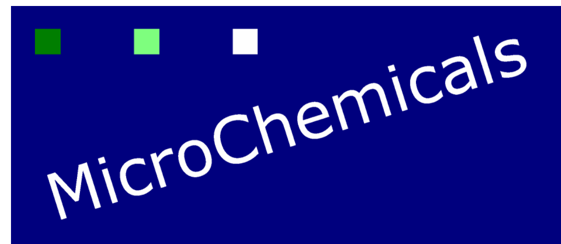
Dry Etching with Photoresist Masks



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www.microchemicals.com/downloads/application_notes.html

Basics of Dry Etching

Basic Dry Etch Mechanism

If the ‘chemical’ mechanism dominates, etching occurs via the strong material selective formation of volatile compounds by radicals in the plasma which – towards high plasma pressure – hit the surface more and more isotropically.

With the ‘physical’ mechanism dominating, etching occurs via the weak material selective sputtering of the substrate by ions which – accelerated by an electrical field – hit the surface with high kinetic energy and – if the free mean path (chamber pressure) is low enough – highly anisotropically.

	Plasma etching	Reactive ion etching (RIE)	Reactive ion beam etching (RIBE)	Sputter etching
Mechanism	Chemical	Chemical + physical	Physical + chemical	Physical
Etching by...	Radicals	Radicals + ions	Ions + radicals	ions
Anisotropy	0	+	++	+++
Selectivity	++	+	0	0
Pressure	» 1 Torr	» 0.1 Torr	» 0.1 Torr	» 0.01 Torr

What Happens in the Plasma

Typical etch gases for SiO_2-etching are mixtures of $C_xF_yH_z$, e. g. CF_4

(1) Formation of Fluoric-radicals by impact ionization: $e^- + CF_4 \rightarrow CF_3 + F + e^-$

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

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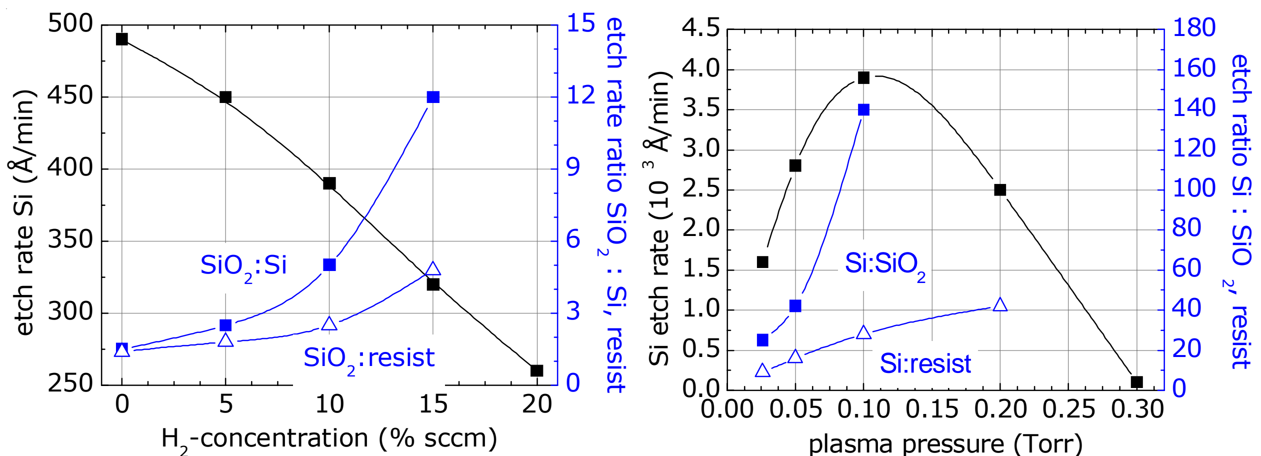
(1) Formation of Fluoric-radicals by impact ionization: $e^- + CF_4 \rightarrow CF_3 + F + e^-$

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

Adjusting the Desired Etch Ratio Si : SiO_2

Addition of O_2: $CF_3 + O \rightarrow COF_2 + F$ increases F-concentration and etch rate.

→ Maximizes Si etch rate for approx. 12% O_2 in CF_4, SiO_2 etch rate for 20% O_2 in CF_4, the etch ratio SiO_2:Si drops. Resist erosion increases with O_2 (combustion).



These plots show how dry etching parameters impact the Si and SiO_2 etch rate.

Addition of H_2: H + F → HF reduces F-concentration and etch rate.

→ Reduces the Si etch rate more than the SiO_2 etch rate (fig. below)

Addition of H_2: CF_4 + H + Si → CH_xF_y causes polymer formation on Si.

→ Preferentially takes place on Si surfaces thus stopping Si etching

Attaining Steep Resist Sidewalls

Suited Photoresists

While resists designed for wet etching predominantly show an optimized adhesion, resists for dry etching such as the AZ® 6600 series, or the AZ® 701 MiR are better suited for attaining steep resist sidewalls.

