AR NEWS

39th Issue, April 2019, Allresist GmbH

Content:

Welcome to the 39th issue of the AR NEWS. Once again, we would like to inform you about the further development of our company and the current research projects.

1. Synthesis week in the new production tract

In the last AR NEWS, we reported extensively on the new extension of our company building by 450 m², which is now fully operational. The endurance test, a complex synthesis week in a three-shift system during which the raw materials for our most popular products CSAR 62, Electra 92 and the bottom resists AR-BR 5400 were produced for the next months, was passed with flying colours. The improved technological possibilities, accompanied by further development works, resulted in a yield increase from 11 to 38 % with regard to the synthesis of the Electra polymer. In the case of the PMMA copolymer synthesis (an important component of bottom resists), it was possible to save 2.5 tonnes of precipitation solvent due to a newly introduced procedure.

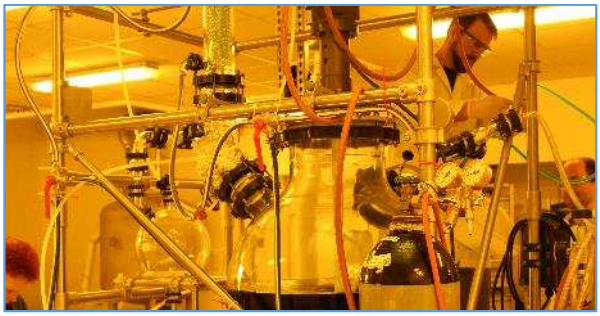

Fig. 1 Synthesis in the reactor of the new production tract

The accomplishment to construct the new building extension in the last year has proven to be very forward-looking. The sales of these three resists currently increase remarkably; they already account for 33 % of our product turnover. And with our latest highlight product Medusa 82 (the HSQ analogue), another top-class new development is now on the starting blocks.

In addition to create new production and synthesis facilities, we also significantly increased our storage capacity. This enables us to store a large supply of strategic raw materials for a cost-effective production on a large scale. Another important objective of this measure is to ensure the supply of tailor-made resists for our batch-loyal key account customers in the long run.

But also the well-being of our Allresist team was an important aspect for us in the construction planning. The newly created and planted 5 x 12 m large atrium separating the "old" laboratories from the new production building turnes out to be quite popular among our employees. The warm spring lures all of us to use this recreational spot during breaks, and in just a few weeks, all plants will be blooming.

Fig 2 New atrium for break times of the Allresist team

2. Allresist at the congresses Triple Beam (EIPBN 2019) and MNE 2019

Our research team was very successful in the recent years and developed many innovative resists that are highly popular around the world. We again attend both congresses to inform trade visitors about the status of our recent developments. Several scientific papers are submitted and we present the respective results in lectures and posters on both congresses.

The highlight of the presentations is undoubtedly Medusa 82. With this resist, we brought an improved alternative to HSQ resists onto the market. Already in the run-up of the EIPBN Conference 2019, the interest in Medusa 82 turned out to be large, especially in the US market.

Gerald Lopez, University of Pennsylvania and co-organizer of EIPBN 2019, initiated a meeting series for Advanced Electron Beam Lithography (MAEBL) in the US, which is sponsored by Allresist. The new resist was already presented on these meetings. Our lecture on Medusa 82 at the EIPBN 2019 in Minneapolis, Minnesota, USA, will thus attract an even larger circle of interested users.

Our most recent results are furthermore presented at the MNE 2019, which this year takes place at the end of September in Rhodes. Beyond Medusa 82, interested users will be informed about new developments concerning Atlas 46, Phoenix 81, and our coloured and fluorescent resists.

You are welcome to visit us at our booths!

3. Medusa 82 passed comprehensive application tests

After first promising results, samples of Medusa 82 were provided to many interested parties with the request to let us know their own results. Every e-beam user has self-developed technologies and tricks which our products have to be compatible with. In the first tests of our users, partly other developers as well as own process parameters were applied which led to results differing from those obtained by Allresist. The results were nevertheless remarkable and showed us further fields of application. All user feedbacks however consistently underlined a positive experience with the new e-beam resist. Some of the results are presented in the following.

