ION IMPLANTATION WITH PHOTORESIST MASKS

In addition to the patterning techniques such as etching, lift-off or electro-plating, microstructuring can also be realized through the local modification of the electrical properties of existing semiconductor substrates.

A common technique for this is ion implantation, in which certain elements are locally defined incorporated into a material as described in the following chapter.

Basics

Principle

Semiconductors such as silicon alter their electronic properties fundamentally when dopants such as phosphorus or boron are incorporated into the semiconductor crystal even in a very low concentration in the ppm range. Such a targeted "contamination" with elements is usually already carried out during the crystal growth of the substrates in question with the aim of defining the electrical conductivity as spatially homogeneous as possible.

However, for electronic components such as diodes or transistors, it is necessary to spatially modify the conductivity or the conduction type (*p*- or *n*-type) on the µm or nm scale. For this purpose ionised dopants which are accelerated in an electric field are incorporated into the semiconductor via *ion implantation*.

Acceleration Voltage and Ion Velocities

An *n* ionised atom of the mass *M* has the velocity *v* after the run-through of a voltage difference *U* (*acceleration voltage*)

$$v = \sqrt{\frac{2\,n \cdot U \cdot e}{M}}$$

which means for a single ionised comparatively heavy atom such as arsenic after an acceleration voltage of 10 keV which is comparatively low for ion implantation, a speed of about 160 km/s, and for n boron ion accelerated with 500 keV, approximately 3000 km/s (approx. 1% of the light speed), for which the above classical view is still in a good approximation.

Scattering Processes between Ions and Solids

In the substrate, the ions are decelerated by impacts, i.e. electromagnetic interactions with the electrons and atomic nuclei of solids.

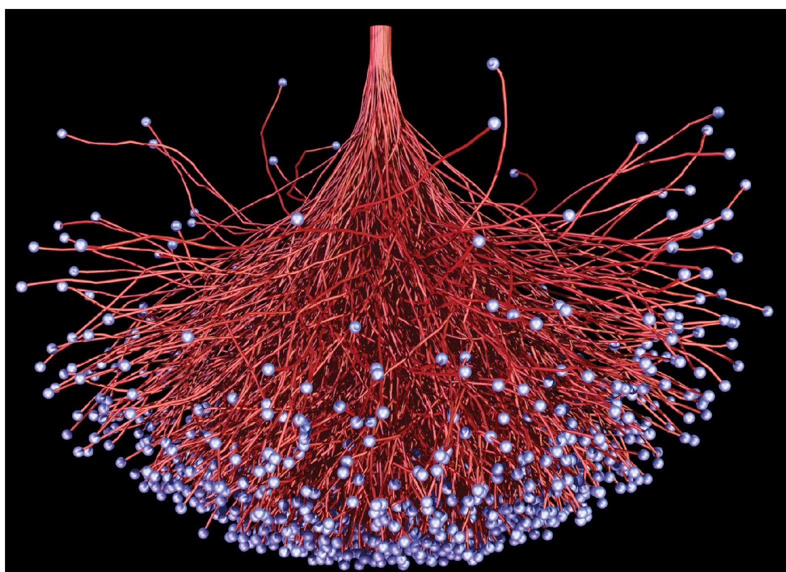


Fig. 125: The numerically modelled covered paths (red) of 1000 ions “shot” into a fictitious solid above centre with an originally ‘downward’ oriented flight direction. The blue spheres mark the places at which the ions come to rest and are implanted in the solid.

Inelastic collisions of electrons cause the excitation or ionisation of the atoms of the host matrix. In the case of ion energies of several 10 eV, which are too low for these processes, i.e., about 1 per thousand of the original energy, a charge exchange between the ion and the solid can take place during the short-term formation of "quasi-molecules" of the ions with the atoms of the matrix.

The collisions with the atomic nuclei of the solid are primarily elastic with a scattering cross-section increasing with decreasing ion velocity. In addition, inelastic collisions can also occur in which the atoms of the host matrix are displaced in the microstructure of the solid, hereby producing point defects in crystalline media.

