New high etch resistant high resolution silsesquioxane based resist for DUV/EUV and e-beam lithography as long shelf-life and more sensitive alternative for HSQ

Tobias Mai, Christian Kaiser, Matthias Schirmer, Maik Gerngroß
ALLRESIST GmbH, Am Biotop 14, Strausberg, D-15344, Germany
tobias.mai@allresist.de

Frank Heyroth, Georg Schmidt
Martin-Luther Universität Halle-Wittenberg, Halle (Saale), Germany

Nicolas Pyka
Raith GmbH, Dortmund, Germany

Lothar Hahn
Institute of Microstructure Technology, Karlsruhe Institute of Technology, Germany

The good and reliable properties of HSQ are well known by all e-beam operators. However, the biggest disadvantages when processing HSQ are the relatively short shelf life of the resist and the small processing window between layer preparation and exposure. The complete decomposition of well-prepared layers easily occurs within hours whereby resolution will reduced subsequently. Nevertheless, the processing window of prepared layers could prolonged when stored under Argon or in vacuum [2]. Therefore, we attempted to stabilize the silsesquioxane for a prolonged the shelf life and processing window while still keeping the advantages like high silicon content for etch resistant and high resolution. We combined our knowledge in our recently developed e-beam resist Medusa 82 (Figure 1) which is silsesquioxane based as well, though it can now processed with the HSQ standard procedure but with a delay of several weeks under standard conditions between layer preparation and exposure; the material tolerated storing periods of several weeks at room temperature (Figure 2). Alongside the bigger processing window by the time of writing Medusa 82 shows a longer shelf life in comparison to HSQ. Within these two different exposures we also showed that Medusa 82 is stable for different developing temperatures similar to the results from Chen et al. [1]. When compared to HSQ Medusa 82 could easily processed following the established standard procedures that result in similar sensitivity and resolution (current investigations with Martin-Luther Universität Halle-Wittenberg). Moreover, the higher stability does not influence cross-linking DUV/EUV, which is still possible as well. Since Medusa 82 is a silsesquioxane too the etching and optical parameters are equal to the HSQ ones. For example, providing an oxygen plasma to lines of Medusa 82 didn't affect the resist pattern (Figure 3). Furthermore, we investigated an additional development to Medusa 82. We generated variations of Medusa 82 with which it is possible to exposure with less energy to cross-link the resist. Furthermore, there are weaker alkaline developer possible and providing a post exposure bake causes a significant enhancement of the sensitivity and the contrast as well (Figure 4).

[1] Chen et al., Effects of developing conditions on the contrast and sensitivity of hydrogen silsesquioxane, Microelectronic Engineering 83 (2006).
[2] Rooks, M., Storing HSQ in liquid nitrogen (2014).

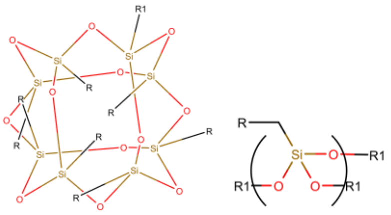

Figure 1: Chemical structure of Medusa 82, left: cluster formula; right: short structural formula.