3.1. Dissolution tests with the sensitive PAG-Medusa 82 (SX AR-N 8250)

Mr. Pyka from the company Raith, Dortmund, compared the properties of Medusa 82 with photoacid generator (AR-N 8250) and without (AR-N 8200). The samples were prepared as follows:

Substrate: 4“ Si-Wafer <100>
Coating: 30 s @ 4500 rpm
Prebake: 90 s @ 180 °C
Exposure: Raith e-Line Plus, 30 kV

In both experiments, development was performed for 90 seconds with AR 300-44.

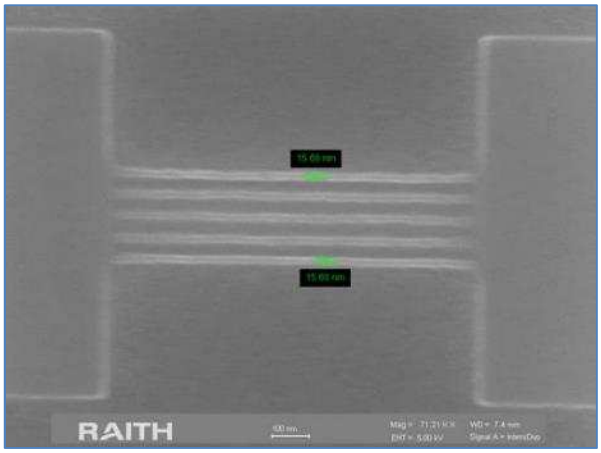

Fig. 3 14-nm lines produced with Medusa 82 SX AR-N 8200.03/1 (no PAG), dosage 7500 µC/cm²

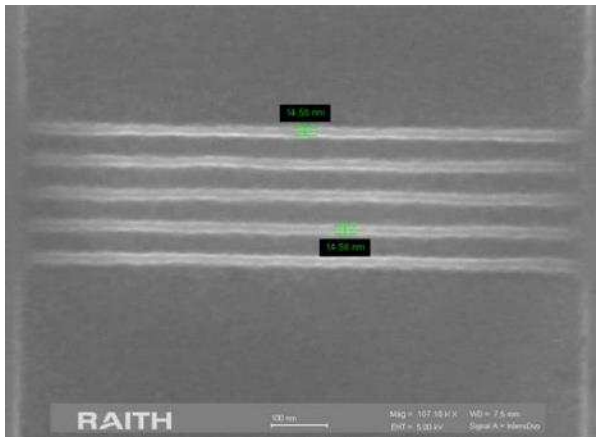

Fig. 4 14-nm lines produced with Medusa 82 SX AR-N 8200.03/2 (with PAG), dosage 1290 µC/cm²

With this test, the sensitivity-increasing effect of the photoacid generator (PAG) was confirmed. Very pleasing was the discovery that the maximum resolution of 14 nm can also be achieved with the considerably more sensitive Medusa variant. Mr. Pyka expressed his praise for the resist properties. Quote: "What I really find fascinating about this resist is the uncomplicated handling. For reasonably good HSQ structures, we have to make a huge effort in our facility. Samples have to be rendered hydrophobic, and the storage of samples and resist is another story. This resist is much easier in this respect."

3.2. Influence of a PEB on the sensitivity of Medusa 82

At the Delft University of Technology, Netherlands, Ms. Anja van Langen-Suurling investigated the sensitivity-enhancing effects of a prebake and a post-exposure bake (PEB). For this purpose, Medusa samples were initially tempered after coating at 140 °C and 170 °C, and then sensitivity and contrast were determined. As developers, MF 321 and MF 322 provided by DOW Chemicals were used.

