

DRY ETCHING

With dry etching, the material is not eroded by the compounds dissolved in a liquid, but by the atoms or molecules of a, at least, partially ionised gas.

This chapter describes the basic physical and chemical processes of this etching process and sets out the specific requirements of the previous photoresist processing to define of the desired resist mask.

Basic Etching Mechanisms and Parameters

Physical and Chemical Processes in Dry Etching

The erosion of the material to be etched can either be carried out physically by the kinetic energy of the particles (neutral or ionized atoms or molecules) from the gas, or through chemical reactions between the material and the gas.

The physical mechanism can be regarded as a partial-elastic collision of ions with the atoms of the medium to be etched. Chemical reactions play no or only a subordinate role, which is why etching is hardly materially selective. Since the ions from the gas are usually accelerated by electric fields perpendicular to the substrate, the material removal in this preferred direction is anisotropic.

If the 'chemical' mechanism dominates, etching occurs via the strong material selective formation of volatile compounds by radicals in the plasma which – towards high plasma pressure – hit the surface more and more isotropically. Compared to the physical erosion, the chemical erosion allows a significantly higher etching rate.

Dry Etching Technologies

Plasma etching is dominated by chemical erosion. In this way Si or SiO₂ is etched usually with chlorinated and fluorinated hydrocarbons isotropic and very material selectively.

With *sputter etching (ion milling)*, the material is eroded physically by inert gas ions accelerated on the substrate.

RIE (Reactive Ion Etching) represents a combination of physical and chemical erosion: Here, chemically reactive radical is formed in plasma and accelerated towards the substrate.

Criteria with Dry Etching

The *etching rate* is defined by the eroded thickness of the material to be etched per time.

The *selectivity* is the ratio of the etching rate of two materials that are simultaneously exposed to the etching. This can be, for example, the photoresist structures of the etching mask, as well as the material to be etched, but also two vertically stacked materials that are to be etched in succession.

The *anisotropy* describes the ratio of etch rates perpendicular and parallel to the substrate surface. The more isotropic the etching process is, the stronger the etching mask is underetched during the etching process.

The *uniformity* describes the homogeneity of the etching rate over the entire substrate.

Plasma Etching of Si and SiO₂

Typical Etching Gases

Typical etching gases for the etching of SiO₂ are fluorinated hydrocarbons (C_xF_yH_z) such as tetrafluoromethane (CF₄)₂. The basic reactions in plasma and on the SiO₂ to be etched are:

(1) Formation of F-radicals through electron impacts: $e + CF_4 \rightarrow CF_3 + F + e$

(2) Formation of volatile Si compounds: $SiO_2 + 4 F \rightarrow SiF_4 + O_2$

Typical etching gases for etching of Si are chlorinated and fluorinated carbon compounds (C_xF_yCL_z), again using the example of tetrafluoromethane:

(1) Formation of F-radicals through electron impacts: $e + CF_4 \rightarrow CF_3 + F + e$

(2) Formation of volatile Si compounds: $Si + 4 F \rightarrow SiF_4$

Adjustment of the Required Etching Rates Ratio Si : SiO₂

The addition of oxygen increases via the reaction $CF_3 + O \rightarrow COF_2 + F$ the concentration of fluorine radicals in the plasma with the following consequences:

- Via the reaction $Si + 4 F \rightarrow SiF_4$ increases the etching rate of silicon to a maximum with a percentage of approx. 12% O₂ in CF₄.
- Via the reaction $SiO_2 + 4 F \rightarrow SiF_4 + O_2$, the etching rate of SiO₂ increases with a maximum of approximately 20% O₂ in CF₄.
- Via O₂ combustion, an existing resist mask is eroded more strongly

The addition of hydrogen to the process gas

- reduces the concentration of fluorine radicals in the plasma via the reaction $H + F \rightarrow HF$ and lowers the etching rate, however, for Si more than for SiO₂.
- leads to the chemically very inert fluorinated polymer deposition on Si surfaces via the reaction $CF_4 + H + Si \rightarrow CH_xF_y$ thus stopping the etching of silicon.

Deep Reactive Ion Etching: The "Bosch Process"

The so-called *Bosch Process* lends itself to the dry chemical etching of structures with steep sidewalls and a very high aspect ratio.

