diluted TMAH as the developer.

Improvements to resolution with decreasing networking density may be correlated to improved contrast, since the side walls of higher contrast resists would be better defined. Additionally, mass transfer limitations during the development of nanopatterns may play an important role in pattern formation. The diffusion of developer molecules into the nm-scale trenches may be much slower than for large features.⁶⁴ Differences in solvent diffusion rates related to networking density would thus increase the chance of scumming and nanobridge defects for the more crosslinked alucone films, in which more unexposed material is trapped by such nanoscale mass transfer effects. The apparent advantages of Al-MeOH-EG are more clearly visible when comparing the three alucone films at 18 nm half pitch (**SI fig. S9**), at which bridging defects and scumming are clearly visible for both Al-EG and Al-glycerol, limiting their resolution.

Contrary to the difference in resolution, there is no clear difference in LER between the three resists (with the HCl developer). We posit that this is related to their similar post-exposure chemical composition: due to the loss of ligands during exposure, their negative tone features exhibit similar aluminum oxide/hydroxide bonding. Thus, they exhibit similar swelling and aggregation characteristics during the development and rinse processes, leading to similar line edge formation.

As the best performing resist, we continue to tune the development process for Al-MeOH-EG because development is known to have a major impact on pattern quality.^{62,65} TMAH is a basic developer often used in industry;⁶⁶ similar to the acid-catalyzed hydrolysis of metal alkoxide bonds occurring during HCl development, TMAH development is expected to promote base-catalyzed hydrolysis resulting in a similar negative tone pattern. Using a commercial solution (MF-319, 2.38% TMAH) diluted at a 1:200 ratio, we were able to pattern line/space patterns as small as 14 nm hp with 1.6 nm LER (**fig. 8b**), which are among the best resolution and LER metrics achieved by MLD resists reported in the literature (**Table 1**). However,

the dose required to pattern such features is even higher than those for patterns developed with HCl. This is likely because alucone is more soluble in TMAH than HCl at the chosen concentrations, resulting in increased etching rate at lower doses (**fig. 9a**). Increased alucone dissolution rate could improve the contrast in solubility between the exposed and unexposed region, leading to enhanced resolution and LER via enhanced removal of scumming/bridging defects and a narrower boundary region in which the line edge is defined. Another difference is that the contrast curve also exhibits a gradual increase in thickness towards a plateau, instead of the shrinkage observed pre-development (**fig. 4b**) or after HCl development (**fig. 4a**). This behavior could be explained by partial dissolution of regions exposed to doses above D_{100} , with higher dissolution rates at lower doses counteracting the film shrinkage at higher doses.

Due to the promising resolution and LER performance of Al-MeOH-EG with EBL, we perform EUV flood exposures on this resist using a synchrotron-based light source to establish a dose calibration curve. After development with 1:200 diluted MF-319, the resist exhibits a similar negative tone behavior to that after EBL (**fig. 9b**). However, the resist thickness drops significantly above the solubility switch threshold, which may indicate a difference in the chemical composition (leading to partial dissolution in the exposed area) compared to the e-beam exposed resist due to the different exposure source.

By fitting the contrast curve, we determine the EUV sensitivity of Al-MeOH-EG to be ~ 2000 mJ/cm². For comparison, commercial metal-based EUV resists exhibit doses-to-size of 40-100 mJ/cm² for features at industrially relevant length scales (**Table 1**).^{25,26} The poor EUV sensitivity of alucone is consistent with its poor e-beam sensitivity compared to common e-beam resists such as methacrylate-based resists or hydrogen silsesquioxane (HSQ), which exhibit sensitivities below 1 mC/cm².⁶⁵