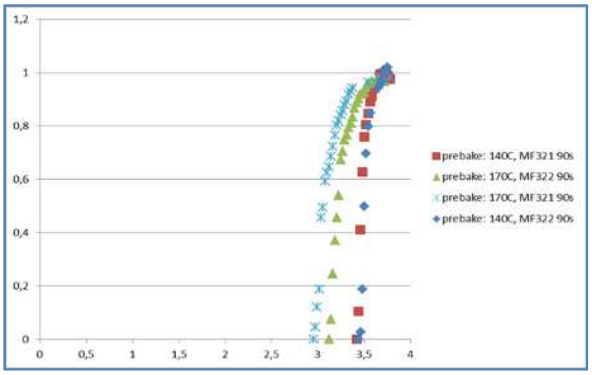

Fig. 5 Contrast curves of Medusa 82 SX AR-N 8200.03/1 after different prebake steps

Process Conditions	D50 [□c/cm²]	□
Prebake 170 °C, MF322 60s	775	4.4
Prebake 170 °C, MF321 60s	467	2.0
Prebake 140 °C, MF322 90s	3163	13.4
Prebake 140 °C, MF321 90s	2950	11.4

Tab. 1 Sensitivity and contrast of Medusa 82 SX AR-N 8200.03/1

The sensitivity can be significantly increased by a prebake (softbake) after coating. However, this came at the expense of the contrast in this experiment, which was lower in both developers. The photoacid generator partially decomposes the structure of the silsesquioxane during irradiation and thus increases the sensitivity. This effect can also be induced thermally with a softbake. Since a thermal decomposition affects the entire surface, also the later unexposed areas become more sensitive and the contrast consequently decreases.

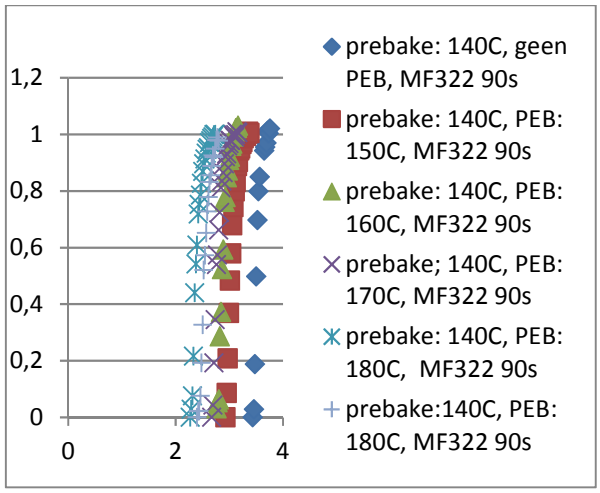

Fig. 6 Contrast curves of Medusa 82 SX AR-N 8200.03/1

Post-Exposure Bake	Sensitivity µC/cm²
no	3163
150	1038
160	730
170	568
180	332

Tab. 2 Sensitivity of Medusa 82 SX AR-N 8200.03/1 after different PEB steps

The contrast was different after a PEB step (see Fig. 6 and Tab. 2). Increasing the PEB to 180 °C resulted in a sensitivity increase by a factor of 10. The high contrast of >10 however remained since the increase in sensitivity only occurs in exposed structures.

In patterning experiments (analogous to Raith), lines up to 13 nm were resolved (Fig. 7). Lines and squares (Fig. 8) could be realized in very good quality.

