

29th issue, October 2014, Allresist GmbH

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Welcome to the 29<sup>th</sup> edition of AR NEWS. We would like to inform you again about the development of the company and its ongoing research projects.

# I. Opening ceremony of our annex building on time for the 22<sup>nd</sup> anniversary of Allresist

We already now look back with pleasure on the year 2014. After two awards for Allresist in spring (Entrepreneur of the State of Brandenburg and Brandenburg Innovation Award for the successful product development of CSAR 62), work on our extension building started in June. Just in time for our 22<sup>nd</sup> anniversary, the construction work was completed after less than 4 months of work.

Further investments will however follow to meet the demands of significantly increased production volumes with consistently excellent quality and to realise the on-site synthesis of CSAR 62 with modern equipment. Allresist now has larger production and storage capacities and thus guarantees short delivery times of 2 days also in the future.

The expansion work was exclusively awarded to Brandenburg companies. Thanks to an efficient project management, the ambitious schedule was precisely adhered to.

We are moreover indebted to the State of Brandenburg. Ralf Christoffers, Minister for Economic and European Affairs. He already last year signed the approval for a GRW-grant (50 % of the total costs), which relieved our project funding noticeably. We also received active and friendly support from the ILB to realise this funding.



We now look forward with anticipation to our opening ceremony. Under the heading "Brandenburg's high tech resist CSAR 62 ... Opening of our annex building ... 22 years Allresist", the Allresist team invites construction workers, key partners, and politicians to celebrate this wonderful linking of three events together on October 16. We are expecting the participation of the Minister for Environment, Health and Consumer Protection of the State of Brandenburg, Anita Tack, as well as the Mayor of Strausberg, Elke Stadeler.



Fig. I New annex building of Allresist GmbH



## 2. New application results with CSAR62 (thicker layers)

The highly sensitive e-beam resist CSAR 62 is meanwhile one of our most successful products. We currently offer 3 standard variants:

AR-P 6200.04 (80 nm / 4000 rpm),

AR-P 6200.09 (200 nm / 4000 rpm), and

AR-P 6200.13 (400 nm / 4000 rpm).

Intense plasma etchings for the fabrication of deeper etch structures however require significantly thicker layers and also have special demands with regard to resolution and contrast.

Resist AR-P 6200.13 reliably produces layers with a thickness of 800 nm at a spin speed of 1000 rpm. Studies conducted at the Martin Luther University in Halle revealed that trenches with a width of less than 100 nm can be generated with a period of 300 nm. The high contrast is made possible by the use of our developer AR 600-546.

By increasing the exposure dose, the degree of the generated undercut could be adjusted specifically ( $\rightarrow$  Fig. 2 - 4). The profile can thus be selected in accordance with the requirements of each user during the lift-off process. For the generation of nano-conductor paths with a metal height of only a few 10 nm, resist layers of 100-200 nm are however still the best choice. In contrast, columns with a height of several 100 nm and diameters of less than 100 nm (e.g. nanowires) can be produced with "thick" lift-off structures.

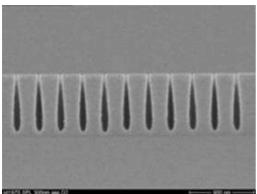


Fig. 2  $\,$  AR-P 6200.13, 823 nm layer, dose: 1200 pC/cm  $\,$ 

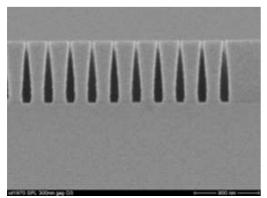


Fig. 3 AR-P 6200.13, 823 nm layer, dose: 1440 pC/cm

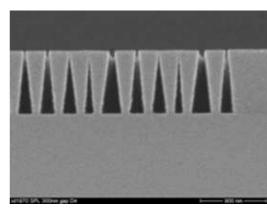


Fig. 4 AR-P 6200.13, 823 nm layer, dose : 1728 pC/cm

For applications that require even thicker layers, we offer a special variant of CSAR 62 which produces a very high contrast if used with developer AR 600-546: SX AR-P 6200/10 (1.5  $\mu$ m/1000 rpm). In 2015, this variant will be offered as one of our standard products with the designation AR-P 6200.18.