Alternating anisotropic Si etching and the formation of a fluorinated polymer layer (which is inert against the plasma) on the etched sidewalls as well as the sidewalls of the resist structures allows aspect ratios > 50, Si etching rates > 10 µm/min, etching rate ratios > 450 (Si : SiO₂) and > 150 (Si : photoresist).

Plasma Etching of Certain Metals

Aluminium

Aluminium can be etched using gases such as hydrogen bromide (HBr) or chlorine-containing gases such as under the formation of sufficiently volatile compounds of aluminium bromide (AlBr₃) or aluminium chloride (AlCl₃).

Tungsten

Tungsten is etched with fluorine-containing gases with the formation of volatile tungsten hexafluoride (WF₆), the densest known gas under standard conditions.

Titanium

Due to the very low vapour pressures of titanium chloride (TiCl₄) and titanium fluoride (TiF₃), pure plasma processes with accordingly halogenated process gases are not suitable for the dry etching of titanium which is why argon is usually added to increase the erosion with sputter etching.

Copper, Silver, and Gold

These metals do not form sufficiently volatile halides for adequately high plasma etching rates at temperatures below 150°C. With the help of hydrogenous process gases however (unstable) hydrides of the metals can form, which via ion or photon-assisted processes can be desorbed from the surface at etching rates of a few nm/min.

Photoresist Processing Requirements

Vertical Resist Sidewalls

For the steepest possible resist profiles, a high-contrast, photoresist, as well as process parameters optimised for high contrast are required, i.e.

- depending on the desired resist film thickness and required thermal stability of the AZ[®] 701 MiR for resist film thicknesses below 1 µm, the AZ[®] ECI 3000 series for 1 - 3 µm resist film thickness, or AZ[®] 9260 for even thicker layers,
- the reduction of the dark erosion and maintenance of a possible high development rate of positive

resists via, among other things, optimised softbake parameters, and

- the use of a highly selective, i.e. optimally diluted developer such as the MIF developers AZ[®] 326 and AZ[®] 726 or the AZ[®] 400K or AZ[®] 351B in a sufficiently high dilution.

Resist Lenses

If ellipsoid resist structures in the substrate are to be transferred, a normally processed resist profile with a rectangular cross-section is usually softened by heating via the softening temperature of the resist. For this process, all positive resists are suitable. The series AZ[®] 1500, AZ[®] 4500 and 9200 have a relatively low softening temperature of approx. 100 - 110 °C.

Removal of the Photoresist Mask after Etching

All standard strippers are generally suitable to remove the resist mask after dry etching. In case of increased temperatures during dry etching, possibly supported by the deep UV background radiation from the plasma, the resist structures can cross-link near their surface. If the removability of the resist mask suffers after the etching process, the measures listed in the following section can be applied against excessive heating. Ultrasonic treatment during stripping also supports removal of the resist structures.

For highly cross-linked positive resists which can not be removed with standard removers, the high-performance stripper TechniStrip[®] P1316 is recommended for positive resists or the TechniStrip[®] NI555 for many Novolak based negative resists such as the AZ[®] nLOF 2000 series.

Measures Against the Thermal Softening of Resist Structures

Heat development during etching can soften the edges of the used photoresist mask which is transferred to the substrate during dry etching. Possible remedial measures are

- an optimised heat coupling of the substrate to its holder (e.g. some drops of turbo pump oil for proper heat transfer from strained, curved substrates)
- a sufficiently high heat buffer (massive substrate holder construction) or
- heat removal (e.g. black anodised aluminium as rear infrared radiator) from the substrate holder
- a reduced deposition rate and/or a multi-stage deposition with cooling interval(s) in between or
- a thermally more stable photoresist like the AZ[®] 701 MiR or the AZ[®] ECI 3000 series
- a sufficient softbake to minimise the residual solvent content.

Measures Against Bubble Formation in the Resist Layer during Dry Etching

Appearance

Sometimes, bubbles in the resist or even a foam-like resist appearance is observed after dry-etching. In most cases, nitrogen or evaporating solvent or water is the reason for this behaviour.

Evaporation of Residual Solvents

Another possible source of vapour bubbles is water which has penetrated during development in the resist film and can be evaporated after development with another baking. In this case, a baking step after development at approx. 80 - 100°C (always below the resist softening point!) helps reduce the water concentration and a thermal deformation of the resist structures.

Evaporation of Water

An insufficient softbake (too short/too cool) may cause the evaporation of the remaining solvent from the resist forming bubbles.