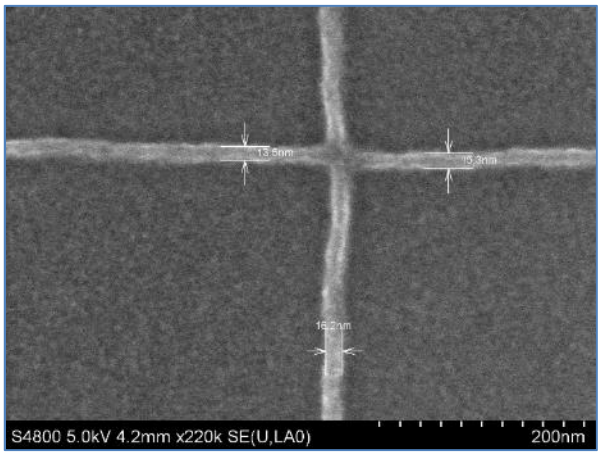

Fig. 7 Crossing lines up to a resolution of 13 nm

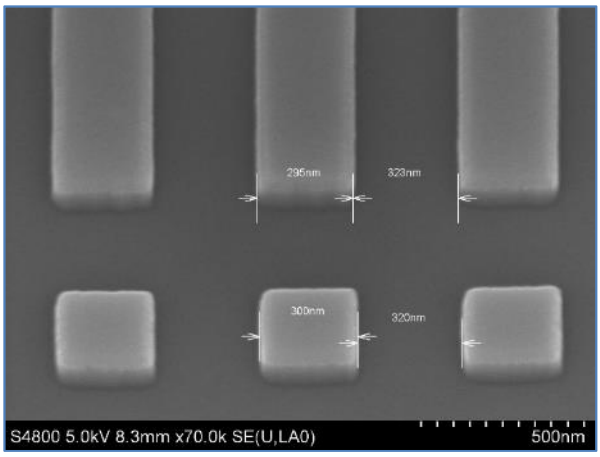

Fig. 8 High imaging quality of Medusa structures

3.3. Plasma etching tests with Medusa structures

Laurent Markey from the University of Bourgogne, France, produced a waveguide structure with Medusa 82. The following process parameters were used:

Si wafer with 4 µm SiO_2 + 230 nm TiO_2
Coating MEDUSA 82 resist:
Wafer dehydratised for 5 min at 120 °C on a hotplate
1000 rpm spinning speed
150 °C hotplate bake, 5 min
EBL condititions of Raith Pioneer EBL system:
20 kV accelleration speed
Area dosage of 300 µC/cm^2
Dose factor was varied around 1 -> df = 0.7 yielded the best result (210 µC/cm^2)
Development AZ 726 MIF developer, 30 sec.

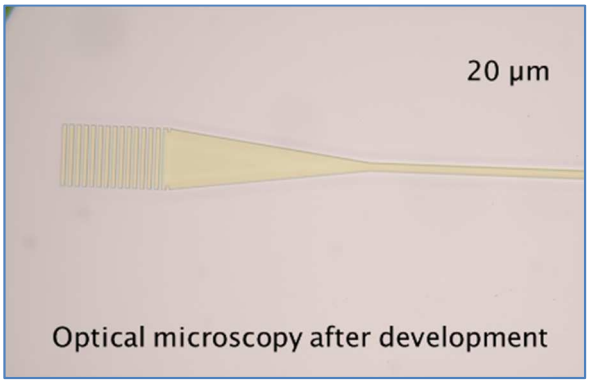

Fig. 9 Waveguide structure of Medusa, film thickness 199 nm, dosage 210 µC/cm², 20 kV

These Medusa 82 structures were subsequently etched in an oxygen plasma:

Plasma etching parameters:

RIE O_2, 80 W, 50 mTorr, 5 min

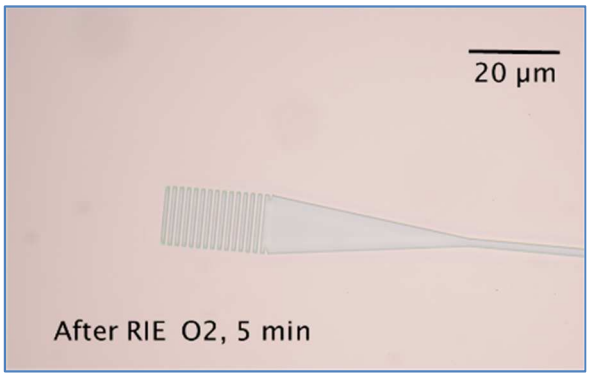

Fig. 10 Medusa struktures after O_2 etching, film thickness still 140 nm

Etched structures showed a very good quality; the resulting layer thickness of 140 nm was quite sufficient for the following process steps.

