SOFTBAKE

In contrast to dry films, coated films from liquid resists still have a too high solvent-content for subsequent processing and have to be sufficiently dried by means of a softbake or prebake.

This chapter describes the purpose and the physical mechanisms of this baking step, the effects of substrate and equipment used on the result as well as the interaction of the applied softbake parameters with the following lithographic steps.

**Purpose of the Softbake**

After the coating, the resist film has a residual solvent concentration of typically 10 - 35 %, depending on the film thickness and the solvent used. The purpose of the softbake is to reduce this residual solvent concentration to ...

- avoid the contamination of the photo mask with resist as well as mask sticking to the resist,
- prevent nitrogen popping or foaming of DNQ-based resists during exposure as a side product of the photoreaction,
- improve the resist adhesion to the substrate,
- minimise the dark erosion of positive resists during development,
- allow multiple resist coating without dissolving the already coated resist film by the next one,
- prevent bubbling by evaporating solvent during subsequent thermal processes such as metallisation or dry etching and increase the softening point of the resist for subsequent thermal processes such as metallisation or dry etching,
- to increase the stability of the resist structures during electroplating and to suppress a contamination of the electrolyte with remaining solvent.

**Processes in the Resist Film: Some Physics**

**Diffusion in the ResistFilm**

Before the solvent molecules can evaporate, they have to diffuse to the resist film surface.

Their diffusion constant $D$ depends on the temperature $T$, as well as the local remaining solvent concentration $C$ ($0 = $ solvent-free ... $1 = $ pure solvent) as follows:

$$D(T, C) = D_0 \cdot \exp \left( - \frac{E_1}{kT} \right) \cdot \exp \left( - \frac{C}{a + b \cdot C} \right)$$

where $D_0$ is a constant, $E_1$ the diffusion activation energy, and $a$ and $b$ resist- and solvent specific parameters. Thus, the solvent diffusion of the solvent molecules decreases with its concentration where the given temperature rapidly slows the further drying (Fig. 64).

In an in-house research project, which we were able to carry out, we could evaluate experimental data using the above formula for typical AZ® resists numbers $D_0 = 0.000767 \, \text{(m/s)}^3$, $E_1 = 1.426 \, \text{eV}$, $a = 0.00394$ and $b = 0.0218$ with phenol resin and PGMEA as a solvent.

**Evaporation from the Resist Film**

Solvent molecules at the resist surface with a kinetic energy exceeding the evaporation enthalpy $E_2$ (whose size we have determined at 0.47 eV) resulting in a solvent partial pressure $p$ over the resist surface as follows:
with \( C_0 \) as the relative resist surface solvent concentration \((1 = \text{pure solvent}, 0 = \text{solvent-free resist surface})\).

**Diffusion and Convection over The Resist Surface**

Above the resist film, a diffusion boundary film forms as over any liquid, whose thickness depends on the air speed above the surface. The higher this is, the shorter the distance the already evaporated solvents have to travel by diffusion in the atmosphere in order to pass over into the air flow through convection.

**The Role of Temperature and Air Movement**

While the diffusion in the resist film as well as the evaporation are thermally activated, the removal via convection depends on the air movement above the substrate.

The average time in which the solvent molecules pass through the diffusion boundary layer depends on the temperature (thermally activated diffusion) as well as on the air movement (stronger flow = thinner diffusion boundary layer).

**Mean Solvent Concentration of the Resist Film**

Fig. 65 shows the measured time flow, over which the solvent concentration of two differently thick resist films averaged over the entire resist film (The 1 \( \mu \)m thick resist film starts after the softbake at 21\% residual solvent content, the 12 \( \mu \)m resist film at 26\%) during the softbake as a function of time with different temperatures.

After a short time, the residual solvent content begins to saturate since the decrease in the residual solvent content suppresses the diffusion of the solvent from deeper resist films. At higher temperatures, this saturation begins earlier, but at a lower level.

Accordingly, the 90 - 100°C customary for softbake processes is necessary in order to lower the residual solvent concentration to values below 5\% in a reasonable time.

Even at 115°C saturates the value at 2\%. Such a strong drying is not necessary however but often detrimental for most processes because this increases the mechanical stresses in thick resist films.

**Solvent Concentration Gradient in the Resist Film**

For many process steps, the solvent concentration depth profile in the resist film is more important than the average solvent concentration. A low solvent concentration at the substrate/resist interface improves the resist adhesion and lowers the danger of \( N_2 \) bubble formation of DNQ-based (especially thick) resists during exposure, while a solvent-depleted resist surface prevents mask sticking.

Since the solvent diffusion from the bulk of the resist film cannot keep up with the evaporation from the film surface, a depth profile of the solvent concentration forms, most pronounced near the resist surface. This gradient increases in the vicinity of the resist film surface because the diffusion in the already solvent-depleted boundary layer is strongly suppressed.