During the development of thicker films, a considerable amount of polymer is dissolved in the developer. Layers should be briefly rinsed with fresh developer and/or MIBK immediately afterwards. The deposition of polymer residues and particles from the developer solution on the substrate can thus be avoided effectively. The subsequent stopping is carried out in AR 600-60.

This trick can also be used for thinner resist layers, if small amounts of particles might remain on large structures. A further preventive option is to increase the exposure dose by about 20 %.

# 3. Start of Eurostar project PPA-Litho on November 1, 2014

In early October, Allresist was granted approval for the European project PPA-Litho:

"Development and manufacture of resists based on structure-optimised polyphthalaldehydes for advanced lithographic applications".

Goal of the joint project is the production and first commercial availability of a new high-performance resist based on polyphthalaldehydes (PPA) for new lithographic methods for nanostructuring.

The particular properties of PPA allow an application in two main fields: as base material for a self-developing resist, and for new innovative lithography processes, especially for thermal probe nanolithography and direct laser writing.



In addition, other applications are also conceivable. In the near future, these materials may be of interest for electron beam lithography as well as for "normal" photolithography.

It is therefore necessary to synthesize new and structurally optimized polymeric materials on the basis of PPA, and corresponding resists have to be developed and adapted to these specific applications. In order to achieve this goal, several partners from Switzerland, Austria and Germany cooperate in the joint project. Their core competencies are the synthesis of organic polymer materials, the development, production and sales of photo and electron beam resists, and the production of lithography systems for nanostructuring.

Objective of the subproject implemented by Allresist is to ensure the manufacture of novel, thermally developable resists for advanced lithography applications. Allresist's task is to develop equipment and procedures for the production of the PPAs. Various nano-resists will be designed for different microstructuring techniques.

Polyphthalaldehyde (PPA) opens the door to new lithographic methods. Solutions of this polymer can be processed into stable, thin films by spin coating - a prerequisite for all lithographic procedures.

Of particular importance is in this case that the polymer is degraded into volatile monomer units when heated to approximately 150 °C. This thermally initiated depolymerisation can be narrowed down locally, so that the process only occurs where e.g. the heated tip of an atomic force microscope contacts a polymer layer (see Fig. 5) and the resist layer only evaporates in this particular area. With this method, structures in the nanometre range of up to 10 nm resolution can be fabricated without the need for wet-chemical or plasma-based etching procedures. The complete evaporation of degradation products is another advantage of this contamination-free direct inscription method.

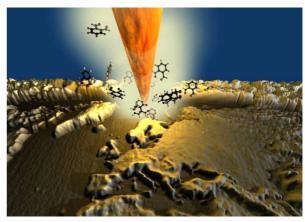


Fig. 5 Generation of Europe using the NanoFrazor-method (Source: SwissLitho)

The NanoFrazor prototype has successfully been tested for several months (see Fig. 6). This device is an affordable alternative to commonly used ebeam writers, and Allresist will develop nanoresists especially suitable for this process. In addition, PPA resists with addition of light- or radiation-sensitive components will be profiled for applications in laser-, e-beam, and photolithography.

We invite all interested parties to contact us with ideas or wishes on this issue. If you e.g. need to process a substrate under completely anhydrous conditions, this procedure might be a solution. We are looking forward to your comments.



Fig. 6 NanoFrazor device



#### 4. New developments of Allresist

#### 4.1. Thermostable positive resist

In the penultimate AR NEWS (Issue 27), we reported on thermally stable negative resists SX AR-N 4340/6 and SX AR-N 4340/10. Structures of these resists are able to withstand temperatures of up to 350 °C with high structural accuracy (→ Fig. 7), and shrinkage of less than 20 % is observed. (→ Fig. 8).

