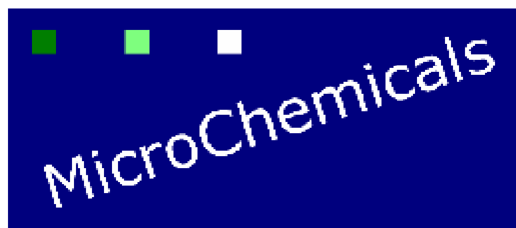
Lithography Trouble-Shooter



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The following issues and work-arounds are just the core of our litho-know-how. We would be glad to discuss your technical questions, please do not hesitate to contact us! Our contact data as well as the link to the application notes marked with (*) can be found at the end of this document.

Strange Appearance of the Photoresist

Discolouring? Positive tone and image reversal resists darken over the months. Hereby, the photo active compound forms azo-dyes having a strong absorbance in the visible part of the spectrum without any impact on the UV sensitivity. The discolouring proceeds very slowly and therefore is often noted when starting with a new resist lot.

Bubbles and Comet-Like Structures After Spin Coating? Possible reasons and work-arounds are listed in the section „Bubbles or Particles in the Resist Film After Coating“.

Rough Resist Surface After Coating? Expired resist or resist stored on wrong (temperature) conditions, as well as resist diluted too strong or with unsuited solvents, may form particles. In early stage averaging, the coated resist reveals a silky resist surface. Strongly deteriorated resist may also show bigger lumps and coating failures. Please contact us for recommended storage conditions and suited thinner!

Edge Bead - Prevention and Removal

Circular Substrates? For edge bead removal on round substrates, we recommend to dispense a thin stream of PGMEA = AZ® EBR Solvent onto the edge bead of the substrate rotating at approx. 500 rpm. After the edge bead removal (typically taking approx. 10-20 seconds) the substrate should continue rotating for some seconds in order to remove the remaining PGMEA.

Edged Substrates? Adjusted spin profiles (see below) or using a gyrset will reduce the edge bead size. Fitting the substrate into a commensurate cavity during spin coating, or alternative coating techniques such as spray coating, roller coating, or dip coating are possible work-arounds. If applicable, remove (break) the outer pieces of the substrate together with the edge bead or alternatively manual clean of the substrate from the edge bead with cleanroom wipes.

Suited Edge Bead Remover? Low-boiling solvents such as acetone are not recommended for edge bead removal due to their high vapour pressure (Resist film thinning during edge bead removal). Additional, the low viscosity acetone promotes droplets splashing onto the resist film hereby causing defects. For edge bead removal, we recommend PGMEA = AZ® EBR Solvent which is also the main solvent of most AZ® and TI resists.

Optimum Spin Profile? High spin speeds lower the edge bead size. In order to attain the desired resist film thickness, adjust the spin time - please contact us for suited spin profiles!

(Very) Thick Resist Films? A multiple coating with an elevated spin speed for each coating cycle gives better results than single-coating of thick resist films.

Optimum Coating Technique? Especially in case of edged substrates, spray coating, roller coating, or dip coating are reasonable alternatives for spin coating. Please contact us for detailed information on these techniques!

Development: Minor Development Rate

Sufficient Rehydration? Positive tone and image reversal resists require a certain water content to allow a reasonable high development rate. After softbake or image reversal bake,

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the now missing water has to diffuse from the air into the resist film requiring a delay time between baking and exposure to rehydrate the entire photo resist film towards the substrate. Therefore, a certain air humidity (at least 40 %), and sufficiently long (dependant on the resist film thickness) delay between baking and exposure is required (details s. *Rehydration of Photoresists**).

Sufficient Exposure Dose? The required exposure dose depends on the resist, the resist film thickness, and the emission spectrum of the light source with respect to the resist to be exposed (details s. *Optical Parameters of Photoresists**). We strongly recommend an exposure dose series when starting with new resists and processes, or after changes of the exposure equipment.

Compatible Developer? Some photoresists require special developers for residual-free development. The document *Resists and Developers** gives detailed information on compatibilities between photoresists and developers.