Fig. 66 shows the results of a numerical simulation of the development of the spatially resolved solvent concentration during the softbake of a thin (1 \( \mu \)m) and thick (10 \( \mu \)m) resist film.
Excessively high Residual Solvent Concentration

An excessively high residual solvent concentration in insufficiently baked positive resist films leads to increased, undesirable removal of the unexposed resist areas (dark erosion) during the development process with the remaining resist structures too small and less sharp than desired. The dimensional accuracy of the resist lines and openings as well as their sidewall steepness also suffers from the developer corrosion on the corners and sidewalls of the resist profile as in Fig. 67 which shows the simulation of the development process of a resist film in cross-section.

Fig. 68 shows the measured dark erosion rate of an AZ® 6632 film at various softbake parameters at various temperatures and times in an unusually strong (AZ® 400K : H₂O = 1 : 2) developer concentration. In conventional developer solutions, the dark removal rate is significantly lower, but this also increases the development time during which the dark erosion can also take effect.

Fig. 66: The chronological development of the solvent concentration profile in a 1 µm (left, initial solvent concentration before softbake = 15 %), and 10 µm (right, initial solvent concentration = 35 %) resist film.

Fig. 67: A numerical simulation of the chronological sequence of the development of a positive resist film. In the upper row, the dark erosion is significantly greater than in the lower row; correspondingly the entire unexposed resist film thins out more greatly up to the development of the exposed areas. The further the developer proceeds into the resist sidewalls also laterally, the flatter resist profiles remain as a result.
In addition to increased dark erosion, an increased alkaline solubility also leads to a stronger corrosion of the resist film in etching media or electrolytes with a pH > 7, which not only changes the shape resist film profiles but can also lead to an organic contamination of the etching medium or of the electrolyte.

In addition, a high residual solvent concentration in the vicinity of the substrate can adversely affect the adhesion of the resist film in wet-chemical processes such as etching or electroplating.

**Decomposition of the Photoinitiator**

Since the unexposed photoinitiator of DNQ-based positive resists is an inhibitor against alkaline solubility (Fig. 40 on page 26), the dark erosion rate of very hot or long baked resists can also increase again due to the associated decomposition of the photoinitiator.

This effect occurs only significantly in very long and/or hot softbake steps.

**Impact of Softbake Parameters on the Development of Negative Resists**

**Excessively high Residual Solvent Concentration**

In cross-linked negative resists, excessive residual solvent concentration can inhibit the cross-linking of the resin thereby causing an unwanted erosion of the exposed resist areas during development.

As with positive resists, an excessively high residual solvent concentration can reduce the adhesion of the resist film to the substrate, as well as its stability in wet-chemical media.

**Thermal Cross-linking**

Even if with negative resists, where the cross-linking of the resin is initiated or done via an exposure, a more or less strong cross-linking can take place at higher temperatures even without previous exposure.

In Fig. 70, this context is shown as an example of our AZ® nLOF 2070 negative resist.

As a result, a softbake which is too hot and/or longer than necessary can reduce the later development rate or make development difficult or, impossible especially in the case of small holes or narrow trenches to be cleared.
Optimum Softbake Parameters

**Always a Compromise**

Resist films which are baked too cool or/and too short can promote a higher proportion of undesired erosion in the developer as well as deteriorate the resist adhesion and stability in wet-chemical media. Temperatures which are too high or baking times which are too long during the softbake can partially decompose the positive resists or cause a thermal cross-linking of the resin of negative resists.

**Temperature and Time**

Unless otherwise specified in the technical data sheets, a temperature of 100°C for 1 minute/μm resist film thickness is often suitable as a starting point for further specific optimisations for common AZ® and TI photoresists.

In the case of temperature-sensitive substrates or with a focus on fast process times, also in the case of thick resist films, the parameters temperature and time can be varied within limits: The baking time can be halved per 10°C temperature increase in the range between 80 and 110°C and vice versa. These numerical values for temperature and time are based on the conditions directly in the resist film.

Depending on the substrate and equipment used, it must be taken into account that there may be more or less large differences between the temperature set point at the heating source and the temperature profile on the substrate (=in the resist film) over time.

**Problems with the Softbake of Thick and very Thick Resist Films**

As a rough approximation, the softbake time of a resist film at a given temperature required to lower the average remaining solvent concentration to a certain value quadratically increases with the resist film thickness. However, DNQ-based thick positive resists require sufficient drying in order to prevent the formation of \( \text{N}_2 \) bubbles especially in the vicinity of the substrate during exposure, the occurrence of which is promoted by large resist film thicknesses. A complete drying of several 10 μm thick resist films up to the substrate would require temperatures and times which would damage the resist films via a thermal decomposition of the photoinitiator or a thermal indexed cross-linking of negative resists, which would result in unreasonably long development times for thick resists.

Additionally, with an increasing resist film thickness, a too extended softbake causes mechanical stress in the resist film making it vulnerable to crack formation which is problematic for subsequent wet-chemical processes such as etching or plating.