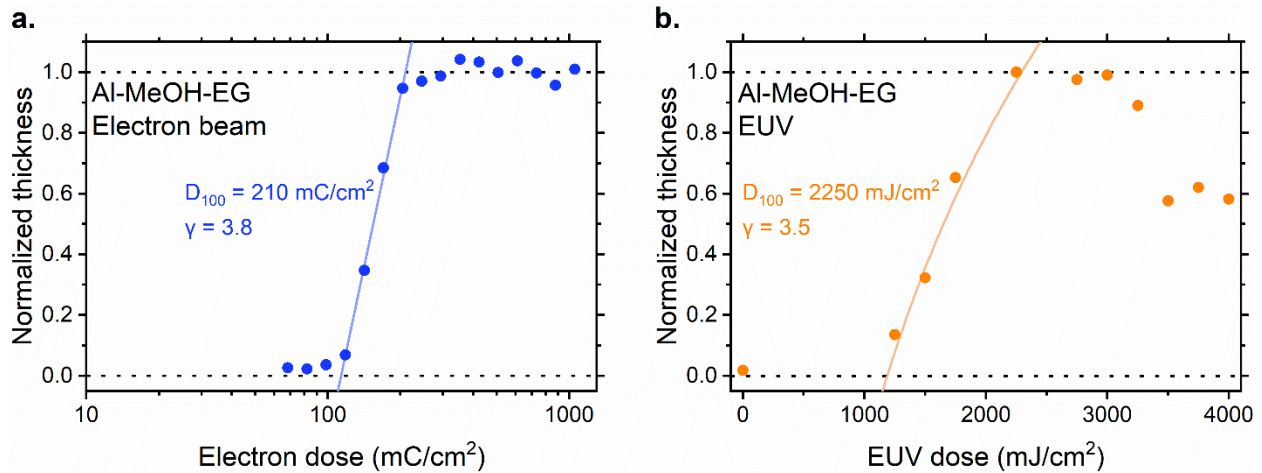


Figure 9. Contrast curves for Al-MeOH-EG exposed with (a) electron beam or (b) EUV exposure and developed with 1:200 diluted MF-319 (TMAH developer). Note that the x-axis is log-scale in (a) and linear scale in (b).

Table 1. Performance metrics of representative MLD resists and other negative-tone metal-organic resists in the literature. Dose-to-size, contrast, and LER corresponds to the smallest pitch 1:1 line/space patterns demonstrated by each resist. An empty entry indicates that the information was not provided in the reference.

Resist	Exposure source	Resolution (full pitch, nm)	LER (nm)	Dose-to-size	Contrast/ γ	Ref.
Al-MeOH-EG (this work)	EUV			2000 mJ/cm ²		
	EBL (100 kV)	28	1.6	294 mC/cm ²	3.7	
Zn-3MP	EUV	32	1.37	60 mJ/cm ²	6.46	39
	EBL (100 kV)	28	2.39	2.175 mC/cm ²		
Zn-imidazolate	EBL (30 kV)	40	3.47	200 mC/cm ²	0.87	28
HfO ₂ -DMA (5% PAG)	EUV	40	6.1	2.2 mJ/cm ²		20
Inpria MOR	EUV	24	1.9	39.5		25
Lam Research dry resist	EUV	24		42		26

To better understand the EUV-induced behavior of Al-MeOH-EG, we perform TEY and RGA measurements during EUV flood exposure to observe secondary electron generation and outgassed species, respectively. Results from both measurements are broadly consistent with the proposed e-beam reaction mechanism, due to evidence of film densification and ligand oxidation/outgassing. **Figure 10a** shows the TEY signal over time of Al-MeOH-EG, with PMMA and bare silicon as references. After a sharp initial spike attributable to charging effects, the alucone TEY gradually rises over time, attributed to the loss of organic ligands and increasing fraction of EUV-absorbing Al atoms over time.⁶⁷ Concurrently, RGA (**fig. 10b**) confirms the EUV-induced evolution of gaseous species. Examination of the outgassing at each mass-to-charge (m/z) reveals that the outgassing signal is dominated by molecular hydrogen (H₂) (**fig. 10c**). Signals corresponding to outgassed ethylene glycoxide (C₂H₄O₂) and methoxide (CH₃O) fragments – including C₂H_xO, CH_xO, CH_x, CO – are also present, although they are difficult to distinguish from chamber contaminants (observed during exposure of uncoated silicon substrates, **SI fig. S10**). Both molecular hydrogen and outgassed ligands can be produced from dehydrogenation reactions converting alkoxide ligands into carbonyl and alkenyl groups.³² Dehydrogenation, oxidation of alkoxide ligands, and loss of ligands have also previously been observed during the degradation of alucone in ambient conditions,⁴⁶ suggesting that this reaction mechanism is particularly favorable.

In addition to confirming the similar reaction mechanisms between e-beam and EUV exposure of Al-MeOH-EG, these *in situ* experiments also help to pinpoint the cause of its poor EUV sensitivity. The resist sensitivity may be bottlenecked at any step in the mechanism for EUV-induced solubility switch: poor EUV absorption, slow reaction kinetics, poor selectivity towards solubility-switching reactions, or a large ligand loss threshold to cause insolubility.