Developer Expired? CO_2-absorption from air limits the lifetime of open developer baths to few days. A N_2 curtain reduces CO_2-absorption and hereby can decelerate the developer neutralisation. Even well-closed containments are permeable for CO_2, therefore the developer activity may decrease after the expiry date. A developed resist concentration too high also exhausts the developer: As a rule of thumb, approx. one promille resist solved in typical developers significantly reduces the development rate.

Proper Developer Dilution? The KOH-based AZ® 400K and NaOH-based AZ® 351B are typically applied in a 1 : 4 dilution with water. AZ® Developer can be applied as concentrate (high development rate), or in a 1 : 1 dilution (improved selectivity). The TMAH-based ready-to-use developers AZ® 326 MIF, 726 MIF, and 826 MIF are generally applied undiluted.

HMDS applied correctly? In case of spin-coating of HMDS, a too thick HMDS film forms on the surface. After resist coating during the softbake, this excess of HMDS releases ammonia which diffuses into the resist and chemically modifies the resin near the substrate. As a consequence, through-development may become impossible.

Thermal Decomposition of the Photo Active Compound? The photosensitive compound of photoresists is partially decomposed during baking steps. If the softbake temperature and -time are higher than recommended, the development rate decreases (Details in *Softbake of Photoresist Films**).

Resist Film Thickness Higher than Expected? The resist film thickness attained via spin coating depends on the resist solvent concentration (potentially reduced by frequent opening of the resist bottles), and the temperature. In case of thicker resist films, the required exposure dose also increases.

Changed Substrate Reflectivity? Especially in case of thin (< 2 µm) resist films, the exposure energy absorbed by the resist depends on the substrate properties (reflection coefficient and scattering). For this reason, the exposure dose required for a certain resist film depends on the substrate material.

Development: Dark Erosion too High

Proper Developer Dilution? The KOH-based AZ® 400K and NaOH-based AZ® 351B are typically applied in a 1 : 4 dilution with water. AZ® Developer can be applied as concentrate (high development rate), or in a 1 : 1 dilution (improved selectivity). The TMAH-based ready-to-use developers AZ® 326 MIF, 726 MIF, and 826 MIF are generally applied undiluted.

Optimum Softbake Conditions? A softbake too cool/too short keeps the remaining solvent concentration at high values, thus increasing the dark erosion rate in developers. The optimum softbake parameters (time and temperature) depend on the resist film thicknes, the solvent, the subtsrate material and -geometry, and the equipment used for softbake (hotplate or oven). For further details, plase consult our document *Softbake of Photoresist Films**.

Thermal Decomposition of the Photo Active Compound? If not exposed, the photosensitive compound of photoresists is a solubility inhibitor in alkaline solutions, thus decreasing the dark erosion in developers. If the softbake temperature and -time are higher than recommended, this inhibitor is partially decomposed (details in *Softbake of Photoresist Films**).

Compatible Developers? Certain developers such as AZ® Developer or AZ® 826 MIF reveal

slightly higher dark erosion rates for photoresist. The document *Resists and Developers** gives detailed information on recommended developers for each photoresist and substrate material.

In Case of Image Reversal- or Negative Tone Resists? Image reversal resists and negative tone resists require i) a certain minimum exposure dose and ii) a certain post exposure bake temperature/-time. Otherwise, the alkaline solubility of the resists parts which should remain after development is too high, with a high „dark" erosion as a consequence.

Exposure Dose too High? In this case, light scattering in the resist film may expose „dark" parts of the resist, which hereby become soluble in developers.

Exposure Artefacts? A gap between resist surface and mask, textured or transparent substrates, or incident white light are able to expose resist via scattering, reflection, or diffraction. Hereby, resist parts which should remain after development become soluble in developers.

Inferior Resist Adhesion

Optimum Substrate Pretreatment? Detailed information on substrate cleaning and adhesion promotion are given in our document *Substrate Cleaning Adhesion Promotion**.

Using HF-containing etchants? HF diffuses into the resist film and may lead to a large scale resist peeling either during the etching, or after the subsequent rinsing by resist swelling and large-scale etching of the resist covered substrate material. Work-arounds are i) increasing the resist film thickness (= barrier against HF), and the usage of buffered HF (BOE) (details in *Wet Chemical Etching**).

