

27th issue, October 2013, Allresist GmbH

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#### 1. Prosperous year 2013 for Allresist

Every year in the middle of October – around the time of the company's anniversary - are we able to estimate more accurately the result of the current financial year. After a spectacular year 2012 with our 20th company anniversary and winning the Ludwig Erhard Award, we now look back with joy to a rather "normal", but nevertheless very successful year 2013.

Our ambitious sales targets were so far exceeded in every month. This result is mainly due to our new developments and the acquisition of many new customers. Above all, high sales figures for the CSAR 62 and the new anisole PMMA resists as well as the further increasing export revenues are quite noticeable. Many new customers are attracted by the concept of excellence continuously promoted by Allresist, which also facilitates the initiation of new business contacts.

The fortunately high demand for Allresist products will reach our capacity limits in the near future. In order to further ensure such short delivery times, we thus decided to expand in 2014 the company

building which was constructed in 1999. We in particular intend to increase the production and storage capacity and to expand the logistics segment. The extension is scheduled for the summer 2014 and shall be inaugurated on our 22nd anniversary next year.

We currently also develop new product descriptions which will provide more specific product details. The new folders for photoresists are available to our customers as of January 2014, folders for ebeam resists will follow in March 2014.

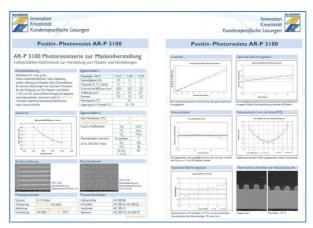


Fig. I Excerpt from a new photoresist product description folder





# 2. Establishment of the "German Innovation Center" in Changzhou

A German-Chinese working group led by Dr. Zhou officially opened the new German Innovation Center on 26.09.2013 in Changzhou. Dr. Zhou, who is also partner of our sales office Germantech in Peking, created after long negotiations the required preconditions so that the Innovation Center is now finally ready to commence work in the new facilities. The involved German companies presented themselves to municipal decisions makers. In addition to Allresist, the companies Raith, Temicon, AMOtronics, Rose Fotomasken and Heidelberg Instruments participated in this event in Changzhou and outlined how a cooperation with this Chinese region could possibly be structured. In a festive signing ceremony on the following day, one German and one Chinese partner each signed a declaration of intent for the joint establishment of a technology cluster which is aimed to realise micro-structuring processes concentrated in one location. Planned is to establish different lithographic processes which are then used to develop customer-specific adaptations. In this context, Allresist will contribute its experience and its technological know-how.

We will inform you in our AR NEWS about the progress of establishing this Innovation Center and the service options which open up also for our customers.



Fig. 2 Dr. Zhou (left) during the official opening of the new rooms of the German Innovation Center (GIC)



Fig. 3 Signing of documents for the GIC

#### 3. Successful introduction of CSAR 62

The introduction stage of our new positive-tone e-beam resist CSAR 62 was successfully completed. The quite complex synthesis can meanwhile also be performed on a large scale at Allresist. The available analytical methods guarantee a reproducible and constantly high quality of the polymers.

The feedback from CSAR users so far was consistently positive in every respect. The sensitivity of this resist reaches, as a direct comparison confirmed, the level of the ZEP 520, while the process stability of CSAR 62 was considered to be even higher. According to a report by a user from Jena, a complicated structure in the sub-100-nm range could be manufactured with CSAR 62 reproducibly without any need for further adjustment, while this had not always been the case when ZEP 520 was used. In particular, also the possibilities for a safe lift-off procedure and the application of CSAR 62 in two-layer systems were perceived as valuable.

The recently finished long-term stability measurements of the liquid resist demonstrated that the resist remains unchanged over a period of 9 month. We will consequently increase our recommended storage temperatures of 4–8 °C (which resulted from our duty of care) in future new product information sheets.

In many discussions at fairs and conferences like e.g. the MNE 2013 in London, the Semicon Europe 2013 in Dresden and the HARMNST 2013 in Berlin, we have noticed an uncertainty of possible users with respect to the "chemical semi-amplified" reaction mechanism of the CSAR 62. A few interested customers assumed that disadvantages which are generally associated with the use of CARs like instability, lower resolution and amine sensitivity are also to be expected for the CSAR 62. These concerns are however unfounded, due to an entirely different operating principle and chemical components which we selected with utmost care. This is also confirmed by the high long-term stability and the fact that a resolution of < 10 nm is not possible with conventional chemical enhancement. In this respect, our designation "chemical semiamplified" may have been somewhat misleading. After successful long-term investigations and many positive user feedbacks we offer with clear conscience a top-quality, not chemically enhanced ebeam resist which is suitable for highly stable processes.



If users should be interested in resists with increased sensitivity, are we able to offer new developers specifically optimised for this purpose in the near future. The new developers are currently investigated at the MLU Halle. First results indicate that the sensitivity can be increased by a factor of 5 as compared to the standard developer X AR 600-54/6.

