# SPRAY COATING

*The spray coating of substrates with a photoresist can then be an alternative to spin-coating if the substrate size or its surface does not allow spin-coating with the required homogeneity.*

*This chapter describes the technology of spray coating, the processes between the formation of droplets on the spray head and the finished resist film and provides explanations and answers to frequently asked problems in connection with the spray coating.*

## Basics of Spray Coating

### Basic Principle

In the case of spray coating, the resist film is deposited from atomised photoresist with typical droplet sizes in the µm range. The droplets are formed via, for example, a nitrogen-filled nozzle and / or via ultrasonic atomisation and land on the substrate surface carried by an air or nitrogen flow where they combine to form a closed resist film.

### Possible Advantages

In addition to a very high resist yield (at least theoretically), the spray coating offers the potential to coat arbitrarily shaped substrates in which spin-coating is not technically feasible or does not provide the results required with respect to homogeneity and edge coverage of the resist film over textures.

For example, it is theoretically possible, in the case of textured substrates, to provide the grooves, sidewalls and edges of the textures with a uniform resist film thickness.

### Limitations

In practice, most of the resist droplets land in the exhaust and only a small portion on the substrate. The attainable resist yield achieves typical values of 5 - 15%, which are still significantly greater than with spin-coating.

Due to micro-turbulences above the surface of textured substrates, the resist film is not uniformly thick over the textures, but rather usually thinned at the top edges, and thickened in the grooves near the sidewalls.

The formation of thin (<1 µm) and closed resist films is difficult because the landing sites of the droplets follow a statistical distribution. Thus, a minimum critical droplet density is required to allow the aggregation of the droplets to a closed film.

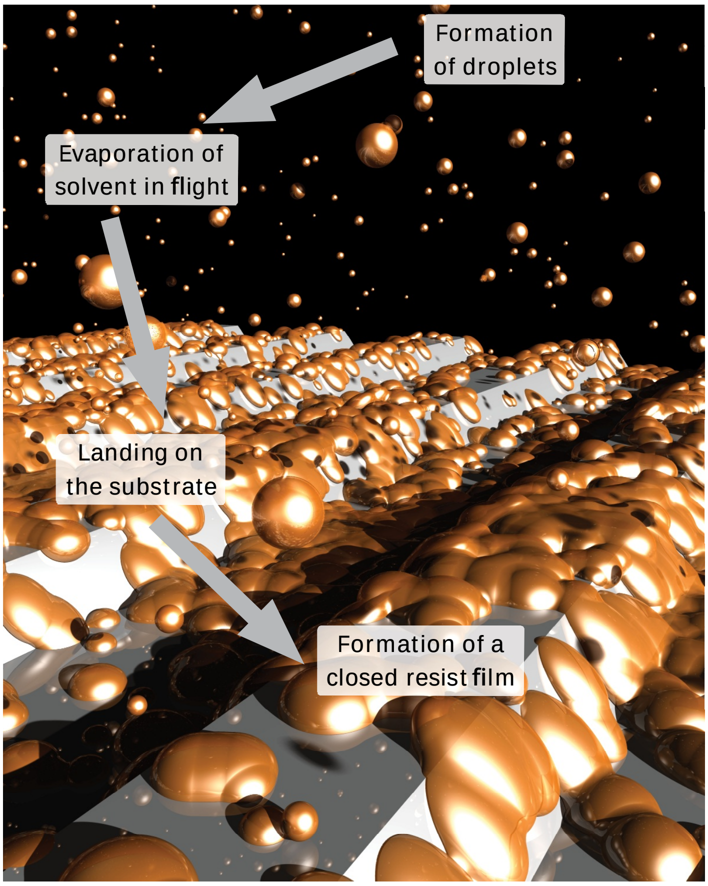



Fig. 60: The schematic way from the atomised resist to a closed film on the substrate

## Atomised Spray Formation

### Equipment

The technically simplest way to produce an atomised spray is the atomisation of the resist from a nozzle as done with conventional airbrush guns. In order to prevent contamination of the resist with particles or atmospheric humidity condensing on the low pressure side of the spray nozzle, it is recommended to use pure nitrogen.

Another possibility is ultrasonic atomisation, in which the resist is atomised via a high-frequency mechanical vibration applied to the resist and is conducted onto the substrate by a carrier gas.