On Noble Metals? The resist wetting and adhesion on noble metals (e. g. silver, gold) is often worse. In this case, resists such as AZ® 111 XFS, AZ® 1514H, or the ECI 3000 series may improve the adhesion. While organic adhesion promoters such as HMDS are not able to significantly improve resist adhesion, a metallic adhesion layer (Titanium or Chromium) results in a very good adhesion to resists. If required, such few nm thick metal films can easily be etched after development or/and after resist removal.

On SiO_2, Quartz, or Glass? Organic adhesion promoters such as HMDS or TI PRIME work well with these substrate materials (details in *(Inferior) Resist Adhesion**).

Optimum Softbake Parameters? A softbake too cool/too short keeps the remaining solvent concentration too high with inferior resist adhesion as a consequence. A softbake too hot/too long embrittles the resist film and causes mechanical strain between resist and substrate. In this case - especially after abrupt cooling after the softbake - the resist film may loose adhesion to the substrate (details in *Softbake of Photoresist Films**).

Positive Tone Resists on Transparent Substrates? Especially in case of too high exposure doses, light can be guided in transparent substrates and hereby expose the resist near the substrate. As a consequence, small resist structures may lift in the developer.

Image Reversal- or Negative Tone Resists? Too low exposure doses or a post exposure bake being too cool/too short will keep the substrate-near resist soluble in the developer. This may cause lifting of especially small resist structures from the substrate during development.

Double-Sided Metalized Substrates? Substrates coated with different metals on both sides may cause a galvanic cell in aqueous solutions, accompanied by gas (H_2-) formation under the resist peeling it from the substrate. A protective coating with e. g. AZ® 520D on the "rear side" of the substrate will help.

Minor Resist Resolution

Suited Photoresist? Positive resists such as AZ® 1505, AZ® 1512HS, or AZ® 6612 allow structure sizes below 1 µm, AZ® 701MiR and the AZ® ECI 3000 series even below 0.5 µm. If high-resolution negative tone resists are required, thin films of the AZ® nLOF 2000 series allow sub-µm features for e. g. lift-off application.

Gap Between Photomask and Resist Surface? Particles, bubbles in the resist film, or an resist edge bead may cause a gap between mask and resist which degrades the theoretical resolution by diffraction and light scattering.

Thermal Decomposition of the Photo Active Compound? If not exposed, the photosensitive compound of photoresists is a solubility inhibitor in alkaline solutions, thus decreasing the

dark erosion in developers. If the softbake temperature and -time are higher than recommended, this inhibitor is partially decomposed (details in *Softbake of Photoresist Films**). Since at the same time the development rate decreases, the contrast of the resist and hereby its resolution performance deteriorates.

Compatible Developers? Certain developers such as AZ® Developer or AZ® 826 MIF have higher dark erosion rates for photoresists than other developers, making them less suited for high-resolution demands. The document *Resists and Developers** gives detailed information on recommended developers for each photoresist and substrate material.

Exposure Dose too High? In this case, light scattering in the resist film exposes also „dark“ parts of the resist, which hereby become soluble in developers and prevents the realization of very small structures .

Bubbles or Particles in the Resist Film After Coating

Resist Bottles Moved? Carrying resist bottles or moving them may inject small air bubbles into the resist. In this case, a delay before coating allows the bubbles to raise to the resist surface. The waiting time depends on the resist viscosity, 1-2 hours should be sufficient in most cases.

Resist Bottles Closed For a While? Over the months, the photo active compound of many resists releases N_2 which dissolves in the resist. When the resist bottle is opened, N_2 bubbles may form which - more or less slowly - raise to the surface. For this reason, a delay with the screw cap set loosely (pressure balance!) on the bottleneck is required to outgas the N_2. The waiting time depends on the resist viscosity, 1-2 hours should be sufficient in most cases.

Manual Resist Dispensing? Dispensing the resist with pipets often leads to air bubbles in the resist. As a work-around, give the resist-filled pipet some time allowing the air bubbles to raise away from the outlet.

Spray Coating? If the fraction of a low-boiling solvent such as MEK or acetone is too high, the resist droplet may already dry during flight and subsequently hit the substrate as resist pellet. Please contact us for suited solvents and dilution recipes!