Sentech Instruments, Berlin, determined the etch rates of Medusa 82 in two plasmas:

Oxygen:
30 sccm O_2, 230 W ICP, HF Bias -317 V, 1 Pa, 20 °C, etch rate: 6 nm/min
Oxygen/tetrafluoromethane:
30 sccm O_2, 5 sccm CF4, 230 W ICP, HF Bias -317 V, 1 Pa, 20 °C, etch rate: 160 nm/min

3.4. Medusa 82 with specifically low contrast

The master thesis of Mr. Voigt, working group of Dr. Hübner, Leibniz-IPHT Jena, deals with the fabrication of three-dimensional structures using the "pure" Medusa resist AR-N 8200.06 and Medusa resist AR-N 8250.06/1 with added PAG. Meanwhile, the first results are available:

Resist: Medusa 82 UV

Thickness: 400 nm
Exposure: 50 keV
Device: Vistec SB350OS (variable shaped beam)
Dosage range: 100 to 1500 µC/cm²
Development time: 30 s
Developer: AR 300-44, rinsed in DI H_2O
Sensitivity:
Do: 55 µC/cm²
D1: 267 µC/cm²
Contrast: y (gamma)= -1.45

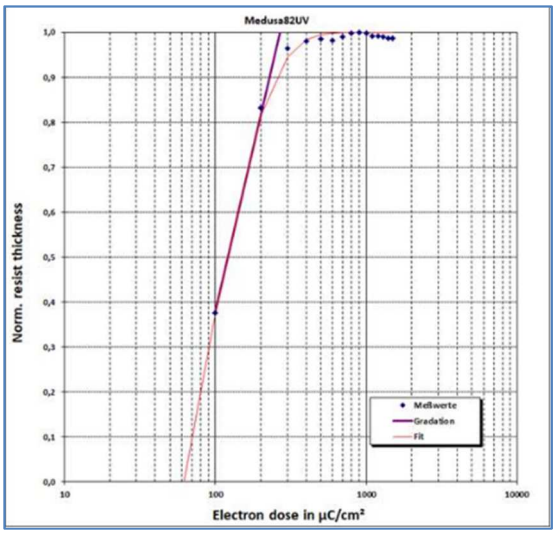

Fig. 11 Contrast curve of Medusa 82 UV

Resist: Medusa 82

Conditions equivalent to Medusa 82 UV
Sensitivity:
Do: 500 µC/cm²
D1: 632 µC/cm²
Contrast: γ (gamma)= -9.8

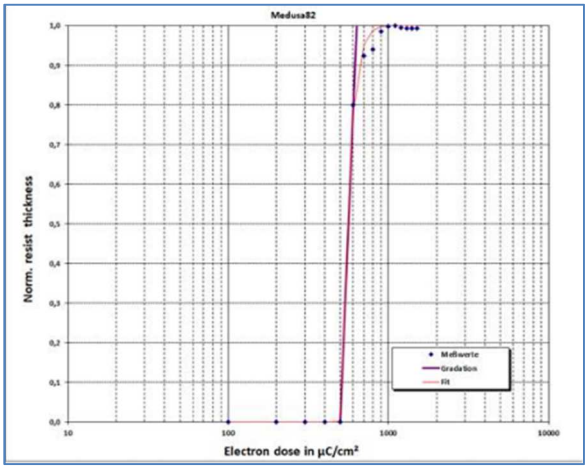

Fig. 2 Contrast curve of Medusa 82

Medusa 82 UV contains in addition a photoacid generator (PAG). The experiments also confirmed that an addition of PAG increases the sensitivity. Conditions and resist formulation were in this experiment however chosen in such a way that the lowest possible contrast could be achieved. For resists with a high contrast (> 10), the structuring of the layer is completed within a few µC/cm². To realize for example 8 different doses for 8 different layer thicknesses, the spacing should ideally only be 1 µC/cm², which is technically impossible to realize. However, with a spacing extending from 100 to 200 µC/cm², several differentiated doses can be applied.