### Resist

Each technology for droplet generation requires a certain low resist viscosity of usually a few cSt. Varying the resist viscosity impacts the droplet generation rate as well as the droplet diameter distribution.

When diluting resists with a solvent, one has to consider possible incompatibilities of certain solvents with the resist, as well as the fact that highly diluted photoresists generally reveal an accelerated ageing of the resist in the diluted state with particle formation as a consequence.

## Processes in Atomised Spray

### Solvent Evaporation

It's important that a certain percentage of the solvent evaporates out of the droplets during flight between spray nozzle and substrate to achieve a sufficient resist edge coverage onto textured substrates: The hereby increased resist viscosity prevents the resist from macroscopically converge on the substrate and withdrawing from the edges of textures. However, the viscosity of the resist film should allow a smoothing of the resist film in the µm-scale.

If, however, too much solvent evaporates during flight, the formation of a closed resist film is inhibited. In the worst case, the droplets lose too much solvent, form resin particles, which not stick to the substrate.

The parameters temperature, droplet velocity (relative to the ambient air) and air solvent vapour saturation as well as the solvent composition and concentration determine the evaporation rate for each droplet as a function of its diameter and its surface solvent concentration. This surface concentration again depends on the temperature and solvent concentration dependant diffusion constant of the solvent from the droplet bulk to its surface.

In practice, the composition of at least two solvents with different vapour pressures (e.g. PGMEA with MEK or Acetone) is used for resist dilution in order to adjust the viscosity for each process.

### Transport of Droplets to The Substrate

The free falling speed of µm-sized spheres in air is very low, for spherical droplets with the density of photoresist far less than 1 mm/s. For a coating, the droplet transport by a carrier gas is therefore required, which is attained by the nitrogen used for the atomisation at the nozzle, in case of ultrasonic atomisation by a corresponding carrier gas flow.

Immediately above the substrate surface to be coated, a laminar flow dominates in part parallel to the surface, in part through a texture-defined turbulent flow, which can make uniform coating of edges and trenches more difficult.

Fig. 62 shows how a closed, smooth resist film forms with time on a smooth substrate (a non-textured silicon wafer) during the spray coating.

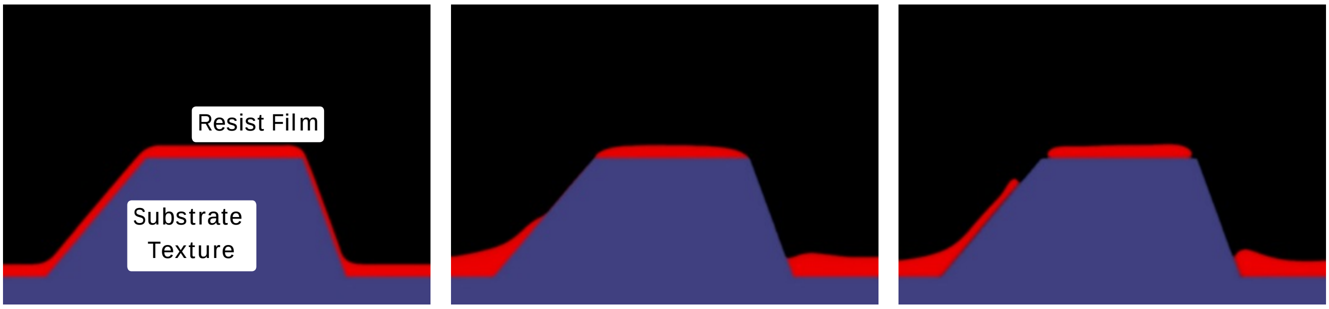



Fig. 61: Modelled cross sections of resist on a textured substrate. The bottom left image reflects optimum edge coverage, while the other two images show what happens if the resist viscosity is too low for too long time (centre) or, respectively, when the resist wetting and adhesion is not optimum (right).