Resist Expired? Expired resist or resist stored under wrong conditions may form particles. This effect especially concerns low-viscosity thin resists with a high concentration of the photo active compound.

Resist Diluted? If a dilution is required, only suited solvents (such as PGMEA or MEK) should be used, and a resist-specific maximum dilution should not be exceeded. Otherwise, the resist may rapidly form particles. Please contact us for suited solvents and dilution recipes!

Bubbles in the Resist Film After Exposure

Optimum Softbake Parameters? A softbake too cool/too short keeps the remaining solvent concentration too high allowing the N_2 formed during exposure to form bubbles in the resist film (details in *Softbake of Photoresist Films**).

Sufficient Resist Adhesion? The N_2 generated during exposure of positive tone and image reversal resists may form bubbles at locations of minor resist adhesion to the substrate. Detailed information on substrate cleaning and adhesion promotion are given in our document *Substrate Cleaning Adhesion Promotion**.

Exposure Intensity too High? The N_2 generated during exposure of positive tone and image reversal resists needs to dissipate from the resist film before its concentration becomes too high. If the exposure intensity is too high, the N_2 cannot timely outgas and therefore forms bubbles or resist cracks due to mechanical stress. Lowering the exposure intensity (= extending the exposure time), or splitting the exposure into several steps with delays in-between will help in this case.

Bubbles in the Resist Film After Thermal Processes

After Baking Steps of Exposed Photoresist? The N_2 generated during exposure of positive tone- and image reversal resists may thermally activated form bubbles in the softening resist during baking steps (post exposure bake or image reversal bake). In this case, a delay between exposure and baking step will help.

After Coating (Sputtering, Evaporation) or Dry Etching? Elevated temperatures may evaporate remaining solvent or water (from development) in the resist. In combination with the low ambient pressure, bubbles may occur. Increasing the softbake time or temperature will reduce the remaining solvent concentration, while a baking step after development reduces the water content. A further reason for bubbling can be the undesired exposure of the resist film during evaporation/sputtering by thermal or recombination UV radiation with N_2 formation as consequence. One work-around is the usage of image reversal resists in image reversal mode or a negative tone resist such as the AZ® nLOF 2000 series. In case of positive tone resists, a flood exposure (without mask) of the developed resist structures with a certain delay to outgas the N_2 formed hereby.

Lift-Off Does Not Work (Well)

Optimum Coating Technique? The more or less isotropic sputtering will also coat the resist sidewalls, while evaporation is much more directed and therefore generally gives better lift-off results, especially in case of thick (> several 100 nm) films.

Suited Photoresist? A pronounced undercut of the resist sidewalls makes the lift-off much easier as compared to perpendicular or even positive sidewalls. Therefore, negative tone resists such as the AZ® nLOF 2000 series, or image reversal resists such as AZ® 5214E or TI 35ES are a good choice. If nevertheless positive tone resists have to be used for lift-off application, the AZ® 6600 series or the AZ® 9260 thick resist allow almost perpendicular sidewalls.

Resist Softening and Rounding During Coating? During coating (evaporation, sputtering, CVD), the resist film may be heated by the evaporation source radiation, the condensing heat of the growing film, or the kinetic energy of the ions, above its softening point (110-130°C for most positive tone and image reversal AZ® resists). Hereby the resist profile starts rounding allowing the coating material to cover also the resist profile sidewalls. As a consequence, subsequent lift-off will work worse or become impossible. Possible work-arounds are i) an optimized heat coupling of the substrate to its holder (e.g. some turbo pump oil for proper heat transfer from strained, curved substrates), ii) a sufficiently high heat buffer (massive substrate holder construction) or iii) heat removal (e.g. black anodized aluminium as rear infrared radiator) from the substrate holder, iv) a reduced deposition rate or/and a multistage deposition with cooling intervals in between, v) UV-curing, or vi) a thermally stable photo resist such as the AZ® 5214E, TI 35ES, or AZ® nLOF 2000 series.

