Development of Photoresists

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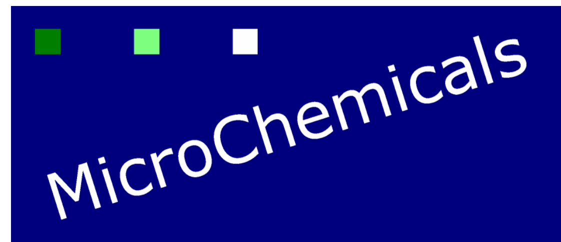
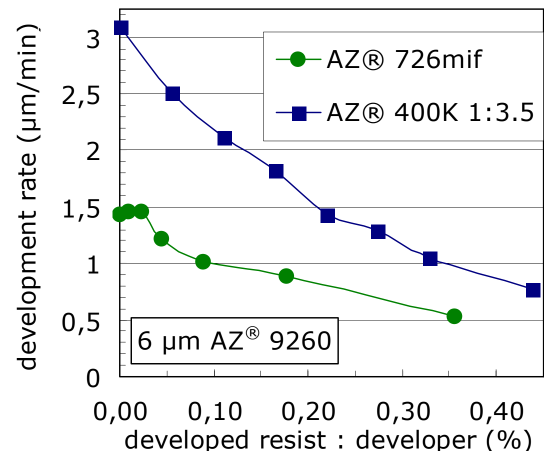


Developers: Storage and Exhaustion



The aging of aqueous alkaline developers originates from **CO_2-absorption** from air, whereby the development rate decreases. Therefore, their storage in well closed original bottles is recommended. With open developer baths over several days, a nitrogen curtain surrounding the bath minimizes the CO_2-absorption. Some developers (e. g. AZ® 400K, AZ® 351B) contain chemical buffers, which suppress the reduction of the pH-value by CO_2-absorption and enable a constant development rate over a long time span as compared with simple NaOH/KOH solutions.

Besides neutralisation by CO_2 absorption from air, also **developed resist** exhausts the developer. As a rule of thumb: When 1 promille (volume or weight) developed resist is solved in the developer, the development rate already drops by some 10 %, and the developer should be renewed. When the ratio resist : developer increases towards 1 %, almost all OH^--ions are consumed, and the development drops towards zero.

Compatibilities between Developers and Resists/Substrates

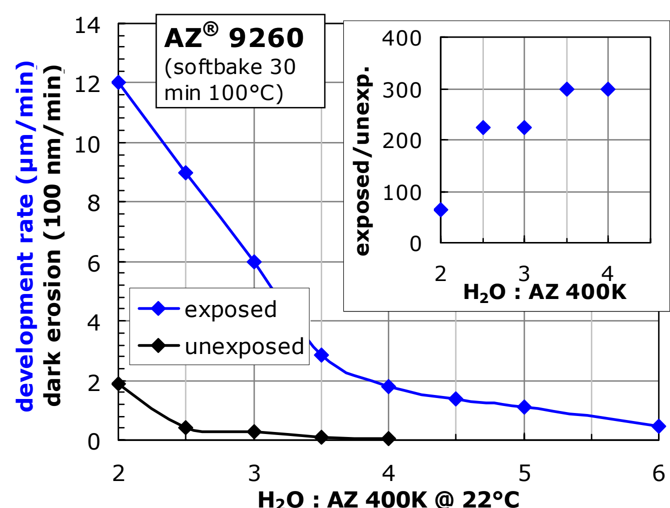
The general compatibilities between resists and developers are described in the document *resists and developers* (same source).

Additionally it has to be checked if **metal ion free** (with e. g. AZ® 326MIF, 726MIF, 826MIF) developers have to be used, or **metal ion containing** developers (such as AZ® 400K, AZ® 351B) are possible. Another selection characteristics is the demand for *ready-to-use* developers, or if alternatively diluted concentrates are preferred/possible.