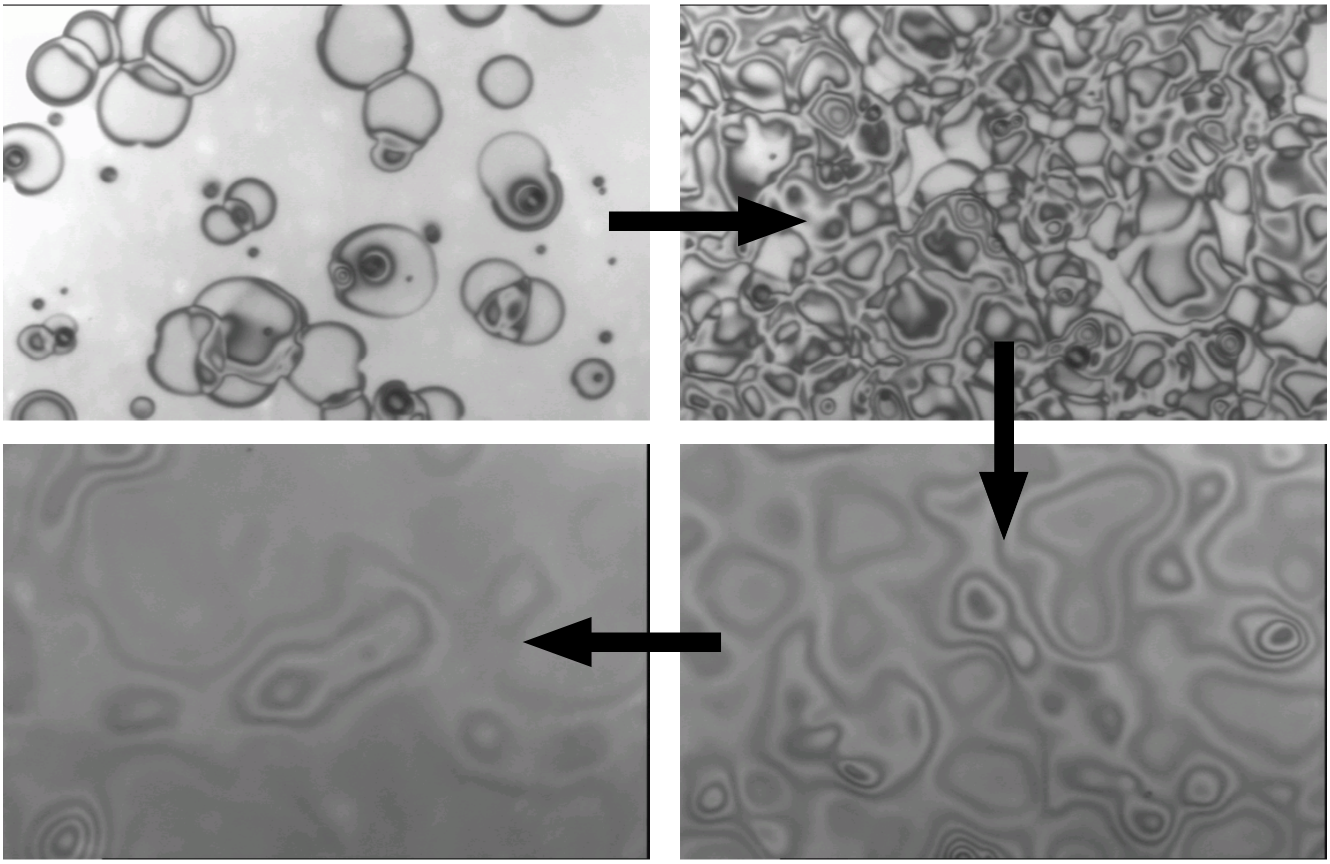


Fig. 62: The figures above show snapshots during the formation of a resist film via spray coating in chronological order from top left clockwise: Stochastically dispersed particles landing on the substrate increasingly overlap and begin to form a closed resist film that begins to smoothen due to the still high residual solvent content.

## Wetting, Edge Coverage and Roughness of the Resist Film

### Wetting

An optimised substrate pretreatment is required to improve the wetting of the resist droplets on the substrate which is a precondition for the formation of a closed resist film.

A good wetting or adhesion can be attained using an optimised substrate pre-treatment.

### Smooth Resist Surface and Optimised Edge Coverage: Always a Compromise

A resist film viscosity that is too low (or, respectively, a remaining solvent concentration that is too high) for a long time causes macroscopic resist flowing thereby reducing the edge coverage of the resist film in the case of textured substrates which can be covered here only very thinly or not at all by the resist. The resist film surface, however, becomes comparably smooth.

