SUBSTRATE PREPARATION

The cleaning from chemical impurities and particles, the heating for the desorption of water, and a treatment with an adhesion promoter are all part of the preparation of the substrate for the resist coating.

None of these measures described in the following sections is absolutely essential for all litho processes. Each step should be considered for each individual process and, if necessary, adjusted.

Cleaning the Substrate

Adsorbed Water

For clean substrates, a baking out is recommended at approx. 120°C for a few minutes for the desorption of water molecules usually adsorbed on surfaces exposed to air humidity. This step can, in principle, be skipped with if the substrates have been cleaned immediately prior to this either with isopropanol or heated to above 100°C in another process step (metallisation, oxidation, etc.).

To maximise adhesion to oxidised surfaces (native or thermally oxidised Si, quartz, glass, most metals), the baking out temperature can be increased to above 140°C. In this process, the OH bonds generally present on oxidised surfaces exposed to air humidity for a while, are broken, the hydrophobic character and thus the wetting and adhesion of the resist increases further.

Depending on the amount of relative humidity and substrate material, a water film can again adsorb onto the substrate surface after a short time. Therefore, the subsequent resist coating should be carried out as soon as possible after baking out, but not before cooling of the substrate down to room temperature.

Particles

In order to remove particles, rinsing in isopropanol (purity VLSI or better) is recommended. Subsequent rinsing in DI water is not necessary and can, in the case of insufficiently clean DI water (e. g. organic impurities), destroy the cleaning effect of isopropanol.

Organic Impurities

For substrates contaminated with organic impurities, two-stage substrate cleaning with acetone is recommended to remove organic impurities, followed by isopropanol, which removes contaminated acetone before it can form streaks on the substrate. Again, subsequent rinsing in DI water is neither necessary nor recommended.

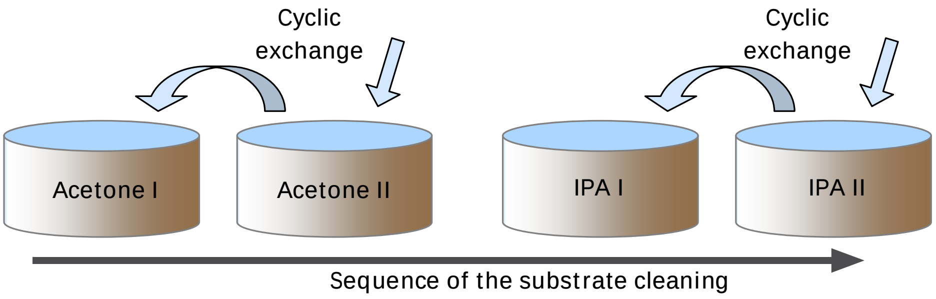


Fig. 46: An efficient, solvent-saving method of substrate cleaning of particles and organic impurities

In the case of strong impurities (e.g. resist residues) or larger series of substrates, it is advisable to have two acetone and isopropanol steps following each other in order to minimise the carry-over of impurities. A "cascadic" mode of operation (acetone vessel I → acetone vessel II → isopropanol vessel I → isopropanol vessel II) is suitable for minimising solvent consumption. In certain cycles, the more heavily contaminated solvent (I) is then disposed of and replaced with the cleaner one (II), which is then replaced by a fresh solvent.

Piranha Etching and RCA Cleaning

In the case of stronger impurities with organic or metallic substances as well as before high-temperature processes, a Piranha etching with subsequent RCA cleaning is recommended for silicon wafers, which runs in the following order:

- In Piranha solution ($H_2O_2 : H_2SO_4 = 1 : 2$) SiO_2 grows on (in) the Si

- After removal of the SiO_2 in 1-5% HF followed by *RCA-1* (H_2O_2 : NH_4OH : H_2O = 1 : 1 : 5) at 70 - 75°C for 10 minutes
- The approximately 10 - 15 Å SiO_2 is removed in 1-5% HF
- Then the *RCA-2* (HCl) follows : H_2O_2 : H_2O = 1 : 1 : 8) at about 80°C for 10 minutes, optionally followed by a dip in 1-5% HF to remove the grown SiO_2

The quantities of all substances refer to their standard concentrations.