As mature and stable product, CSAR resists will replace our stand products next year. These resists will be offered in addition to the currently available variant (6200/2: 200 nm/4.000 rpm) in two further film thicknesses; a thin resist for 80 nm at 4.000 rpm and a thicker resist for 400 nm at 4.000 rpm. CSAR resists thus cover a range of 60 nm to 800 nm. Films with lover thickness values can of course be adjusted by individual dilutions of the user or utilising pre-adjusted dilutions which we provide for a small additional charge. We currently adapt a CSAR resist on demand specifically for a film thickness of 3 µm.

Investigations performed with 80 nm layers demonstrated that a maximum resolution of 6 nm can be achieved.

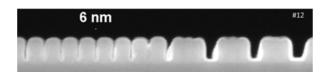


Fig. 4  $\,$  6 nm trenches of SX AR-P 6200/6 at a film thickness of 80 nm  $\,$ 

Electron beam exposure was performed (as in previous experiments) with the Pioneer writer of the company Raith at 30 kV and developer X AR 600-54/6, but the development step was carried out at only 6 °C. Under these conditions, the development time increased by a factor of 3. The required dose for single lines was 260 pC/cm and thus twice as high as compared to a development at room temperature. It is therefore evident that a low development temperature exhibits a positive effect on the resolution.

All results will be included in the new product descriptions which are available at the beginning of 2014. We will provide separate information with respect to particularly interesting details to all readers of the AR NEWS.

# 4. Mask blank production in preparation

The word-wide mask blank production is firmly in Japanese hands (Hoya and others). Only in the USA and in China a few smaller mask producers exist. Allresist resists were for a while also used for the coating of mask blanks and distributed by Schott Lithotec AG, a subsidiary of Schott AG in Meiningen (PMMAs, AR-P 617). The Schott AG shifted the production to the USA in 2006, and production was unfortunately discontinued in 2007.

Since then Allresist endeavours to initiate mask blank production in Germany, but without much success so far. After the development of CSAR 62 however the idea to use Allresist resists for mask blanks was given a strong new impetus. We currently evaluate in cooperation with a partner if a mask blank production could be realised in China. We hope to get support and ideas from the German Innovation Center (see item 2) and intend to produce first test samples of mask blanks with CSAR 62 in a few weeks.

This is why we now turn to you, dear customers. Please inform us if you need mask blanks, and if so, which size, kind of mask blank material or which resist you would prefer. This may also be a resist which is not yet specifically adapted for the coating of masks. We intend to offer for example also the negative e-beam resist SX AR-N 7520/4 which is characterised by a very good long-term stability. But also the AR-P 617 (formerly AR-P 610 or PSKL) could make a comeback. And, of course, CSAR masks would definitely be less expensive than ZEP-variants. We would also like to ask users whose masks are written by other companies (e.g. by Photronics, Dresden or compugraphics (formerly ML&C), Jena to communicate your desired masks (format, resist). This would be very helpful for us in order to organise our mask blank production. We look forward to your feedback!

# 5. Thermally stable negative resists

The thermally stable two-layer lift-off system SX AR-N 4340/10 – AR-P 5460 was already presented as resist of the month in July. In many lift-off applications, the resist layer is subjected to high thermal loads. Specifically during sputtering processes without additional cooling, temperatures of 150 to more than 200 °C may occur. Positive resists based on novolacs begin to melt at such high



temperatures, thus rendering a subsequent lift-off impossible.

Allresist therefore develops a series of temperature-stable negative resists. One of the first samples, the SX AR-N 4340/10, is currently investigated in the Center for Intelligent Sensors, Erfurt, by Mr. Preuß with respect to its resistance to higher temperatures.

<u>Process:</u> In a first step, the light-insensitive photo-insensitive bottom resist AR-P 5460 is applied and tempered at 150 °C. The new negative photoresist SX AR-N 4340/10 is then spun onto the bottom resist and dried at 85 °C.

After UV-exposure, cross-linking and development with AR 300-44, the desired undercut is adjusted. Almost any desired undercut is possible, which is clearly demonstrated in Fig. 5.

In this case, the top resist collapsed after a too long development step (undercut of more than 15  $\mu$ m!) due to mechanical stress (own weight).

The resist structure with "normal" undercut was then again tempered at 200 °C. In this process, the undercut was fully preserved (see Fig. 6).

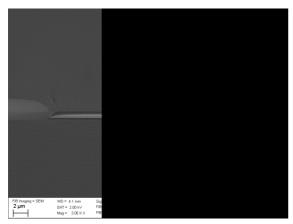


Fig. 5 Collapse of 15- $\mu m$  undercut structure

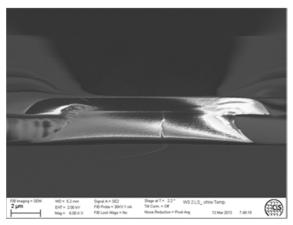


Fig. 6 Lift-off structure after second bake step at 200 °C

Further investigations with thermally stable resists as single layer (which were also conducted at the Center for Intelligent Sensors in Erfurt) provided evidence that structures of the new temperature-resistant negative resist SX AR-N 4340/6 are stable to up to at least 350 °C. The resist was exposed using standard conditions, cross-linked and developed under aqueous-alkaline conditions. The line structures which were obtained with high sensitivity (and with comparably high resolution as for AR-N 4340) were subsequently heated stepwise to up to 350 °C. SX AR-N 4340/6 was able to tolerate these temperatures without any problems, and no significant rounding of edges could be observed.