An excessively high viscosity of the droplets landing on the substrate (or the already formed resist film) prevents the resist from flowing thereby improving the edge coverage. The resist film surface, however, becomes rather rough - in extreme cases, the droplets keep sticking there in their original form on the substrate where they have landed.

### Parameters for Influencing the Edge Coverage and Smoothness of the Resist Film

In order to find the optimum compromise between a smooth resist film, and (if required), a good edge coverage, the resist film viscosity and its time dependency after the droplets landed onto the substrate has to be adjusted. For this purpose, many parameters can be varied.

An improved edge coverage with the compromise of a tendency toward a less smooth resist film can be attained if the resist droplets landing on the substrate through an accelerated evaporation in flight between the spray head and the substrate are sufficiently highly viscous which is possible via:

- A low initial fraction of high-boiling solvents (such as PGMEA) in the spray resist
- Smaller droplet diameters (e.g. via a higher initial solvent concentration or by adjusting the spray nozzle settings)
- Increasing the distance (and thus the droplet flight time) between the spray nozzle and the substrate surface

Alternatively or in addition an accelerated evaporation from the just-formed resist film can improve the edge coverage via:

- A substrate heated to approx. 40-60°C
- A reduced spray rate gives the growing resist film more time for solvent evaporation

The opposite measures can help to improve the smoothness of the resist film - but at the expense of a tendency towards an inferior edge coverage.

## Suitable Spray Resist

By means of a suitable solvent composition, it is principle possible to apply a spray resist made from any resist, which is why, in the case of the resist selection, one should primarily evaluate which positive, image reversal or negative resists are required with which resolution for which application of the developed resist film.

The optimal composition with high-boiling and low-boiling solvents depends, on the one hand, on the substrate and on the criterion of whether a smooth resist film or maximum edge coverage is most important and on the other hand, on equipment-driven parameters such as the technology used for atomised spray generation, spray rate and the distance between the spray nozzle and the substrate.

With resists such as the AZ® 4999 or the TI spray, there are some ready-to-use spray resists suitable for most applications. Adjustments to the solvent composition for an optimisation of the coating result may nevertheless be advisable. We will gladly advise you.

## 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<br>AZ® 1512 HS<br>AZ® 1514 H<br>AZ® 1518 | ≈ 0.5 µm<br>≈ 1.0 - 1.5 µm<br>≈ 1.2 - 2.0 µm<br>≈ 1.5 - 2.5 µm | AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer | AZ® 100 Remover,<br>TechniStrip® P1316<br>TechniStrip® P1331 |
| | | AZ® 4500 | AZ® 4533<br>AZ® 4562 | ≈ 3 - 5 µm<br>≈ 5 - 10 µm | AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 2026 MIF | |
| | | AZ® P4000 | AZ® P4110<br>AZ® P4330<br>AZ® P4620<br>AZ® P4903 | ≈ 1 - 2 µm<br>≈ 3 - 5 µm<br>≈ 6 - 20 µm<br>≈ 10 - 30 µm | AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 2026 MIF | |
| | | AZ® PL 177 | AZ® PL 177 | ≈ 3 - 8 µm | AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 2026 MIF | |
| | Spray coating | AZ® 4999 | | ≈ 1 - 15 µm | AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 2026 MIF | |
| | Dip coating | MC Dip Coating Resist | | ≈ 2 - 15 µm | AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 2026 MIF | |
| | Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating | AZ® ECI 3000 | AZ® ECI 3007<br>AZ® ECI 3012<br>AZ® ECI 3027 | ≈ 0.7 µm<br>≈ 1.0 - 1.5 µm<br>≈ 2 - 4 µm | AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer | |
| | | AZ® 9200 | AZ® 9245<br>AZ® 9260 | ≈ 3 - 6 µm<br>≈ 5 - 20 µm | AZ® 400K, AZ® 326 MIF, AZ® 726 MIF | |
| | Elevated thermal softening point and high resolution for e. g. dry etching | AZ® 701 MiR | AZ® 701 MiR (14 cPs)<br>AZ® 701 MiR (29 cPs) | ≈ 0.8 µm<br>≈ 2 - 3 µm | AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer | |
| 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<br>AZ® 12 XT-20PL-10<br>AZ® 12 XT-20PL-20<br>AZ® 40 XT | ≈ 3 - 5 µm<br>≈ 6 - 10 µm<br>≈ 10 - 30 µm<br>≈ 15 - 50 µm | AZ® 400K, AZ® 326 MIF, AZ® 726 MIF | AZ® 100 Remover,<br>TechniStrip® P1316<br>TechniStrip® P1331 |
| | | AZ® IPS 6050 | | ≈ 20 - 100 µm | | |
| Image Re-versal | Elevated thermal softening point and undercut for lift-off applications | AZ® 5200 | AZ® 5209<br>AZ® 5214 | ≈ 1 µm<br>≈ 1 - 2 µm | AZ® 351B, AZ® 326 MIF, AZ® 726 MIF | TechniStrip® Micro D2<br>TechniStrip® P1316<br>TechniStrip® P1331 |
| | | TI | TI 35ESX<br>TI xLift-X | ≈ 3 - 4 µm<br>≈ 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<br>AZ® nLOF 2035<br>AZ® nLOF 2070 | ≈ 1.5 - 3 µm<br>≈ 3 - 5 µm<br>≈ 6 - 15 µm | AZ® 326 MIF, AZ® 726 MIF, AZ® 2026 MIF | TechniStrip® NI555<br>TechniStrip® NF52<br>TechniStrip® MLO 07 |
| | | 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)<br>AZ® 15 nXT (450 cPs) | ≈ 2 - 3 µm<br>≈ 5 - 20 µm | AZ® 326 MIF, AZ® 726 MIF, AZ® 2026 MIF | |
| | | | AZ® 125 nXT | ≈ 20 - 100 µm | AZ® 326 MIF, AZ® 726 MIF, AZ® 2026 MIF | TechniStrip® P1316<br>TechniStrip® P1331<br>TechniStrip® NF52<br>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. Not compatible with Au.