Usage of Adhesion Promoters

Mechanism of Action

While the purpose of the substrate cleaning is the removal of all substances not belonging to the substrate, an adhesion promoter should modify the substrate surface itself with regard to an optimised resist wetting and adhesion.

SiO_2 in the form of quartz, glass or silicon with (native) oxide as well as most base metals form polar OH bonds on their surface after a sufficiently long exposure to atmospheric humidity. The substrate in question is thereby hydrophilic ("water loving") and therefore exhibits a poor affinity for the non-polar or low polar resin molecules of the photoresist.

In order to make such a substrate surface hydrophobic (water-repellent and thus photoresist-attractive), non-polar molecules of adhesion promoters such as HMDS or TI Prime can be chemically bound on it.

HMDS

HMDS (HexaMethylDiSilazane) is an adhesion promoter commonly used on semiconductor surfaces, its simplified reaction mechanism shown in Fig. 48: HMDS bonds on oxygen-free surfaces with its Si atom to the oxygen atoms (if necessary with the breakdown of OH groups) of oxidised substrate surfaces, releasing ammonia.

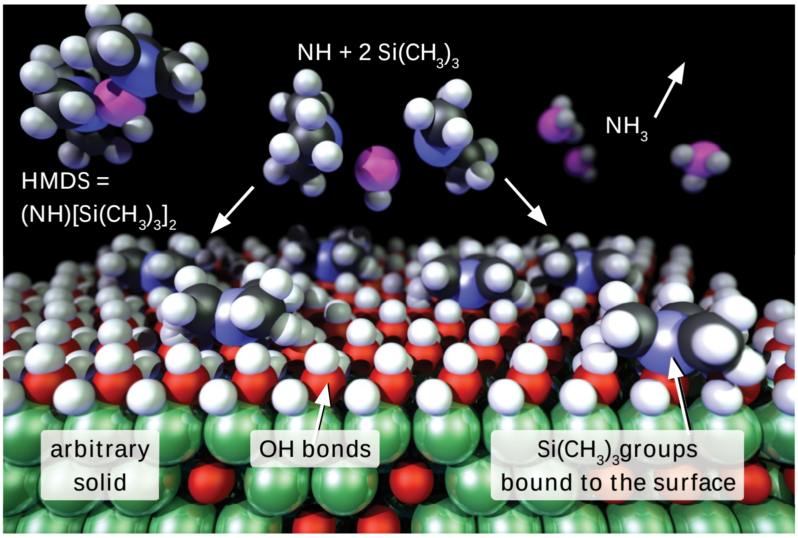


Fig. 48: HMDS bonds to surfaces with OH bindings under NH_3 splitting off

The non-polar methyl groups directed away from the substrate form a hydrophobic surface with correspondingly good resist wetting and adhesion.

Correct Use of HMDS

The right application of HMDS is very important for the result: HMDS vapour transported in a so-called "bubbler" at room temperature by dry nitrogen and passed to the heated (75-120°C) substrate on whose surface HMDS chemically bonds as a monolayer.

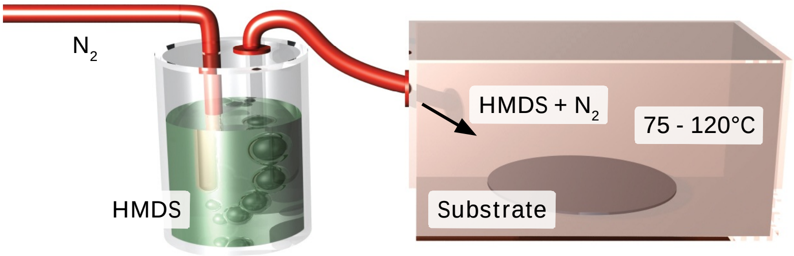


Fig. 47: HMDS is applied on heated substrates via a bubbler (left) from the gas phase when used correctly.

Incorrect Application of HMDS

If, on the other hand, liquid HMDS is spun on, the resulting HMDS layer is bound only physically and can therefore not act adhesion-improving, on the other hand chemically active: After the coating, the ammonia (Fig. 49), which is thermally activated by the softbake splits off from the HMDS and cross-links the resist areas near the substrate and thus suppresses its development.

For this reason, HMDS may not be applied in the spin coaters with which coatings are also done: Due to the slow evaporation of HMDS, HMDS vapours penetrate into the resist film a long time later during subsequent coatings and can partially cross-link them thermally activated during the softbake. This reduces the development rate, which means that the resist profile as well as the attainable resolution suffer.