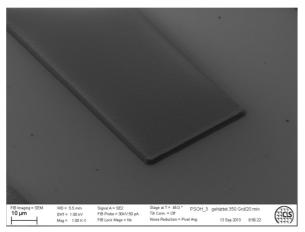


Fig. 7 REM image of SX AR-N 4340/6 structure tempered at 350  $^{\circ}\text{C}$  with smooth surface and sharp edges

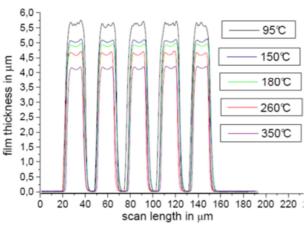


Fig. 8 Temperature-dependent shrinkage, measurement on Dektak 150

Several customers also asked for thermostable positive resists. For this purpose, we assessed combinations of thermally stable polyhydroxystyrenes and light-sensitive components. After numerous test series, the best sample yielded structures of strong resistance to high temperatures as they occur in intensive etching or implantation processes. The temperature-stable positive resist SX AR-P 3500/8 is currently being tested by customers.

Most commercial removers dissolve resist layers after thermal loads of up to 130 °C easily. At high-

er temperatures however, the aqueous-alkaline remover AR 300-73 has to be used. Structures hardened above 150 °C are inert to solvents and thus allow applications in microfluidics. Samples of the new positive resists are now available on request.

## 4.2. Sensitive negative PMMA resist (CAR)

PMMA resists are mainly used for electron beam applications or as protective coatings in aggressive wet-chemical etching techniques. In principle, a structuring of PMMA layers by deep UV-exposure (220 - 266 nm) is also possible, but the sensitivity is low in this case and long exposure times are required.

If the advantageous properties of PMMA structures are desired e.g. for transparent coatings, PMMA negative resists can be used. For this purpose, Allresist offers X AR-N 4800/16 which can be structured by deep UV and i-line exposure (365 nm). The resist provides however, like all conventional PMMAs, only medium sensitivity.

This motivated us to search for a PMMA variant with higher sensitivity. After several weeks of work, our research team finally succeeded in transferring the principle of chemical amplification to PMMA polymers. The new chemically amplified formulation is characterised by a very good sensitivity in the wavelength range of 300 - 410 nm; g-line-exposure is however also possible (436 nm). With the new experimental sample SX AR-N 4810/1, resist thicknesses of up to 5  $\mu$ m can be realised. The developer is composed of an anisole-solvent mixture. First samples will be available at the beginning of 2015.

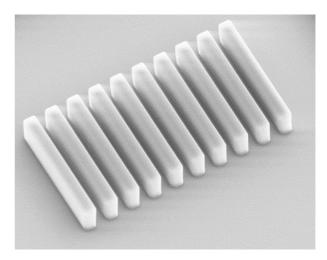


Fig. 9 5-µm bars with SX AR-N 4810/1



#### 4.3. Safer solvent PMMA resist

The protective coatings AR-PC 503 and AR-PC 504 have been used successfully for many years by our customers in aggressive KOH etchings. These resists are traditionally produced with the solvent chlorobenzene. In order to not only offer the best quality, but also the highest possible level of health protection for our customers, we designed a PMMA resist with the safer solvent anisole.

In-house tests showed that the excellent protective effect of the PMMA layer is retained even in anisole; but good adhesion to various customer substrates still has to be verified. Currently, users conduct own tests with SX AR-PC 5040/I samples.

While our research team was working on a solvent replacement for protective coatings, new ideas developed for an optimisation of their coating properties. Protective coatings tend to produce "cotton candy" effects under certain conditions during spin coating, i.e. fine PMMA strings occur.

We now produced samples that reduce this effect. First samples of the protective coatings based on safer solvent and with optimized coating performance will be available at the beginning of 2015.

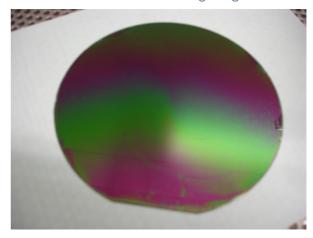


Fig. 10 Wafer with SX AR-PC 5040/1 after 6 h etching in 30 % KOH at 85 °C

We hope that you could find some inspiration and we encourage you to communicate us your particular wishes.

The next edition of AR NEWS will be published in April 2015. Until then, we wish you and us a successful time.



Strausberg, 16.10.2014
Matthias & Brigitte Schirmer
in the Team of Allresist