Suited Lift-Off Medium? Using solvents with a high vapour pressure such as acetone as lift-off medium sometimes promotes the re-adsorption of material already lifted onto the substrate. We recommend NMP as lift-off medium, which can be heated up to 80°C if required. If necessary, ultrasonic treatment assists the lift-off process.

Photoresist Removal Does Not Work (Well)

Organic Solvents as Remover? Acetone sometimes used as stripper promotes resist residuals on the substrate due to the fast evaporation. Heating acetone for faster stripping is absolutely not recommended due to the low flash point and the high fire hazard. NMP is a much better lift-off medium due to its low vapour pressure. In case of cross-linked resists, heating the NMP up to 80°C may be required for resist removal.

Alkaline Remover? As an alternative to organic solvents, AZ® 100 Remover is optimized for stripping photoresists residual-free and striation-free. In case of Al (-containing) substrates, even traces of water have to be avoided in order to prevent Al attack. NaOH or KOH (> 2%) can also be used as stripper, a higher cross-linking degree may require higher concentrations and elevated temperatures.

Hardbake? Negative tone resists such as the AZ® nLOF 2000 series already cross-link during the post exposure bake (PEB) and stronger cross-link even at moderate hardbake temperatures. All cresole-resin-based (AZ®-)resists thermally cross-link from approx. 150°C on. If applicable, lowering the hardbake temperature will improve the solubility of the resist in the remover.

After Coating (Evaporation, Sputtering, CVD)? If the resist film is strongly heated by the evaporation source radiation, the condensing heat of the growing film, or the kinetic energy of

the ions, cross-linking of the resist may decrease its removability. Possible work-arounds are i) an optimized heat coupling of the substrate to its holder (e.g. some turbo pump oil for proper heat transfer from strained, curved substrates), ii) a sufficiently high heat buffer (massive substrate holder construction) or iii) heat removal (e.g. black anodized aluminium as rear infrared radiator) from the substrate holder, iv) a reduced deposition rate or/and a multistage deposition with cooling intervals in between.

After Dry Etching? Generally consider what is mentioned in the previous subsection. Additionally, re-deposition of material already etched onto the resist may prevent resist removal. In this case, the re-deposited material first has to be etched wet-chemically.

Disclaimer of Warranty

All information, process guides, recipes etc. given in this brochure have been added to the best of our knowledge. However, we cannot issue any guarantee concerning the accuracy of the information. We assume no liability for any hazard for staff and equipment which might stem from the information given in this brochure. In general, it is in the responsibility of each staff member to inform herself/himself about the processes to be performed in the suited (technical) literature, in order to minimize any risk for man and machine.

Contact and References

* The documents referred can be freely downloaded from our homepage via
http://www.microchemicals.eu/technical_information

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Our Photoresists

Sales Volumes : Units of 250 ml, 500 ml, 1 L, 2.5 L, 5 L*

Thin Positive (Thickness 0.5 ... 2.5 µm)

AZ® 1500 Series → Improved adhesion for wet etching
AZ® 111 XFS → Improved adhesion for wet etching
AZ® 6612, 6624 → High thermal stability for dry etching

Medium Positive (Thickness 2.5 ... 5.0 µm)

AZ® 4533 → Improved adhesion for wet etching
AZ® 6632 → High thermal stability for dry etching

Thick Positive (Thickness 5.0 ... 50 µm)

AZ® 4562 → Improved adhesion for wet etching
AZ® 9260 → Outstanding aspect ratios

High Resolution

AZ® 701MiR → High thermal stability, dry etching
AZ® ECI 3000 Series → Wet and dry etching

Image Reversal

AZ® 5214E → High resolution for thin films
TI 35FS → Resist film thickness 3 ... 5 µm

Negative (High Thermal Stability, alkaline developable)

AZ® nLOF 2000 series → Resist film thickness 1 ... 15 µm

Special Application

AZ® 4999, TI Spray → Spray coating
AZ® 520D → Protective coating

Our Etchants

Sales Volumes : Bottles of 2.5 L in VLSI quality*

Ammonia Solution (25 %)

Ingredient of the RCA-1 solution

Acetic Acid (99.8 %)

Thinner, wetting agent and chemical buffer in various etching solutions such as Al-etchants

Hydrofluoric Acid (Various Concentrations) and BOE

Used for etching of SiO_2 and (together with HNO_3) - etching of silicon.