The low contrast of 1.45 is documented in Fig. 11. If structures with different, increasing doses are now generated in the range of 55-267 µC/cm², increasing layer thicknesses are obtained for each dose (Fig. 14). This is how gray value grids and DOEs can be written.

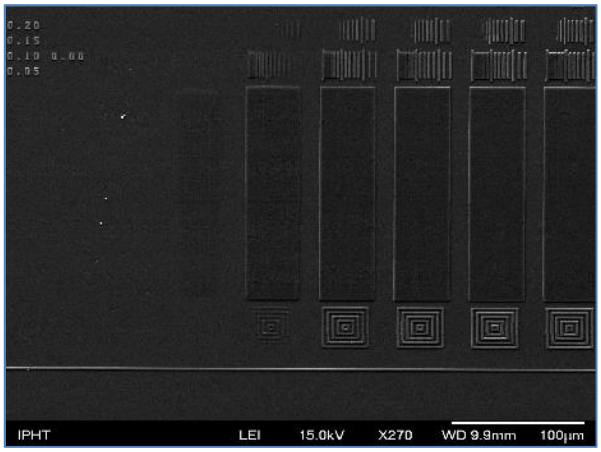

Fig. 13 A grey tone wedge produced with Medusa 82 UV structures

Further results will be presented at the MNE 2019 in Rhodes. We are currently preparing a joint paper with the Leibniz-IHPT for the MNE.

4. Five coloured negative resists on one glass wafer

We presented the first results of our coloured Atlas resists already on the MNE 2018.

Fig. 14 Coarse test structures on a glass wafer

The development of coloured resist continued, and we were thus able to provide various qualified coloured Atlas samples to Precision Optics Gera GmbH (POG). Mr. Hermeyer from POG tested our samples and produced a demonstration wafer with five differently coloured structures that were successively applied.

At first, the yellow-coloured "Siemens star" was irradiated, crosslinked and developed, wile

unexposed areas were removed. Subsequently, the second resist was spun on.

The already existing structures did not interfer with this process and were not dissolved. The second layer was also exposed, crosslinked and developed. Sucessively, all five colours were deposited on the wafer in the same manner.

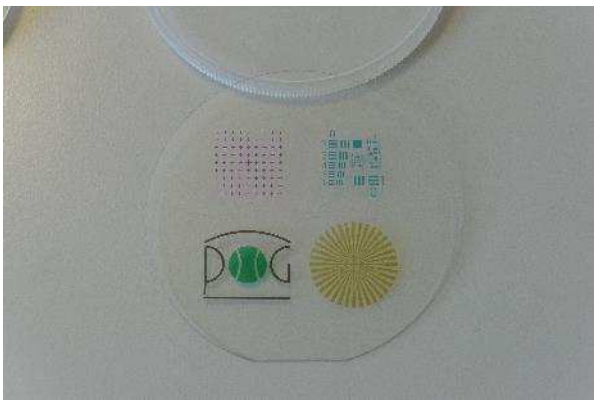

Fig. 15 Test wafer with five different colours

An important feature of the coloured structures is long-term stability, which was not yet given in the single samples. New dyes evaluated in cooperation with the University of Potsdam and Precision Optics Gera GmbH give legitimate reasons for hope that a very good long-term stability can be achieved with these resists in the future. A ZIM project will be applied for to support the work.

We hope that you found interesting and helpful suggestions for your own applications and would highly appreciate your feedback. And if the way to Minneapolis or Rhodes should be too far ☺, we will inform you in our next issue!

We present the next regular issue of the AR NEWS in October 2019.

Until then, we wish you and us successful times!

Strausberg, 30.04.2019
Matthias & Brigitte Schirmer in the Team of Allresist