Thus, the time/temperature process window for the softbake narrows with increasing resist film thickness and has to be carefully optimized with respect to the individual process requirements. If even the optimisation of the softbake parameters does not result in a sufficiently solvent-poor, but still undamaged resist film, the following workarounds might be an option:

**Workarounds for Very high Resist Film Thicknesses**

A multiple coating with a softbake after each coating step allows a homogeneous low solvent concentration through the entire resist film with a moderate overall softbake time, which would not suffice if applied once for the finished resist film. This, however, results in a resist film with an increasing softbake time for each layer towards the substrate. In order to minimise this effect, each partial softbake can be performed at a lower temperature (e.g. 80°C for 1 minute per μm thickness of the film coated immediately before), and 100°C for the same time after the final coating.

Alternatively, drying the resist film in a vacuum at moderate temperatures (vacuum hotplate) or even...
at room temperature might be beneficial. At a base pressure below the solvent vapour pressure, the solvent evaporates very quickly from the resist film. It is also very important to make sure that no air bubbles from coating are embedded in the resist film: Otherwise such bubbles strongly expand in a vacuum thereby causing severe defects. If bubbles cannot be avoided during resist coating, a moderate softbake (e.g. 5 minutes at 100°C) under standard conditions before the vacuum bake makes the resist film more resistant to expanding bubbles.

Non-Ideal Softbake Conditions

Massive or Non-planar Substrates

In the case of massive or non-planar (curved) substrates, or substrates with a comparably low heat conductivity such as glasses, ceramics or polymers, it takes a certain time on a hotplate until the substrate heating up is finished, and the resist film temperature remains constant. Additionally, the final temperature of the resist film may be significantly lower than the hotplate temperature.

Fig. 71 shows the measured substrate (left: Si-wafer, right: glass mask blank) surface temperature as a function of the time on a 100°C hotplate with different gaps between hotplate and substrate. With small air gaps, the very good heat conductivity of silicon in combination with a low heat capacity of the 575 µm thick wafer results in a fast temperature rise, while the 3.3 mm thick glass substrate requires more time to reach the final temperature. With bigger gaps, the influence of the substrate type decreases, and the measured substrate surface temperature profile is determined more by the size of the gap.

The experiment has shown, that the temperature profile of the Si wafer and small (<100 µm) gaps significantly depends on the surface treatment (polished or rough) of the wafer rear side facing the hotplate. Additionally, for a desired real contact (0 µm gap), an applied contact pressure causes a strongly temperature rise towards the hotplate temperature. This shows, that a real 0 µm contact between substrate and hotplate is hard to realise which significantly impacts on the attained temperature profile especially for substrates with low heat capacity.

Therefore, depending on the substrate, longer softbake times and elevated temperatures might be required for a sufficient softbake of the resist film on such non-ideal substrates.

Using an Oven Instead of a Hotplate

The heat transfer in a convection oven via the air is much slower than the heat carriage via conductivity on a hotplate, especially in the case of massive substrates with a high heat capacity such as glass or
ceramics. Thus, it takes much longer for the resist film to attain the target temperature, which is more problematic in the case of short baking times for only a few minutes (Fig. 72).

Without direct heat contact to flat, massive metallic surfaces (oven hotplate), we recommend adding approx. 2 - 10 minutes (depending on the substrate) to the softbake time in an oven as compared to a hotplate process.

Even with this adjustment, possible temperature differences between different locations in an oven make reproducible results of temperature-critical processes difficult. After opening and loading the oven, the temperature-hysteresis during heating can exceed the temperature significantly beyond the target temperature, which can damage the resist film as a too long or hot softbake does.

**Measuring the Effective Resist Temperature**

For substrates which thermally conduct well such as planar, thin and high thermal conductivity substrates on a hotplate, it can be assumed to a good approximation that the effective resist temperature corresponds to the temperature of the hotplate with only a short delay.

Unfortunately, it's almost impossible to measure the resist film temperature during softbake using a technically justifiable effort: The absorption characteristics of thermal elements (e.g. undoped or weakly doped Si wafers transmit most of the thermal radiation of the hotplate) and thermal inertia of the thermocouple gives the wrong results.

Thus, in most cases, it is reasonable to empirically optimise the softbake conditions by varying the softbake parameters temperature and time, and correlating them with the final process results.

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Fig. 72: The slow heating of the substrate in an oven as compared to a contact hotplate requires an extension of the softbake time. The evaporation rate of the solvent is halved per approx. 10°C below the target temperature, here shown schematically by time intervals with a corresponding "time factor".
**Inorganic Developers**

**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**

**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® N1555 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® N1555 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® N1555 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™ NFS2 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 monocristalline 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: www.microchemicals.com/products/wafers/waferlist.html

**Further Products from our Portfolio**

**Plating**

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

**Solvents (MOS, VLSI, ULSI)**

Acetone, isopropyl alcohol, MEK, DMSO, cyclopentanone, butylacetate, … www.microchemicals.com/products/solvents.html

**Acids and Bases (MOS, VLSI, ULSI)**

Hydrochloric acid, sulphuric acid, nitric acid, KOH, TMAH, …

**Etching Mixtures**

www.microchemicals.com/products/etchants.html

www.microchemicals.com/products/etching_mixtures.html
Further Information


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

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All information, process descriptions, recipes, etc. contained in this book are compiled to the best of our knowledge. Nevertheless, we cannot 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.

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