KOH Solution (44 %)

Also used for anisotropic etching of silicon

Phosphoric Acid (85 %)

Ingredient of aluminium etchants, and etching solutions for Ga-containing III/V-semiconductors

Nitric Acid (70 %)

Ingredient of the silicon etchant, and etching solutions for Ga-containing III/V-semiconductors.

Hydrochloric Acid (37 %)

Ingredient of aqua regia and etching mixtures for various III/V-semiconductors such as InP

Sulfuric Acid (96 %)

Ingredient of the piranha-etch as well as etching solutions for Ga-containing III/V-semiconductors

Our Solvents

Sales Volumes : Bottles of 2.5 or 5 L L in VLSI quality*

Acetone

Recommended for substrate cleaning (organic impurities and particles), second cleaning step (e. g. isopropyl alcohol) required for residual-free surfaces

Cyclopentanone

Developer for certain e-beam resists

Ethyl Lactate

Suited thinner for AZ® and TI photoresists

Isopropyl Alcohol

Recommended for rinsing contaminated acetone during substrate cleaning, particle removal from surfaces, additive for anisotropic Si-etching.

MEK (Methyl Ethyl Ketone)

Additional thinner for spray coating resists

Methanol

Substrate cleaning (substitute for isopropyl alcohol)

NMP (1-Methyl-2-Pyrrolidone)

Powerful lift-off medium, very well-suited stripper for photoresists

Our Developers

Sales Volumes : 5 L Bottles*

AZ® 326 MIF (Metal Ion Free, Ready-To-Use)

2.38% TMAH (TetraMethylAmmoniumHydroxide)

AZ® 726 MIF (Metal Ion Free, Ready-To-Use)

2.38% TMAH + surfactant for fast, homogeneous wetting

AZ® 826 MIF (Metal Ion Free, Ready-To-Use)

2.38% TMAH + surfactant for fast, homogeneous wetting – scum-remover for resist residual removal

AZ® 400K (KOH-Based Concentrate)

Chemically buffered, optimized for AZ® 4500 resist series

AZ® 351B (NaOH-Based Concentrate)

Chemically buffered, optimized for the AZ® 1500 resist series

AZ® Developer (Sodium Metasilicate)

Optimized for low Al attack

Our Etching Mixtures

Sales Volumes : 2.5 L Bottles*

Aluminium Etchant ($H_3PO_4/HNO_3/CH_3COOH$)

Mixtures of nitric acid (→ Al oxidation to Al_2O_3), phosphoric acid (→ solving the Al_2O_3 formed), and optionally acetic acid (→ wetting agent and buffer for HNO_3)

Chromium Etchant ($(NH_4)_2[Ce(NO_3)_6]/HClO_4$)

Mixtures of perchloric acid and ceric ammonium nitrate

Silicon Etchant (HF/HNO_3)

Mixtures of nitric acid (→ oxidation of Si to SiO_2), hydrofluoric acid (→ SiO_2 etching), and optional acetic acid (→ wetting agent and buffer for HNO_3).

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Our Ancillaries

Sales Volumes : Bottles of 1 ... 5 L*

HMDS Adhesion Promoter

HMDS should only be applied from the vapor phase onto heated substrates. Otherwise, water cannot sufficiently desorb from the wafer surface. Additionally, a HMDS film thickness being too high (caused by e. g. spincoating of HMDS) is able to crosslink substrate-near resist parts during baking steps (e. g. softbake).

TI PRIME Adhesion Promoter

TI PRIME adhesion promoter is designed for being spin-coated. In contrast to HMDS it has to be mentioned that TI PRIME is NOT metal ion free.

Resist Removal / Lift-Off

AZ® 100 Remover is a strongly alkaline remover for positive and negative tone AZ® and TI resists.
AZ® Kwik Strip is an amine-free, pH-neutral stripper for positive and negative tone AZ® and TI resists.
NMP is an organic solvent which can be heated up to 80°C for better performance. NMP is also a powerful lift-off medium.

***Your request for available sales volumes, quality, and pricing: sales@microchemicals.eu**