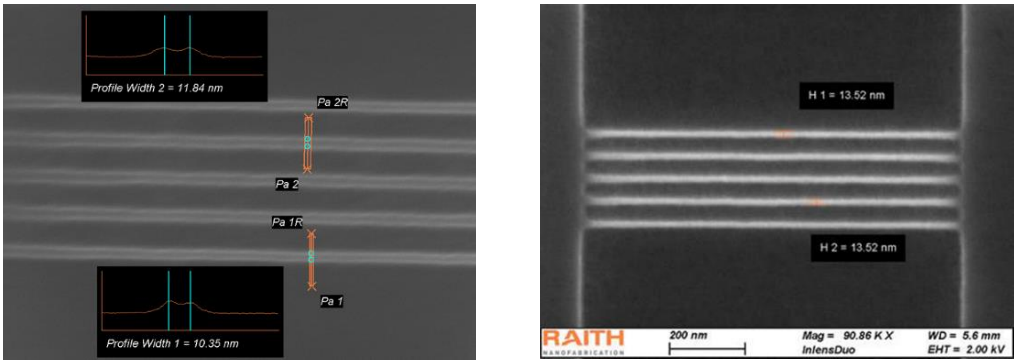

Figure 2, left: 12 nm lines of SX AR-N 8200.03/1 in SEM, 50 nm film thickness, soft bake 10 min at 120°C, exposure at 30 kV Raith Pioneer, development with AR 300-44 for 90 s at 23°C; *right:* Realized 13 nm lines from a coated substrate that was stored at room temperature for 22 days, process conditions as described before.

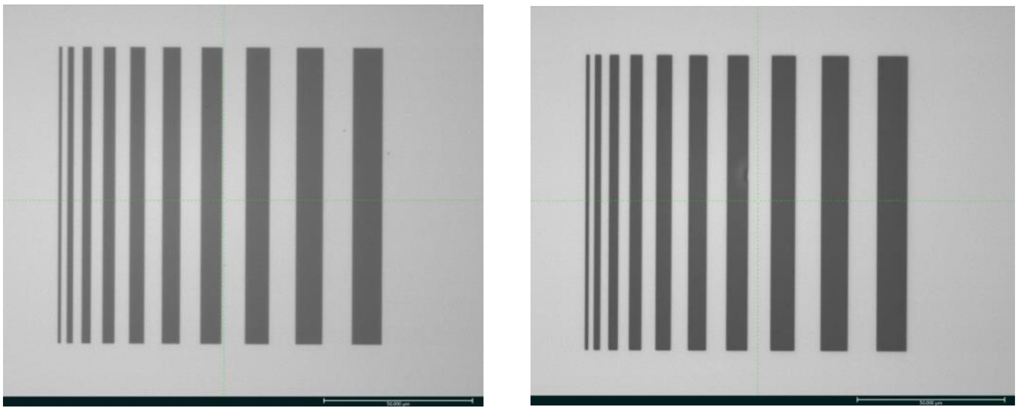

Figure 3 left: Bars of SX AR-N 8200.06/1 in optical microscope view, film thickness 100 nm, exposure dosage 2.000 µC/cm^2 at 100 kV, development with AR 300-44 for 90 s at 23°C; *right:* Resist bars after a 10 minutes treatment with oxygen plasma.

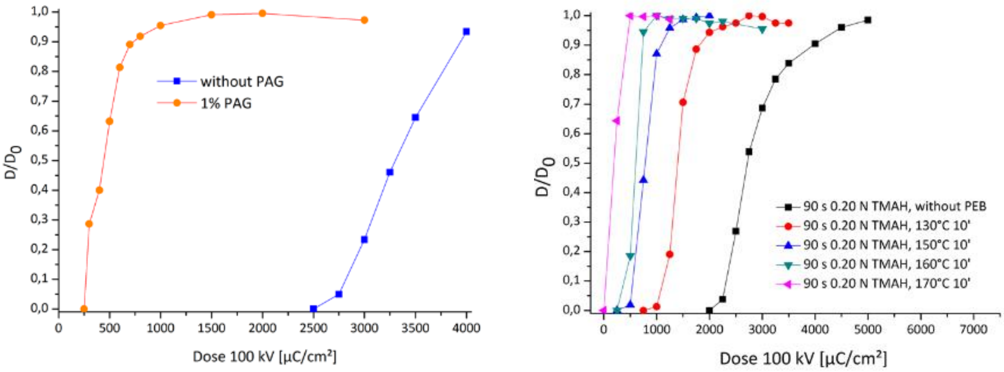

Figure 4, left: Gradation plot of SX AR-N 8200.06/1 with and without PAG, film thickness 100 nm, soft bake 10 min at 130°C, exposure at 100 kV, development with AR 300-44 for 90 s at 23°C; *right:* Enhancement of sensitivity by PEB variation, SX AR-N 8200.06/1 without PAG, film thickness 100 nm, soft bake 10 min at 130°C, exposure at 100 kV, development with AR 300-47 for 90 s at 23°C.