Nitrogen Formation

The developed resist structures of DNQ-based positive resists are still photo-active and can be exposed by the short-wave thermal or recombination radiation from plasma forming larger amounts of nitrogen. To ensure all photoinitiator has been converted and all nitrogen has been released from the resist film before the dry etch process, we recommend a flood exposure without mask, followed by a delay to out-

gas the nitrogen formed before the substrate is introduced to the dry etching.

Image reversal resists in image reversal mode are no longer photoactive after development and negative resists don't release nitrogen during exposure, so these resists are not affected by this problem.

Our Photoresists: Application Areas and Compatibilities

Recommended Applications ¹		Resist Family	Photoresists	Resist Film Thickness ²	Recommended Developers ³	Recommended Removers ⁴
Positive	Improved adhesion for wet etching, no focus on steep resist sidewalls	AZ [®] 1500	AZ [®] 1505	≈ 0.5 μm	AZ [®] 351B, AZ [®] 326 MIF, AZ [®] 726 MIF, AZ [®] Developer	AZ [®] 100 Remover, TechniStrip [®] P1316, TechniStrip [®] P1331
			AZ [®] 1512 HS	≈ 1.0 - 1.5 μm		
			AZ [®] 1514 H	≈ 1.2 - 2.0 μm		
			AZ [®] 1518	≈ 1.5 - 2.5 μm		
	AZ [®] 4500	AZ [®] 4533	≈ 3 - 5 μm	AZ [®] 400K, AZ [®] 326 MIF, AZ [®] 726 MIF, AZ [®] 826 MIF		
		AZ [®] 4562	≈ 5 - 10 μm			
	AZ [®] P4000	AZ [®] P4110	≈ 1 - 2 μm	AZ [®] 400K, AZ [®] 326 MIF, AZ [®] 726 MIF, AZ [®] 826 MIF		
AZ [®] P4330		≈ 3 - 5 μm				
AZ [®] P4620	≈ 6 - 20 μm					
AZ [®] P4903	≈ 10 - 30 μm					
AZ [®] PL 177	AZ [®] PL 177	≈ 3 - 8 μm	AZ [®] 351B, AZ [®] 400K, AZ [®] 326 MIF, AZ [®] 726 MIF, AZ [®] 826 MIF			
Spray coating	AZ [®] 4999		≈ 1 - 15 μm	AZ [®] 400K, AZ [®] 326 MIF, AZ [®] 726 MIF, AZ [®] 826 MIF		
Dip coating	MC Dip Coating Resist		≈ 2 - 15 μm	AZ [®] 351B, AZ [®] 400K, AZ [®] 326 MIF, AZ [®] 726 MIF, AZ [®] 826 MIF		
Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating	AZ [®] ECI 3000	AZ [®] ECI 3007	≈ 0.7 μm	AZ [®] 351B, AZ [®] 326 MIF, AZ [®] 726 MIF, AZ [®] Developer		
		AZ [®] ECI 3012	≈ 1.0 - 1.5 μm			
		AZ [®] ECI 3027	≈ 2 - 4 μm			
AZ [®] 9200	AZ [®] 9245	≈ 3 - 6 μm	AZ [®] 400K, AZ [®] 326 MIF, AZ [®] 726 MIF			
	AZ [®] 9260	≈ 5 - 20 μm				
Elevated thermal softening point and high resolution for e. g. dry etching	AZ [®] 701 MiR	AZ [®] 701 MiR (14 cPs)	≈ 0.8 μm	AZ [®] 351B, AZ [®] 326 MIF, AZ [®] 726 MIF, AZ [®] Developer		
		AZ [®] 701 MiR (29 cPs)	≈ 2 - 3 μm			
Positive (Chem. amplified)	AZ [®] XT	AZ [®] 12 XT-20PL-05	≈ 3 - 5 μm	AZ [®] 400K, AZ [®] 326 MIF, AZ [®] 726 MIF		
		AZ [®] 12 XT-20PL-10	≈ 6 - 10 μm			
AZ [®] 40 XT	AZ [®] 12 XT-20PL-20	≈ 10 - 30 μm				
	AZ [®] 40 XT	≈ 15 - 50 μm				
AZ [®] IPS 6050		≈ 20 - 100 μm				
Image Re-verseal	AZ [®] 5200	AZ [®] 5209	≈ 1 μm	AZ [®] 351B, AZ [®] 326 MIF, AZ [®] 726 MIF		
		AZ [®] 5214	≈ 1 - 2 μm			
	TI	TI 35ESX	≈ 3 - 4 μm			
TI xLift-X		≈ 4 - 8 μm				
Negative (Cross-linking)	AZ [®] nLOF 2000	AZ [®] nLOF 2020	≈ 1.5 - 3 μm	AZ [®] 326 MIF, AZ [®] 726 MIF, AZ [®] 826 MIF		
		AZ [®] nLOF 2035	≈ 3 - 5 μm			
	AZ [®] nLOF 2070	≈ 6 - 15 μm				
	AZ [®] nLOF 5500	AZ [®] nLOF 5510	≈ 0.7 - 1.5 μm	TechniStrip [®] NI555, TechniStrip [®] NF52, TechniStrip [®] MLO 07		
Improved adhesion, steep resist sidewalls and high aspect ratios for e. g. dry etching or plating	AZ [®] nXT	AZ [®] 15 nXT (115 cPs)	≈ 2 - 3 μm	AZ [®] 326 MIF, AZ [®] 726 MIF, AZ [®] 826 MIF		
		AZ [®] 15 nXT (450 cPs)	≈ 5 - 20 μm			
AZ [®] 125 nXT		≈ 20 - 100 μm	AZ [®] 326 MIF, AZ [®] 726 MIF, AZ [®] 826 MIF			

