Etching with Hydrofluoric Acid

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Etching of SiO_2, Quartz, and Glasses with HF

Hydrofluoric acid is the only etchant which attacks amorphous SiO_2, quartz, or glasses at significant high etch rate.

However, HF is not only a strong corrosive, but also highly toxic towards higher concentrations: Local effects include tissue destruction and necrosis, deaths have been reported from concentrated acid burns to as little as 2.5 % body surface area. Besides personal protective equipment, it's recommended not to handle higher concentrations of HF than required, and use ready-diluted mixtures instead of making own dilutions. We supply HF in a concentration of 1, 10, and 50% as well as buffered HF (BOE 7 : 1) in semiconductor-quality (VLSI).

The following sections deal with common questions and problems concerning HF-etching with photoresist masks.

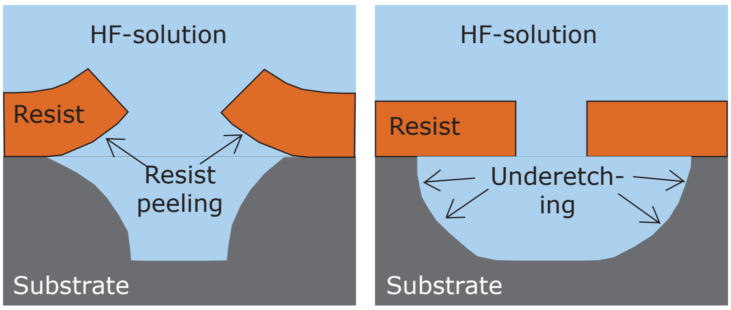
Stability of Photoresists against Hydrofluoric Acid

All common photoresists are sufficiently stable against HF, which is only a weak acid with a pK_s-value (degree of dissociation) of 3.14. Even 50% HF over several hours does not chemically attack the resist mask.

An insufficient „stability" in most cases points towards the frequently observed underetching or peeling of the resist film from the substrate during etching after a certain etch time, as explained in the following sections.

"Real" Resist Adhesion Problems during HF Etching

In contrast to the large-scale resist peeling described in the following section, a "real" poor adhesion causes an underetching underneath the resist mask more pronounced than one would expect assuming isotropic etching. Strong underetching might also be accompanied by a peeling of small or narrow resist structures during etching or the subsequent rinsing.



The etched profile reveals if either the resist adhesion is poor (left), or only the inevitable underetching in case of isotropical etching occurs (right).

In order to improve the resist adhesion, the following work-arounds concerning substrate pretreatment and resist processing are:

- Substrates contaminated with organic impurities can be cleaned with a two-stage cleaning process: Acetone removes organic impurities, a subsequent rinse in isopropyl alcohol removes the contaminated acetone thus avoiding striations.
- In the case of clean substrates (virgin wafer or wafer with fresh thermal oxide), baking at 120-140°C for several minutes is sufficient for the desorption of H_2O. At 150°C, the OH-bonds apparent on SiO_2 and glasses decompose thus further increasing the resist adhesion. If applicable, the resist coating should be applied immediately after cooling the substrate from baking to room temperature in order to avoid re-adsorption of water.
- Incomplete (with remaining oxide) etching of the substrate with HF before resist coating results in a very poor and non-reproducible resist adhesion, which can be restored with a

bake at temperatures > 700°C.

- The usage of resists with optimized adhesion such as the AZ® 1500 series (resist film thickness range approx. 0.5 - 3 µm via the AZ® 1505, 1512 HS, 1514 H, and 1518), or the AZ® 4533 (3 - 5 µm). The deeper into the substrate one has to etch, the ticker the resist film should be. If this requires a high aspect ratio, we recommend the high-resolution AZ® ECI 3000 series (resist film thickness range 0.5 - 4 µm) or the AZ® 4562 or 9260 (> 5 µm resist film thickness). The document Photoresists, Developers, and Removers gives more details on these resists and their processing.
- In order to improve the resist adhesion, a hardbake at 140-150°C for 5-10 minutes after development can be beneficial. Since the resist film hereby embrittles, the cooling down to room temperature should not take place abruptly, and the handling be done carefully, in order to prevent the formation of cracks. A higher hardbake temperature will make it difficult or impossible to remove the resist after etching due to thermal cross-linking of the resin. Further details on the hardbake can be found in the document Hardbake of Photoresist Structures.

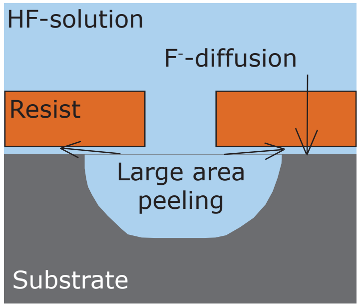
"Spurious" Resist Adhesion Problems During HF Etching

When etching with hydrofluoric acid or HF-containing mixtures, often a large-scale resist peeling is observed after a certain etch time or during the subsequent rinsing. This effect originates from the following mechanism:

- Resist swelling caused by the etchant diffusing into the resist film, and
- large-scale etching of the resist covered substrate after the etchant has diffused through the resist film towards the substrate.

Besides an adjusted etchant, both mechanism can be reduced by a thicker resist film. As a rule of thumb, doubling the resist film thickness allows a four times longer etching time in HF.

Additionally, the usage of buffered HF (BOE) significantly prolongs the time until resist peeling occurs, since the HF_2^--ions formed in BOE are less permeable in the resist film as compared to the F^- ions of unbuffered HF.



F^--ions diffuse through the resist film towards the substrate, etch the substrate material, followed by a large-scale resist peeling.

Etching of Doped Glasses

Unlike SiO_2, glasses with various compositions show a strong dependency between their etch rate and additives in the etch. Such additives (e. g. HCl, HNO_3) dissolve surface films formed on the glass during etching, which are often chemically inert in HF and would stop or decelerate glass etching with pure HF.

Therefore, such additives allow a continued etching at a constant and high rate. This allows one to increase the etch rate at a reduced HF-concentration (= increased stability against resist peeling).

Our Resists and Etchants

We supply all mentioned resists also in 250 ml, 500 ml, and 1.000 ml units, and HF in a concentration of 1%, 10%, and 50% as well as buffered HF (BOE 7 : 1) in 2.5 L units. Please ask us for further technical 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.