Due to sintering processes, the film thickness decreased by approximately 20 % as expected (see Fig. 7). The very high surface quality and the structural geometry were fully preserved in this process (see Fig. 8). Structures which were tempered at high temperatures can be removed again in aqueous-alkaline remover.

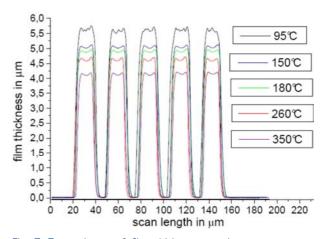


Fig. 7 Dependency of film thickness on the temperature, measurement performed at Dektak  $150\,$ 

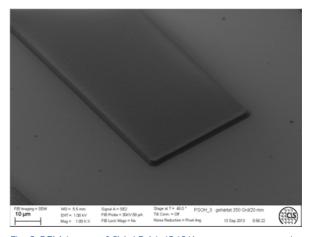


Fig. 8 REM image of SX AR-N 4340/6-structure tempered at 350  $^{\circ}$ C with smooth surface and sharp edges



Entirely new fields of application thus open up for technologies involving high thermal strain like for example an application in soldering or bumping processes. A further major advantage of our new development is the aqueous-alkaline development and its compatibility with standard photolithographic processes. In addition to a high temperature resistance, SX AR-N 4340/6 is also characterised by high plasma etch resistance and good insulating properties.

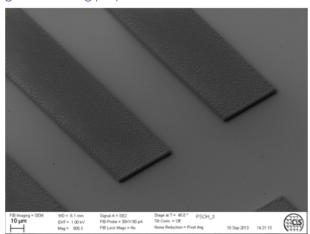


Fig. 9 Line structures of SX AR-N 4340/6 after aqueous-alkaline development (prior to tempering)

#### 6. Conductive resist for e-beam lithography

Resist SX AR-PC 5000/90.1 is utilized by several customers to avoid a charging during e-beam lithography. This charging in particular occurs for glass or quartz substrates, but it may also cause troublesome effects on GaAs-wafers. SX AR-PC 5000/90.1 could however so far only be used for PMMA layers, since novolac-based resists were attacked by the solvent mixture and the resist surface consequently roughened up.

In a well-established cooperation with the IDM e.V., we were able to synthesise a polyaniline in the past few weeks that is applicable in thin layers, water-soluble and characterised by considerably higher conductive properties than SX AR-PC 5000/90.1. With this new conductive coating SX AR-PC 5000/90.2, all resist types (PMMA and novolac-based resists as well as CSAR 62) can be coated. A first experiment conducted last week at the MLU Halle confirmed that the resist is well suited for this purpose.

The experimental parameters of these first tests were as follows:

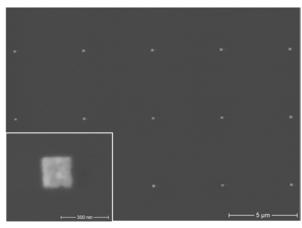


Fig. 10 200nm Ti/gold squares with  $5\mu m$  spacing on glass, thickness of I mm (object slide)

# Sample preparation:

Clean glass object slide  $25mm \times 25mm \times 1mm$ Coated with:

PMMA two-layer system AR-P 679.02 (950k) top layer, AR-P 669.04 (600k) bottom layer (total thickness approx. 340nm)

As well as with protective coating AR-PC 5000/90.2 (coated at 2500 rpm = 40nm)

Exposed in Raith/Pioneer at 30kV and beam current of 150 pA.

=> No charging problem due to the protective coating!!

# Developed:

60s  $H_2O$  for removal of protective coating + 60s MIBK: IPA = 1:2 + 60s  $H_2O$ 

Coating 10nm Ti / 25nm gold Lift-off with acetone

[Dr. F. Heyroth, Dr. B. Fuhrmann, G. J. Prof. Schmidt, IZM, Martin-Luther-University, Halle]

Further investigations to optimise the coating features and measurements of conductivity will follow in the near future. Since we are aware of the fact that a well-working conductive resist is of high interest for all e-beam users, we already now publish the first highly promising results.

On completion of the qualification procedure, we will submit the product information for SX AR-PC 5000/90.2 to all customers.



# 7. Allresist on the Semicon Europe 2013

Already for the 4<sup>th</sup> time, Allresist presented itself on the Silicon Saxony stand in Dresden. Again in particular the new developments (e-beam resist CSAR 62 and the new, highly improved conductive resist SX AR-PC 5000/90.2) attracted the attention of the customers. Topic of many discussions were however also the standard products and our customer-specific developments. We shared many trustful conversations with long-term customers which were mainly aimed at the perspective development of business contacts and the introduction of new products.



We hope to have presented a few interesting suggestions to you and encourage you to contact us with your wishes.

The next issue of the AR NEWS will again be presented in April 2014. Successful times until then!



Strausberg, 15.10.2013 Matthias & Brigitte Schirmer Team of Allresist