¹ In general, almost all resists can be used for almost any application. However, the special properties of each resist family makes them specially suited for certain fields of application.
² Resist film thickness achievable and processable with standard equipment under standard conditions. Some resists can be diluted for lower film thicknesses; with additional effort also thicker resist films can be achieved and processed.
³ Metal ion free (MIF) developers are significantly more expensive, and reasonable if metal ion free development is required.

Our Developers: Application Areas and Compatibilities

Inorganic Developers

(typical demand under standard conditions approx. 20 L developer per L photoresist)

AZ[®] Developer is based on sodium phosphate and –metasilicate, is optimized for minimal aluminum attack and is typically used diluted 1 : 1 in DI water for high contrast or undiluted for high development rates. The dark erosion of this developer is slightly higher compared to other developers.

AZ[®] 351B is based on buffered NaOH and typically used diluted 1 : 4 with water, for thick resists up to 1 : 3 if a lower contrast can be tolerated.

AZ[®] 400K is based on buffered KOH and typically used diluted 1 : 4 with water, for thick resists up to 1 : 3 if a lower contrast can be tolerated.

AZ[®] 303 specifically for the AZ[®] 111 XFS photoresist based on KOH / NaOH is typically diluted 1 : 3 - 1 : 7 with water, depending on whether a high development rate, or a high contrast is required

Metal Ion Free (TMAH-based) Developers

(typical demand under standard conditions approx. 5 - 10 L developer concentrate per L photoresist)

AZ[®] 326 MIF is 2.38 % TMAH- (TetraMethylAmmoniumHydroxide) in water.

AZ[®] 726 MIF is 2.38 % TMAH- (TetraMethylAmmoniumHydroxide) in water, with additional surfactants for rapid and uniform wetting of the substrate (e. g. for puddle development)

AZ[®] 826 MIF is 2.38 % TMAH- (TetraMethylAmmoniumHydroxide) in water, with additional surfactants for rapid and uniform wetting of the substrate (e. g. for puddle development) and other additives for the removal of poorly soluble resist components (residues with specific resist families), however at the expense of a slightly higher dark erosion.

Our Removers: Application Areas and Compatibilities

AZ[®] 100 Remover is an amine solvent mixture and standard remover for AZ[®] and TI photoresists. To improve its performance, AZ[®] 100 remover can be heated to 60 - 80°C. Because the AZ[®] 100 Remover reacts highly alkaline with water, it is suitable for this with respect to sensitive substrate materials such as Cu, Al or ITO only if contamination with water can be ruled out..

TechniStrip[®] P1316 is a remover with very strong stripping power for Novolak-based resists (including all AZ[®] positive resists), epoxy-based coatings, polyimides and dry films. At typical application temperatures around 75°C, TechniStrip[®] P1316 may dissolve cross-linked resists without residue also, e.g. through dry etching or ion implantation. TechniStrip[®] P1316 can also be used in spraying processes. For alkaline sensitive materials, TechniStrip[®] P1331 would be an alternative to the P1316. Nicht kompatibel mit Au oder GaAs.