For resists films thicknesses exceeding 5 µm, the AZ® 9260 with its superior aspect ratio is a good option.

Optimized Softbake Parameters

An adjusted softbake temperature and time are important to attain the maximum contrast (high development rate, low dark erosion) of a given positive resist as a basic requirement for steep sidewalls. If the softbake is performed to short or/and too cool, the high remaining solvent concentration in the resist film causes a high dark erosion rate. If the softbake has been applied too long or/and too hot, a significant amount of the photo active compound will be thermally decomposed which lowers the development rate.

We recommend a softbake at 100°C for 1 minute per µm resist film thickness on a hotplate. Detailed information on softbaking can be found in the document Softbake of Photoresists.

Sufficient Rehydration

DNQ-based resists (= almost all AZ® positive resists) require a certain water content during exposure in order to subsequently attain a high development rate. A high development rate keeps the total dark erosion low and therefore is a requirement for steep sidewalls.

After the softbake, the resist film is almost water-free and requires the absorption of water from the air. Thus, a resist film thickness dependant delay at a certain air humidity (*rehydration*) between baking steps and exposure is required for positive resists with the demand of steep sidewalls. Please consult the document Rehydration of Photoresists for more details on this topic.

Contact Exposure

A gap between photomask and resist surface extends the diffraction pattern and therefore makes it impossible to attain steep sidewalls. Possible (unintended) reasons for a gap are:

- Particles in the resist caused by either insufficient cleanroom conditions, contaminated substrates, or expired photoresist,
- bubbles in the resist film caused during dispensing, or an insufficient delay time after refilling/diluting/moving the resist,
- mask contamination by particles, or resist from previous exposure steps,
- rough, textured, or curved (strained) substrates,
- an edge bead, or a mask attached upside-down ☺.

Optimized Exposure dose

An optimized exposure dose is another requirement for attaining the maximum aspect ratio of a given resist: If the exposure dose is too low, the development time increases which increases the total dark erosion. Too high exposure doses cause an undesired exposure by scattering, diffraction, and reflection of the part of the resist which should not be exposed, making it soluble in the developer.

The optimum exposure dose can be determined with an exposure series which is very recommended for all new or changed processes: At a certain dose D_{opt}, the development rate starts to saturate and will not further increase towards higher exposure doses. For most processes, the optimum exposure dose is close to D_{opt}. The document Exposure of Photoresists gives more information on this topic as well as recommended exposure doses for various resists.

High Developer Selectivity

Steep sidewalls require a developer allowing a high development rate of the exposed resist, and a minimized dark erosion of the unexposed resist.

In the case of positive resists, the dark erosion grows faster with the developer concentration than the development rate. Therefore, a proper dilution is required for a high selectivity (= development rate : dark erosion ratio). For high-resolution photoresist processes, it can be beneficial to apply a higher developer dilution than usual: An AZ® 400K : H_2O or AZ® 351B : H_2O dilution ratio of 1 : 5 ... 1 : 6 (instead of typically 1 : 4), or a moderate dilution (2 : 1 ... 1 : 1) of MIF developers such as AZ® 326 or 726 MIF which are usually applied undiluted.

Developers with an intrinsic high dark erosion should not be used: The AZ® 826 MIF, the AZ® Developer, and the AZ® 303 have a lower selectivity than the developers AZ® 400K, AZ® 351B or AZ® 326/726 MIF.

The document Resists, Developers, and Removers explains which developers are recommended for certain resists.

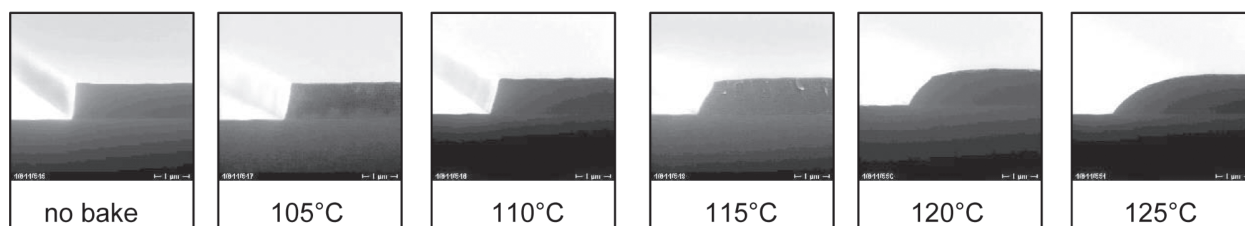
Thermal Stability

During dry etching, elevated temperatures beyond the softening point of the resist will rounden the resist structures hereby deteriorating the steep sidewalls attained before. In order to maintain steep sidewalls during dry etching, we recommend the following techniques:

Using Resists with Elevated Thermal Stability

Non-crosslinking positive resists start softening from approx. 110°C on (holds for e. g. the AZ® 1500, 4500, 9200, or ECI 3000 series), or, respectively, from approx. 130°C on (e. g. the AZ® 6600 series the AZ® 701 MiR, and the AZ® 5214E) also depending on the process parameters such as the softbake conditions. Hereby the upper resist edges rounden, while the contact points of resist and substrate do not move (compare image series below).