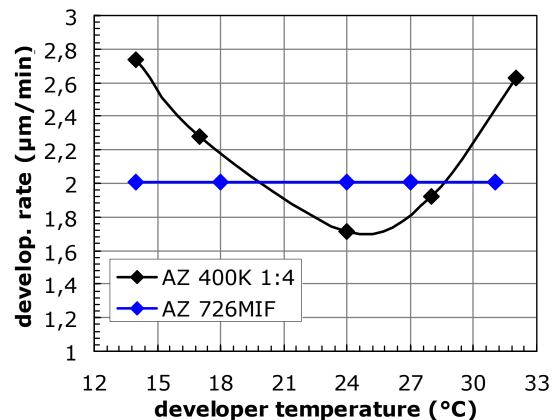
The **substrate compatibility** of developers has also to be considered: Alkaline developers attack aluminium and Al-containing alloys/compounds and hereby may contaminate the substrate with Al traces. 'AZ® Developer' (metal ion containing) is optimized for lowest aluminium attack, but shows a higher dark erosion for photoresists.

Developer Concentration and Selectivity

The development- and dark erosion rate (= how fast completely exposed and unexposed, respectively, photoresist film thickness vanishes in the developer) both strongly increase towards higher **developer concentration**. Therefore, using developer concentrates such as AZ® 400K or AZ® 351B requires a dilution matched to the individual process requirements. As the plot right-hand shows, a dilution ratio of 1:3.5 to 1:4 for AZ® 400K or AZ® 351B allows a reasonably high development rate at a high **selectivity** (ratio of development rate and dark erosion) at the same time.



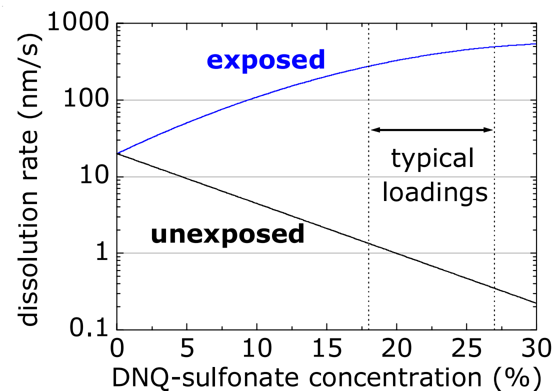
Temperature Dependency



Besides the developer and the developed resist, the temperature dependency of the development rate depends on the thermal activation energy of physical transport mechanisms of the developer and the developed resist, as well as chemical reactions involved in the development and complex formation.

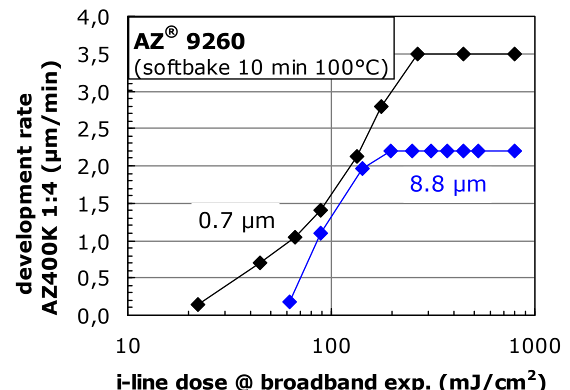
Therefore, critical processes either require a constant developer temperature, or an individual investigation if, how (development rate decreases/ increases with temperature), and how strong the temperature impacts on the development rate.

Exposure Dose and Development Rate



The **Meyerhofer plot** (fig. right-hand) opposites the alkaline solubility of unexposed and completely exposed photoresists as a function of the photo active compound concentration. Before exposure, the inhibitor DNQ-sulfonate *decreases* the development rate by 1-2 orders of magnitude, which is similar to the development rate *increase* caused by the product of the photoreaction, the indene carboxylic acid.

The fig. right-hand, bottom shows the dependency of the exposure dose and the development rate of a thin (illumination penetration depth > resist film thickness), and a thick (penetration depth < film thickness) photoresist: From a certain exposure dose on, the photo active compound is sufficiently converted into the indene carboxylic acid to allow a constant high development rate. The impact of bleaching becomes clearly visible for the thick resist film: Below a certain exposure dose, the resist cannot be cleared.