TechniStrip[®] P1331 can be an alternative for TechniStrip[®] P1316 in case of alkaline sensitive materials. TechniStrip[®] P1331 is not compatible with Au or GaAs.

TechniStrip[®] NI555 is a stripper with very strong dissolving power for Novolak-based negative resists such as the AZ[®] 15 nXT and AZ[®] nLOF 2000 series and very thick positive resists such as the AZ[®] 40 XT. TechniStrip[®] NI555 was developed not only to peel cross-linked resists, but also to dissolve them without residues. This prevents contamination of the basin and filter by resist particles and skins, as can occur with standard strippers. TechniStrip[®] NI555 is not compatible with Au or GaAs.

TechniClean[™] CA25 is a semi-aqueous proprietary blend formulated to address post etch residue (PER) removal for all interconnect and technology nodes. Extremely efficient at quickly and selectively removing organo-metal oxides from Al, Cu, Ti, TiN, W and Ni.

TechniStrip[™] NF52 is a highly effective remover for negative resists (liquid resists as well as dry films). The intrinsic nature of the additives and solvent make the blend totally compatible with metals used throughout the BEOL interconnects to WLP bumping applications.

TechniStrip[™] Micro D2 is a versatile stripper dedicated to address resin lift-off and dissolution on negative and positive tone resist. The organic mixture blend has the particularity to offer high metal and material compatibility allowing to be used on all stacks and particularly on fragile III/V substrates for instance.

TechniStrip[™] MLO 07 is a highly efficient positive and negative tone photoresist remover used for IR, III/V, MEMS, Photonic, TSV mask, solder bumping and hard disk stripping applications. Developed to address high dissolution performance and high material compatibility on Cu, Al, Sn/Ag, Alumina and common organic substrates.

Our Wafers and their Specifications

Silicon-, Quartz-, Fused Silica and Glass Wafers

Silicon wafers are either produced via the Czochralski- (CZ-) or Float zone- (FZ-) method. The more expensive FZ wafers are primarily reasonable if very high-ohmic wafers (> 100 Ohm cm) are required.

Quartz wafers are made of monocrystalline SiO₂, main criterion is the crystal orientation (e. g. X-, Y-, Z-, AT- or ST-cut)

Fused silica wafers consist of amorphous SiO₂. The so-called JGS2 wafers have a high transmission in the range of ≈ 280 - 2000 nm wavelength, the more expensive JGS1 wafers at ≈ 220 - 1100 nm.

Our glass wafers, if not otherwise specified, are made of borosilicate glass.

Specifications

Common parameters for all wafers are diameter, thickness and surface (1- or 2-side polished). Fused silica wafers are made either of JGS1 or JGS2 material, for quartz wafers the crystal orientation needs to be defined. For silicon wafers, beside the crystal orientation (<100> or <111>) the doping (n- or p-type) as well as the resistivity (Ohm cm) are selection criteria.

Prime-, Test-, and Dummy Wafers

Silicon wafers usually come as „Prime-grade“ or „Test-grade“, latter mainly have a slightly broader particle specification. „Dummy-Wafers“ neither fulfill Prime- nor Test-grade for different possible reasons (e. g. very broad or missing specification of one or several parameters, reclaim wafers, no particle specification) but might be a cheap alternative for e. g. resist coating tests or equipment start-up.

Our Silicon-, Quartz-, Fused Silica and Glass Wafers

Our frequently updated wafer stock list can be found here: [è www.microchemicals.com/products/wafers/waferlist.html](http://www.microchemicals.com/products/wafers/waferlist.html)

Further Products from our Portfolio

Plating

Plating solutions for e. g. gold, copper, nickel, tin or palladium: [è www.microchemicals.com/products/electroplating.html](http://www.microchemicals.com/products/electroplating.html)

Solvents (MOS, VLSI, ULSI)

Acetone, isopropyl alcohol, MEK, DMSO, cyclopentanone, butylacetate, ... [è www.microchemicals.com/products/solvents.html](http://www.microchemicals.com/products/solvents.html)

Acids and Bases (MOS, VLSI, ULSI)

Hydrochloric acid, sulphuric acid, nitric acid, KOH, TMAH, ... [è www.microchemicals.com/products/etchants.html](http://www.microchemicals.com/products/etchants.html)