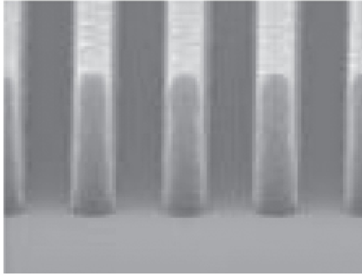
Crosslinking negative resists such as the AZ® nLOF 2000 series, or the AZ® 15 / 125 nXT do not soften at any temperatures. The document Reflow of Photoresists gives further details on this topic.

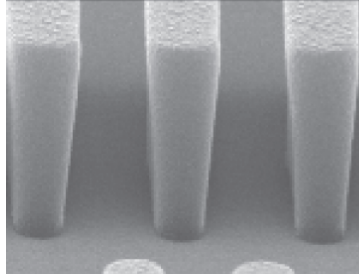


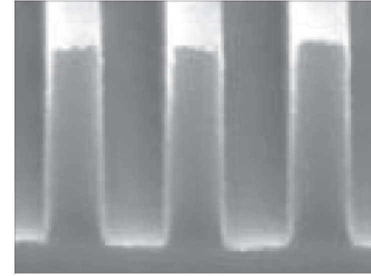
Cross-section of AZ® ECI 3000 resist structures suffering from an increasing temperature. *Source: AZ-EM® AZ® ECI 3000 Product Data Sheet*

Heat development during dry etching close to or beyond the softening point of the resist used causes rounding of the resist profile which becomes transferred into the substrate. Possible work-arounds for lowering the temperature of the resist mask are:

- ➔ An optimized heat coupling of the substrate to its holder (e. g. some turbo pump oil for proper heat transfer from strained, curved substrates),
- ➔ a sufficiently high heat buffer (massive substrate holder construction) or
- ➔ heat removal (e. g. black anodized aluminium as rear infrared radiator) from the substrate holder, and
- ➔ a reduced etch rate and/or multistage etching with cooling interval(s) in between.


300 nm lines and spaces with the AZ® 701 MiR @ 0.8 µm


700 nm lines and spaces with the AZ® nLOF 2020 @ 2.0 µm


450 nm lines and spaces with the AZ® ECI 3012 @ 1.2 µm

Required Resist Film Thickness and Resolution

High Resolution Photoresists

For very thin (200 nm ... 1 µm) resist films and highest resolution requirements, we recommend the thermally stable AZ® 701 MiR which can easily be diluted with PGMEA to adjust the resist film thickness. The thermally stable AZ® 6600 series covers the thickness range from 1 ... 5 µm. If a higher resist film with high aspect ratio is required, the AZ® 9260 is a good choice, which, however, has a lower softening temperature of approx. 110°C.

Process Conditions for High Resolution

The conditions and for attaining a maximum resolution are generally the same required for steep sidewalls explained in the section *Attaining Steep Resist Sidewalls* of this document:

➔ Optimum softbake parameters for a high contrast of the resist,
➔ a sufficient rehydration,
➔ an optimized exposure dose with using contact exposure without proximity gap, and
➔ a developer with high selectivity.

The document High Resolution Photoresist Processing gives further information on this requirement.

Photoresist Removal after Dry Etching

After dry etching, it is often hard or even impossible to remove the resist film. There are several possible mechanism responsible for this issue:

- From temperatures of approx. 150°C on, positive photoresists thermally cross-link which makes them chemically stable in organic solvents.
- Cross-linking also takes place optically activated under deep-UV radiation (wavelengths < 250 nm) in combination with elevated temperatures which occurs during dry-etching.
- Material re-deposited on the resist structures during dry etching will also make it difficult to remove the resist film.

Possible work-arounds for lowering the temperature of the resist mask are ...

➔ an optimized heat coupling of the substrate to its holder (e. g. some turbo pump oil for proper heat transfer from strained, curved substrates),
➔ a sufficiently high heat buffer (massive substrate holder construction) or
➔ heat removal (e. g. black anodized aluminium as rear infrared radiator) from the substrate holder, and
➔ a reduced etch rate and/or multistage etching with cooling interval(s) in between.

The document Photoresist Removal gives further information on this requirement.

Interested?

We supply all mentioned resists also in 250 ml, 500 ml, and 1.000 ml units. Please contact us for further information!

Disclaimer of Warranty

All information, process guides, recipes etc. given in this brochure have been added to the best of our knowledge. However, we cannot issue any guarantee concerning the accuracy of the information.

We assume no liability for any hazard for staff and equipment which might stem from the information given in this brochure.

Generally speaking, it is in the responsibility of every staff member to inform herself/himself about the processes to be performed in the appropriate (technical) literature, in order to minimize any risk to man or machine.

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