If HMDS can only be applied by means of spin-coating equipment, some things should be considered: A desorption of water from the substrate surface by baking the substrates at 100-120°C before the application of HMDS, a subsequent thermal activation (chemical bonding of HMDS to the substrate surface) through a baking step at 100-120°C, and a strict spatial separation of the HMDS application and resist coating to avoid a cross-contamination by HMDS fumes.

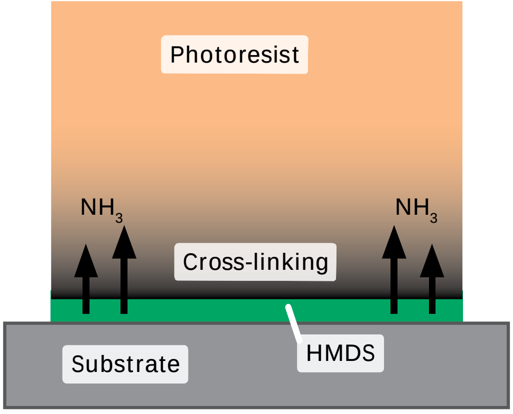


Fig. 49: If HMDS is applied in liquid form, only the physically-bound HMDS releases ammonia during the softbake which can cross-link in the resist which is proximity of the substrate.

TI PRIME

The application of TI PRIME, a highly dilute organic titanium compound, proves to be simpler than the HMDS application: TI PRIME is spun on, whereby through the high dilution of the active substance usually less than one monolayer remains on the substrate. The adhesion promoter is activated in a subsequent baking step at 110 - 120°C for 1 - 2 minutes, followed by the application of the coating as soon as possible after cooling of the substrate down to room temperature.

It should be noted that, under normal conditions, the adhesion-promoting layer formed on the one hand produces a slight yellow colour on transparent substrates, and on the other hand is chemically very stable. This stability can be an etching barrier for HF-free etching, the colouration be problematic in optical components. In either case, it may be useful to dilute TI PRIME (approximately 1 : 2 to 1: 20 with PGMEA as a solvent), or to switch to other adhesion promoters such as HMDS.

The Meaning and Limits of the Use of Adhesion Promoters

Because the use of an adhesion promoter requires several additional process steps, on the other hand, through its influence on the further resist processing and the lithographic processes carried out by means of the resist structures, it may possibly render them less reproducible, the need for adhesion promoters should be questioned with regard to two criteria:

Can an optimised substrate cleaning and/or photoresist processing be sufficient for the adhesion of resists without the additional application of adhesion promoters?

Under the given circumstances (substrate material, photoresist), can the adhesion promoter improve the resist adhesion at all?

Special Problems Regarding Resist Adhesion

After HF Etching

After the SiO_2 etching with hydrofluoric acid, the resist adhesion depends heavily on whether the oxide is completely removed: If this is the case, the hydrogen-passivated Si surface exhibits very good resist adhesion for some time.

Incomplete oxide etching leaves a highly hydrophilic surface with very poor resist wetting and adhesion, which can only be restored by continued, complete oxide etching or baking at high temperatures (about 700°C).

On Metals

Base metals such as Al, Cr and especially Ti show a generally very good resist adhesion.

On noble metals without native oxide formation such as gold or platinum, organic adhesion promoters unfortunately show little or no improvement in the adhesion of the resist since the adhesion promoters cannot chemically bond to the surface. The use of resists optimised for maximum adhesion to metals, such as the AZ® 111 XFS or AZ® 1514 H, can be helpful. A metallic adhesion promoter such as a 10 - 20 nm thick titanium or chromium layer promises a clear adhesion improvement.

Substrates metallised on both sides (e.g. Ag and Al on the front or rear side) form a galvanic element in aqueous solutions. On the one side, gaseous hydrogen can form, as a result of which an overlying resist film is lifted off. In this case, a closed protective resist film is necessary on the other side of the substrate in order to prevent the charge exchange with the liquid (= the electrolyte).

Resist Adhesion and Contact Angle Measurement

Definition of the Contact Angle

The contact angle is the angle between the substrate surface and the tangent of the droplet surface of a droplet sitting on the substrate, at its contact point on the substrate (Fig. 50).