Etching Mixtures

for e. g. chromium, gold, silicon, copper, titanium, ... [è www.microchemicals.com/products/etching_mixtures.html](http://www.microchemicals.com/products/etching_mixtures.html)

Further Information

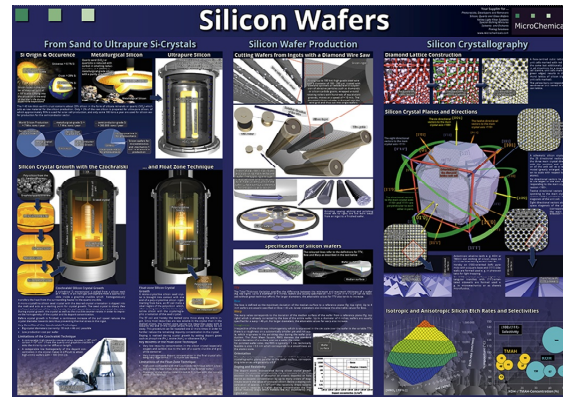
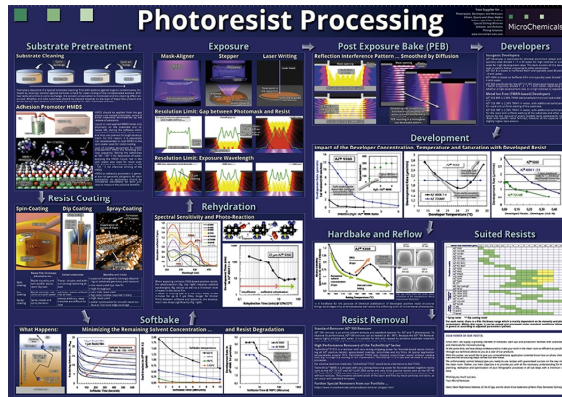
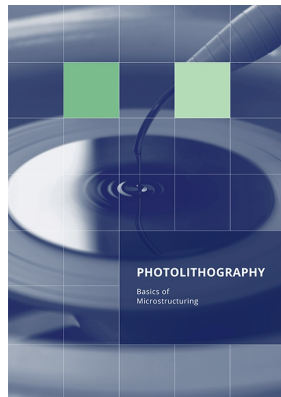
Technical Data Sheets:

www.microchemicals.com/downloads/product_data_sheets/photoresists.html

Material Safety Data Sheets (MSDS):

www.microchemicals.com/downloads/safety_data_sheets/msds_links.html

Our Photolithography Book and -Posters



We see it as our main task to make you understand all aspects of microstructuring in an application-oriented way.

At present, we have implemented this claim with our book **Photolithography** on over 200 pages, as well as attractively designed DIN A0 posters for your office or laboratory.

We will gladly send both of these to you free of charge as our customer (if applicable, we charge shipping costs for non-European deliveries):

www.microchemicals.com/downloads/brochures.html

www.microchemicals.com/downloads/posters.html

Thank you for your interest!

Disclaimer of Warranty & Trademarks

All information, process descriptions, recipes, etc. contained in this document are compiled to the best of our knowledge. Nevertheless, we can not guarantee the correctness of the information. Particularly with regard to the formulations for chemical (etching) processes we assume no guarantee for the correct specification of the components, the mixing conditions, the preparation of the batches and their application.

The safe sequence of mixing components of a recipe usually does not correspond to the order of their listing. We do not warrant the full disclosure of any indications (among other things, health, work safety) of the risks associated with the preparation and use of the recipes and processes. The information in this book is based on our current knowledge and experience. Due to the abundance of possible influences in the processing and application of our products, they do not exempt the user from their own tests and trials. A guarantee of certain properties or suitability for a specific application can not be derived from our data. As a matter of principle, each employee is required to provide sufficient information in advance in the appropriate cases in order to prevent damage to persons and equipment. All descriptions, illustrations, data, conditions, weights, etc. can be changed without prior notice and do not constitute a contractually agreed product characteristics. The user of our products is responsible for any proprietary rights and existing laws.

Merck, Merck Performance Materials, AZ, the AZ logo, and the vibrant M are trademarks of Merck KGaA, Darmstadt, Germany

MicroChemicals GmbH
Nicolai-Otto-Str. 39
89079, Ulm
Germany

Fon: +49 (0)731 977 343 0
Fax: +49 (0)731 977 343 29
e-Mail: info@microchemicals.net
Internet: www.microchemicals.net