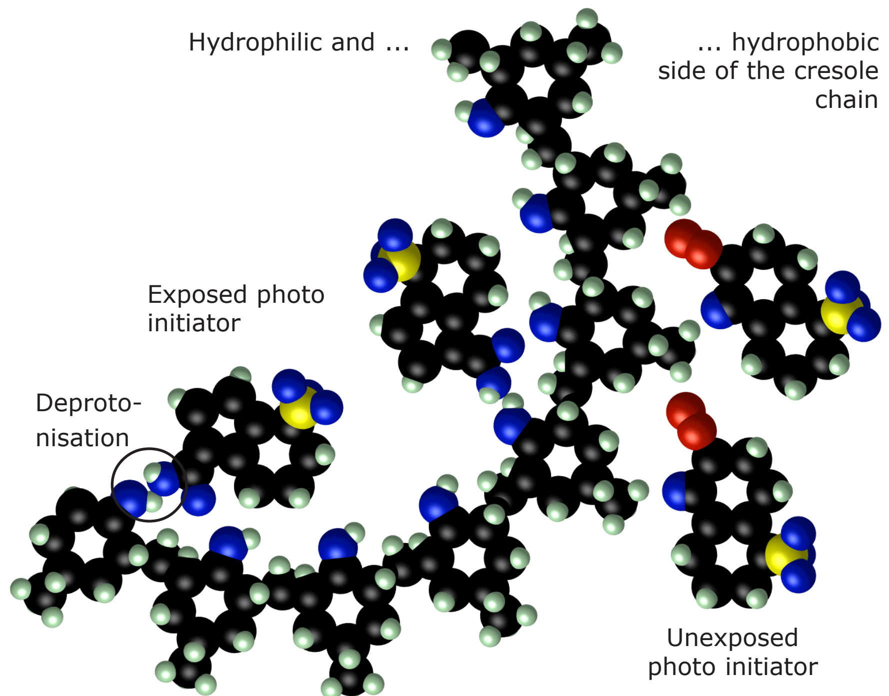
Compatibilities between MIC and MIF Developers

Even small traces of TMAH (which is part of metal ion free developers such as AZ® 326MIF, 726MIF or 826MIF) are able to significantly deteriorate the development rate of metal ion containing developers such as the AZ® 400K or 351B. If both types of developers are used, much care has to be taken to avoid any cross contaminations.

Development: What Happens in Detail

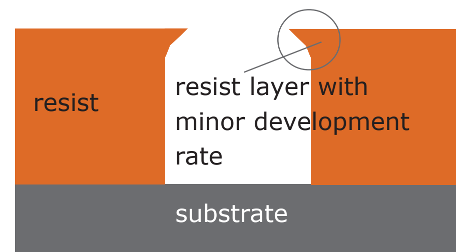
The carboxylic acid formed during exposure (photoreaction, section 9.3) moves from the hydrophobic to the hydrophobic to the hydrophilic part of the cresol chain and promotes the **deprotonisation** of the OH-group increasing the resist solubility in aqueous alkaline developers.

Beside the carboxylic acid, also **acetic acid** (formed by alkaline developers from the resist solvent PGMEA) increases the development rate of exposed and unexposed resist. This explains the higher dark erosion of resist with a remaining solvent concentration too high (e. g. in case of an insufficient softbake).



Surface Inhibition Layer

T-topping sometimes observed on developed resist profiles results from a reduced development rate near the resist film surface. Possible reasons of this so-called *surface inhibition layer* (not to be misunderstood with the desired undercut of image reversal resists in image reversal mode, or negative resists in general) are controversially discussed in literature. This section aims for a short summary of various models trying to explain T-topping:



High energy photons (wavelengths around 250 nm with a penetration depth of few 10th nm, apparent also in g-, h-, i-line exposure) break chemical bonds of the Novolak cresol chains. High temperatures during subsequent baking steps (e. g. post exposure bake) may – promoted by oxidation by O_2 from air – cross-link surface near resist regions making them less soluble in developer. However, typical exposure doses of standard mask aligners allow no sufficient bond braking and cross-linking, and the high diffusion constant of O_2 in resist cannot explain thermally induced oxidation solely limited to the resist surface.

The different (polar/unpolar) nature of the resist/air and resist/substrate interface promotes the spatial segregation of cresol chains. This process is molecule size selective and therefore allows a concentration of the large chain fraction (less soluble in developer) near the resist surface. Additionally, the formation of spatial inhomogeneities of other resist components which impact on the development rate (mainly the indene carboxylic acid formed during exposure, or remaining solvent) are suspected for the creation of the *surface inhibition layer*.

The roughening of the resist surface during the beginning of development (sometimes accompanied by a 'milky' appearance) enhances the resist/developer interface and therefore may explain the often observed reduced dissolution rate in the beginning of development. However, T-topping cannot be derived from this mechanism.