Poor EUV absorption can be ruled out; given the measured film density and atomic composition, its EUV linear attenuation coefficient can be calculated to be $13.4 \mu\text{m}^{-1}$ (**SI note S6**). This is comparable to that of tin-based metal oxide resists ($15\text{--}19 \mu\text{m}^{-1}$), and greater than that of organic resists ($3\text{--}5 \mu\text{m}^{-1}$).⁶⁸ Therefore, secondary electron generation in Al-MeOH-EG should be comparable to that of high EUV-absorbing materials. Additionally, poor EUV absorption would not account for the poor sensitivity in e-beam.

Given sufficient secondary electron generation, another likely bottleneck may be poor reaction kinetics. Electron-matter interactions in the resist may be preferentially directed towards chemically inactive pathways such as autodetachment, radiative cooling, or recombination after dissociation events.¹¹ However, the Al-MeOH-EG total outgassing signal is comparable to PMMA, which is known to produce outgassed species during EUV exposure.^{69,70} Its reaction kinetics is therefore unlikely to be exceptionally poor compared to PMMA, despite its EUV sensitivity being worse by several orders of magnitude.

A more plausible explanation is that multiple reaction pathways are possible, not all of which contribute significantly to solubility switch. The hypothesized solubility switch mechanism requires cleavage of C-O or Al-O bonds for ligand outgassing to occur, followed by formation of Al-O-Al bond networks to cause nanoclustering. Other reactions may also be occurring; for example, dehydrogenation of the alkoxide ligand – a possible reaction resulting in the observed H₂ outgassing – may be a side reaction that does not contribute to ligand loss and aluminum oxide clustering, but acts as a secondary electron trap and reduces the reaction efficiency.

Another possible explanation is that an exceptionally large extent of reaction is required to induce a solubility switch compared to conventional resists. This difference may be because the nanoclustering mechanism requires multiple excitation steps to cleave all coordination sites from each ligand. Ligands that contain at least one intact alkoxide group, and thus cannot be outgassed, could hinder Al-O-Al network formation. Alternatively, the resist solubility could be weakly influenced by each nanoclustering event such that a large extent of reaction is needed, due to a small difference in solubility between alucone and the exposure product, or the lack of an amplification mechanism.