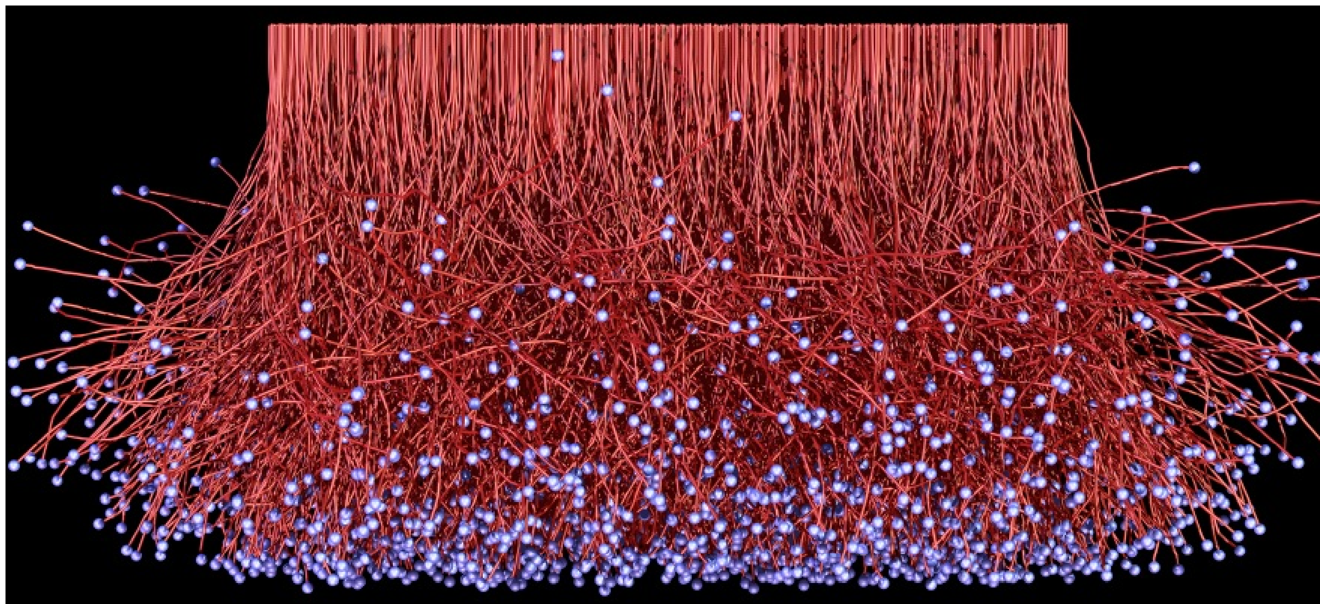


Fig. 126: The numerically modelled covered paths (red) of 5000 ions decelerated in a fictitious solid, injected over a larger area. This results in an overlapping of the scattered cones shown in Fig. 125 a concentration profile of the implanted ions (blue spheres) rel. sharply delimited in depth.

Range and Range Distribution of the Ions in the Solid State

Since the impacts between the ion and the solid are a stochastic process, only a range distribution spread can be defined. Its maximum increases largely linear with the ion energy, i.e. the acceleration voltage. The higher the density of the host matrix and the higher the average atomic number, the lower the average range of implanted ions.

Since each impact also causes a change in the direction of movement of the ion, the distribution of the ions implanted at one location results in the numerically modelled scatter cones as shown in Fig. 125. The important parameter is the range distribution of the ions into the depth of the substrate, that is to say the range distribution projected in the projection direction as in Fig. 126. The border of this distribution far away from the substrate surface is markedly sharper than the upper border, where ions which are spatially more scattered partly also have left the solid body by backscattering.

For crystalline substrates, the anisotropy of the scattering cross-section must also be considered. In crystalline silicon in the {110} direction, hexagonal channels traverse the entire crystal, parallel to those ions travel much deeper in the crystal than along other crystal directions (*channelling effect*).

Photoresist Processing for Ion Implantation

Suitable Photoresists

The photoresist used as a mask for ion implantation does not have any special requirements in addition to the requirement for resist film thickness, lateral resolution and sidewall steepness.

However, the heating of the substrate during the implantation may make it necessary to use a photoresist with a sufficiently high softening temperature.

Necessary Resist Film Thickness

The resist mask must be thick enough to reliably absorb the ions at these sites. Accordingly, the necessary resist film thickness increases with the ionic energy. The higher the density ρ and average atomic number Z of the resist used, the thinner its necessary film thickness for the reliable absorption of the ions can be. Since, with regard to these parameters ρ and Z, phenol-, epoxy- or acrylic-resins of conventional photoresists differ only to a small extent, thus in practice it usually makes little sense to fix the selection of the photoresist used on this criterion.

Removing the Resist Mask

The locally very high energy input of the ions into the material of the resist mask leads to a very strong cross-linking there, which makes the wet-chemical removal of the resist mask after the ion implantation difficult.

If even a high performance remover like the TechniStrip® P1316 or NI555 can remove the resist mask, it can be helpful to increase the resist film thickness slightly:

If the ions are already caught up by the resist mask approximately 1 µm above the substrate, the substrate-near region remains almost non-cross-linked so that the remover can work along this film and can lift off the upper, highly cross-linked region of the resist mask from the substrate.