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

**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**

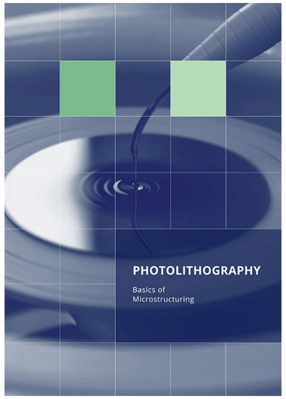
for e. g. chromium, gold, silicon, copper, titanium, ... è www.microchemicals.com/products/etching_mixtures.html

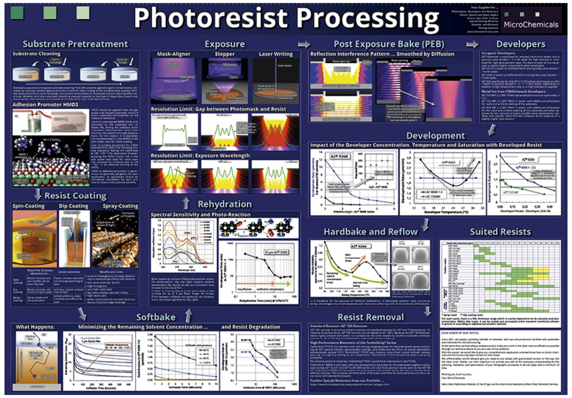
## Further Information

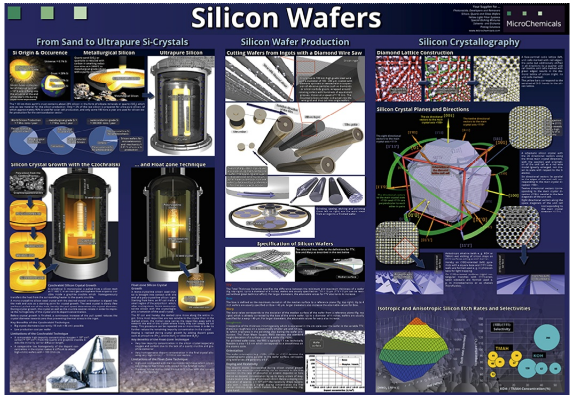
**Technical Data Sheets:** www.microchemicals.com/downloads/product_data_sheets/photoresists.html

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

## Our Photolithography Book and -Posters

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