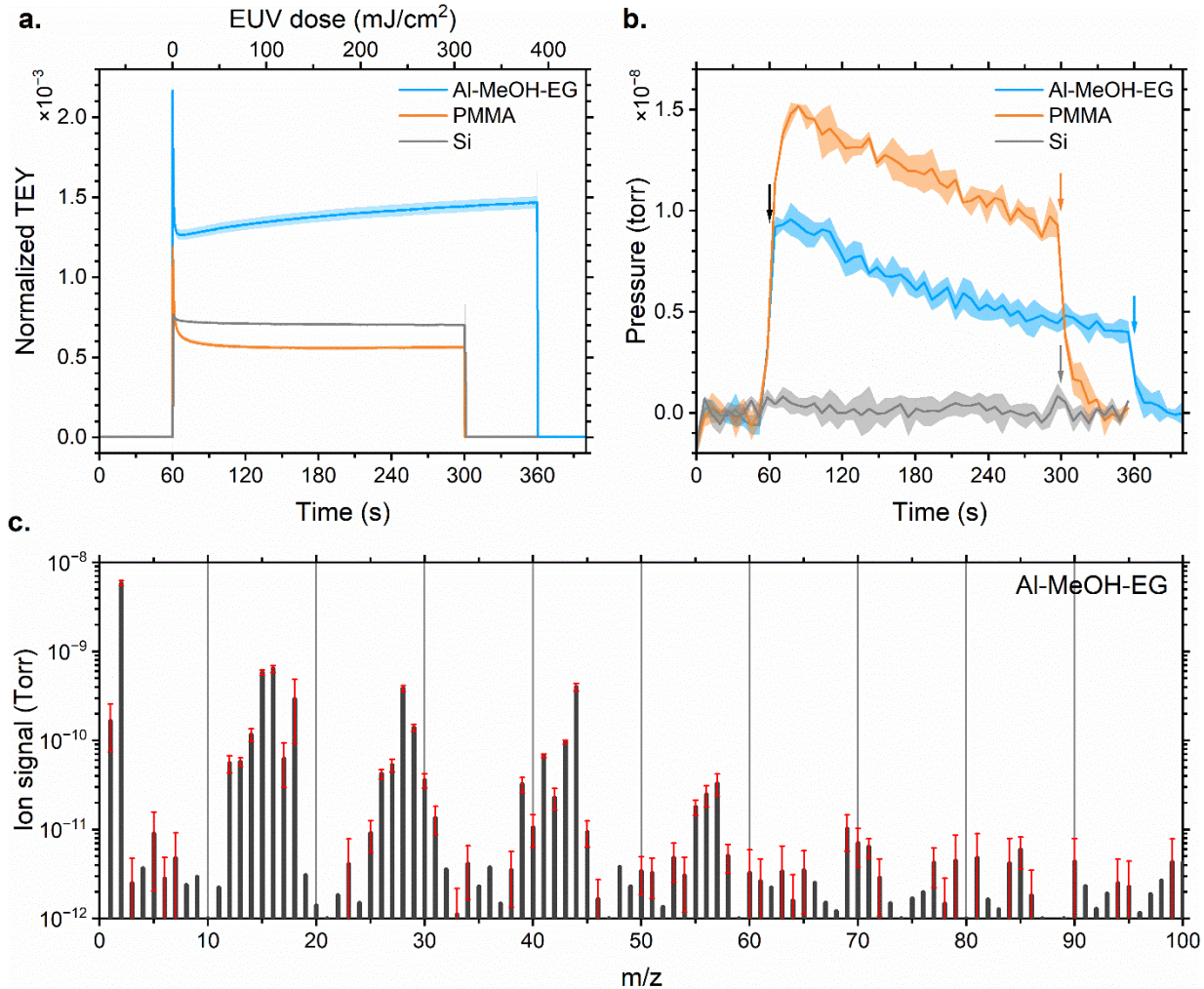


Figure 10. (a) Normalized TEY (drain current/diode current) of Al-MeOH-EG (17 nm film), PMMA (24 nm film), and bare silicon substrate. Samples are exposed to EUV between 60 s and 300 s (PMMA and Si) or 360 s (Al-MeOH-EG). (b) Concurrently measured total outgassing signal of Al-MeOH-EG, PMMA and Si. Arrows indicate the start and end of EUV exposure. (c) Outgassing spectrum of Al-MeOH-EG after background subtraction. The standard deviation from three measurements is indicated by the shaded area in (a) and (b), and by error bars in (c).

Conclusion

In this work, we deposited a series of alucone resists designed to have varying networking density while maintaining the same metal alkoxide chemistry. All three alucone films exhibited similar chemical transformations after e-beam exposure; however, the variation in networking density resulted in differences in resist performance. The most networked film (Al-GL) was significantly less sensitive to e-beam exposure ($D_{100} = 342 \text{ mC/cm}^2$), while the least networked film (Al-MeOH-EG) was more sensitive ($D_{100} = 88 \text{ mC/cm}^2$) and had significantly better contrast ($\gamma = 3.7$). The resolution limit of each resist also followed their structural trend: the least networked resist (Al-MeOH-EG) demonstrated the smallest achievable features. The differences in lithographic performance as a function of network density were attributed to the various kinetic and mass transfer barriers imposed by the polymer network throughout exposure and

development. With the best-performing resist – Al-MeOH-EG – 14 nm hp line/space patterns were resolved via EBL, among the best resolution achieved by MLD resists currently reported in the literature. In addition, its patterning mechanism and negative tone behavior was demonstrated to be similar under EUV exposure. However, its sensitivity is limited compared to conventional resists for both e-beam and EUV.

This work demonstrated that structural differences are significant for hybrid MLD photoresists and, in particular, that resists with low networking density may be advantageous for contrast and resolution. Therefore, selecting chemistries that result in lower networking density, or incorporating network-terminating groups to the MLD process, may be a rational design strategy for improving the resist performance. Additionally, selecting ligand chemistries that more efficiently harness electron-induced reactions may be a strategy that can be applied concurrently to improve resist sensitivity. For example, changing the ligand end group to thiolates or carboxylates can affect the energetics of the ligand cleavage reaction. The ligand chain can also be modified, such as with the addition of unsaturated bonds to promote radical polymerization during exposure, or with halogens and π -conjugated moieties to influence the electron density of the end group. Future studies comparing the influence of such ligand chemistries could help to guide the design of MLD photoresists that could extend the limits of EUV lithography.

Supporting information

XPS before and after GCIB sputtering. Note on XPS binding energy calibration. Developer optimization. MLD saturation curves. XRR and density calculation. Additional details on XPS of patterned features. Method to measure and fit lithographic contrast curves. Note on probability of ligand outgassing. RGA of silicon substrate. Calculation of EUV linear attenuation coefficient.

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