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 AZ® 1512 HS AZ® 1514 H AZ® 1518	≈ 0.5 µm ≈ 1.0 - 1.5 µm ≈ 1.2 - 2.0 µm ≈ 1.5 - 2.5 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	AZ® 100 Remover, TechniStrip® P1316 TechniStrip® P1331
Positive	Improved adhesion for wet etching, no focus on steep resist sidewalls	AZ® 4500	AZ® 4533 AZ® 4562	≈ 3 - 5 µm ≈ 5 - 10 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
Positive	Improved adhesion for wet etching, no focus on steep resist sidewalls	AZ® P4000	AZ® P4110 AZ® P4330 AZ® P4620 AZ® P4903	≈ 1 - 2 µm ≈ 3 - 5 µm ≈ 6 - 20 µm ≈ 10 - 30 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
Positive	Improved adhesion for wet etching, no focus on steep resist sidewalls	AZ® PL 177	AZ® PL 177	≈ 3 - 8 µm	AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
Positive	Spray coating	AZ® 4999		≈ 1 - 15 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
Positive	Dip coating	MC Dip Coating Resist		≈ 2 - 15 µm	AZ® 351B, AZ® 400K, AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
Positive	Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating	AZ® ECI 3000	AZ® ECI 3007 AZ® ECI 3012 AZ® ECI 3027	≈ 0.7 µm ≈ 1.0 - 1.5 µm ≈ 2 - 4 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF, AZ® Developer	
Positive	Steep resist sidewalls, high resolution and aspect ratio for e. g. dry etching or plating	AZ® 9200	AZ® 9245 AZ® 9260	≈ 3 - 6 µm ≈ 5 - 20 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF	
Positive	Elevated thermal softening point and high resolution for e. g. dry etching	AZ® 701 MiR	AZ® 701 MiR (14 cPs) AZ® 701 MiR (29 cPs)	≈ 0.8 µm ≈ 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 AZ® 12 XT-20PL-10 AZ® 12 XT-20PL-20 AZ® 40 XT	≈ 3 - 5 µm ≈ 6 - 10 µm ≈ 10 - 30 µm ≈ 15 - 50 µm	AZ® 400K, AZ® 326 MIF, AZ® 726 MIF	AZ® 100 Remover, TechniStrip® P1316 TechniStrip® P1331
Positive (chem. amplified)		AZ® IPS 6050		≈ 20 - 100 µm		
Image Reversal	Elevated thermal softening point and undercut for lift-off applications	AZ® 5200	AZ® 5209 AZ® 5214	≈ 1 µm ≈ 1 - 2 µm	AZ® 351B, AZ® 326 MIF, AZ® 726 MIF	TechniStrip® Micro D2 TechniStrip® P1316 TechniStrip® P1331
Image Reversal		TI	TI 35ESX TI xLift-X	≈ 3 - 4 µm ≈ 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 AZ® nLOF 2035 AZ® nLOF 2070	≈ 1.5 - 3 µm ≈ 3 - 5 µm ≈ 6 - 15 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	TechniStrip® NI555 TechniStrip® NF52 TechniStrip® MLO 07
Negative (Cross-linking)		AZ® nLOF 5500	AZ® nLOF 5510	≈ 0.7 - 1.5 µm		
Negative (Cross-linking)	Improved adhesion, steep resist side-walls and high aspect ratios for e. g. dry etching or plating	AZ® nXT	AZ® 15 nXT (115 cPs) AZ® 15 nXT (450 cPs)	≈ 2 - 3 µm ≈ 5 - 20 µm	AZ® 326 MIF, AZ® 726 MIF, AZ® 826 MIF	
Negative (Cross-linking)			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

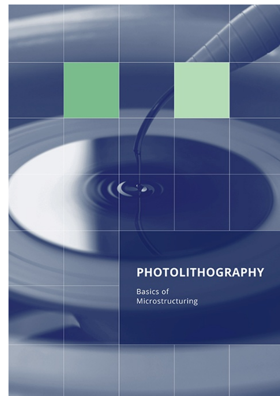
for e. g. chromium, gold, silicon, copper, titanium, ... è www.microchemicals.com/products/etching_mixtures.html

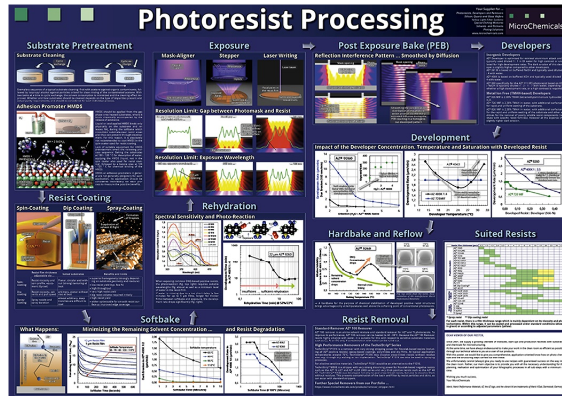
Further Information

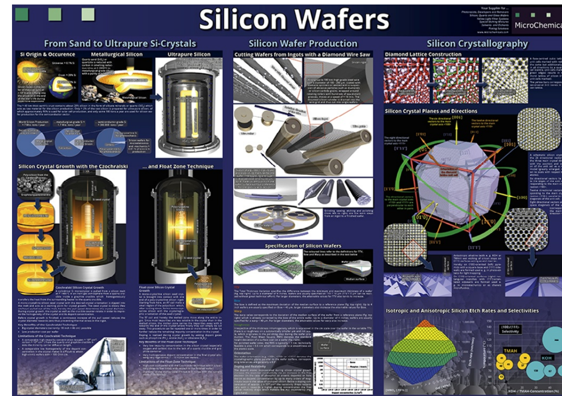
Technical Data Sheets: www.microchemicals.com/downloads/product_data_sheets/photoresists.html

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

Our Photolithography Book and -Posters







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):

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