In theory, the contact angle Θ is derived as follows from the free surface energy ρ_S of the solid, the surface tension ρ_L of the liquid, and the interfacial energy ρ_{SL} between the liquid and the solid:

$$\cos\theta = \frac{\rho_S - \rho_{SL}}{\rho_L}$$

The better the liquid of the droplet wets the substrate, the smaller the contact angle. In the case of water as a liquid, a substrate surface is considered to be *hydrophilic* for $\Theta < 90°$, as *hydrophobic* at $\Theta > 90°$, and as *super-hydrophobic* at $\Theta > 160°$ (Fig. 50).

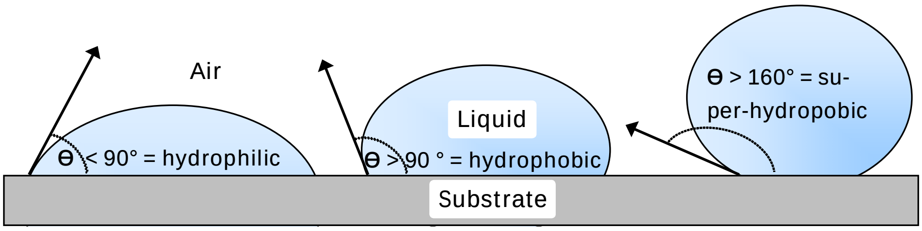


Fig. 50: The contact angle is the angle between the substrate level and the tangent of a liquid droplet at its contact point with the substrate.

Motivation

In many processes of microstructuring with photoresist masks, an optimised resist adhesion is crucial in order to avoid, for example, lateral etching or resist peeling during wet-chemical processes (e.g. etching or electroplating). Since a good adhesion also corresponds to a good wetting of the resist film, contact angle measurements are suitable for controlling the resist adhesion on a particular substrate, whereby the substrate pretreatment can be optimised.

Measurement of Contact Angle

The use of resist droplets on the respective substrate for contact angle measurement is of little help, since hereby the wetting of the solvent on the substrate is determined primarily without being able to make the desired statement about the adhesion of the dried resist itself. However, no droplets can be formed from the solvent-free resist.

Therefore, a trick is used and, as shown schematically in Fig. 51: The two contact angles of an (theoretically) arbitrary liquid are determined on the uncoated substrate (Θ_1) and on the other hand on the soft resist film (Θ_2). The water serves suitability as the liquid since, on the one hand, unlike organic solvents, it does not attack the photoresist film during the measurement, and on the other hand, it is slowly evaporated to allow a reproducible measurement.

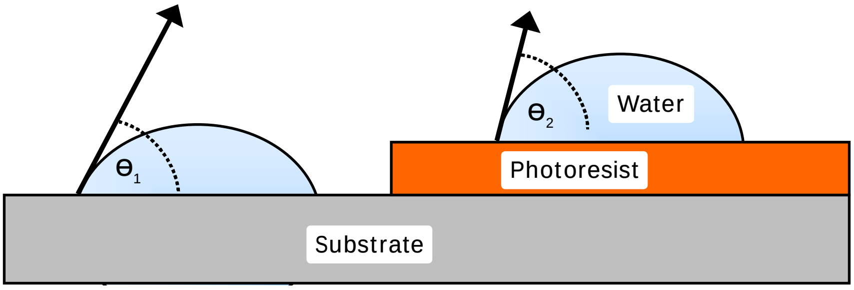


Fig. 51: The contact angle is the angle between the substrate level and tangent of a liquid droplet at its contact point with the substrate.

The resist adhesion is optimal in this case if i) both contact angles are of the same size and ii) are between 45 and 60°, i.e:

$$\Theta_1 = \Theta_2 = 45 - 60°$$

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)	Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating	AZ® XT	AZ® 12 XT-20PL-05	≈ 3 - 5 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF	AZ® 100 Remover, TechniStrip® P1316 TechniStrip® P1331
			AZ® 12 XT-20PL-10	≈ 6 - 10 µm		
			AZ® 12 XT-20PL-20	≈ 10 - 30 µm		
			AZ® 40 XT	≈ 15 - 50 µm		
		AZ® IPS 6050		≈ 20 - 100 µm		
Image Re-versal	Elevated thermal softening point and undercut for lift-off applications	AZ® 5200	AZ® 5209	≈ 1 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF	TechniStrip® Micro D2 TechniStrip® P1316 TechniStrip® P1331
			AZ® 5214	≈ 1 - 2 µm		
		TI	TI 35ESX	≈ 3 - 4 µm		
			TI xLift-X	≈ 4 - 8 µm		
Negative (Cross-linking)	Negative resist sidewalls in combination with no thermal softening for lift-off application	AZ® nLOF 2000	AZ® nLOF 2020	≈ 1.5 - 3 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	TechniStrip® NI555 TechniStrip® NF52 TechniStrip® MLO 07
			AZ® nLOF 2035	≈ 3 - 5 µm		
			AZ® nLOF 2070	≈ 6 - 15 µm		
		AZ® nLOF 5500	AZ® nLOF 5510	≈ 0.7 - 1.5 µm		
	Improved adhesion, steep resist side-walls 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	TechniStrip® P1316 TechniStrip® P1331 TechniStrip® NF52 TechniStrip® MLO 07

[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 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 SiO_2, main criterion is the crystal orientation (e. g. X-, Y-, Z-, AT- or ST-cut)

Fused silica wafers consist of amorphous SiO_2. 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

Further Products from our Portfolio

Plating

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

Solvents (MOS, VLSI, ULSI)

Acetone, isopropyl alcohol, MEK, DMSO, cyclopentanone, butylacetate, ... è 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

Etching Mixtures

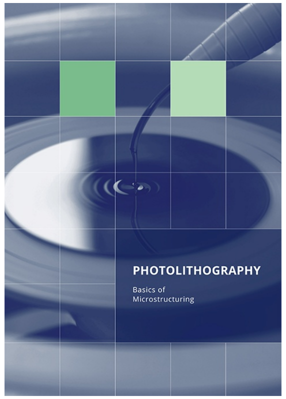
for e. g. chromium, gold, silicon, copper, titanium, ... è www.microchemicals.com/products/etching_mixtures.html

Further Information

Technical Data Sheets: www.microchemicals.com/downloads/product_data_sheets/photoresists.html

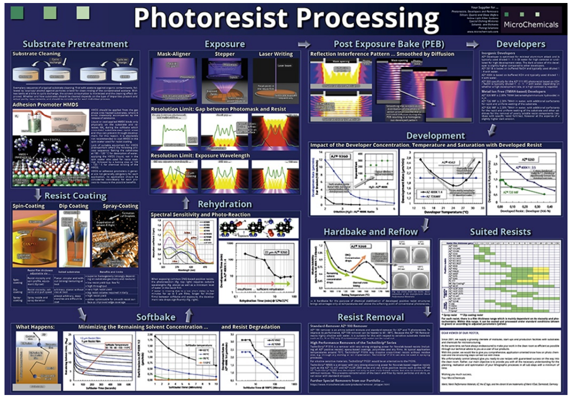
Material Safety Data Sheets (MSDS): www.microchemicals.com/downloads/safety_data_sheets/msds_links.html

Our Photolithography Book and -Posters



PHOTOLITHOGRAPHY

Basics of Microstructuring



Photoresist Processing

MicroChemicals

Substrate Pretreatment

Exposure

Post Exposure Bake (PEB)

Developers

Resist Coating

Rehydration

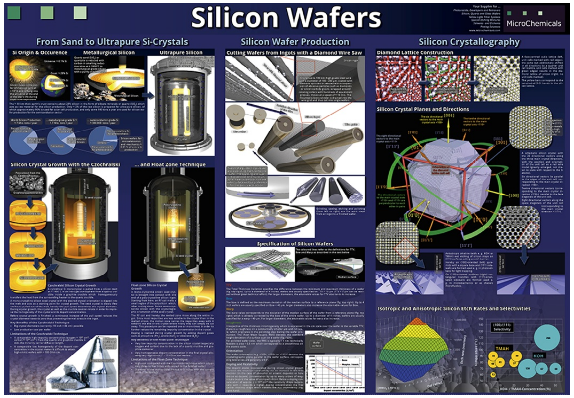
Development

Hardbake and Reflow

Suited Resists

Softbake

Resist Removal



Silicon Wafers

MicroChemicals

From Sand to Ultrapure Si-Crystals

Silicon Wafer Production

Silicon Crystallography

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

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