



# AR NEWS

26<sup>th</sup> issue, February 2013, Allresist GmbH

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Welcome to the 26<sup>th</sup> issue of the AR NEWS. Again, we would like to inform you about the further development of the company and our research projects.

This is an early issue, since we wish to provide already at this point information to you concerning the particular features of our CSAR 62 – the new alternative for the ZEP resist.

## **1. Recognition for the Ludwig Erhard Prize winner Allresist**

With pleasure we informed you in November 2012 about our 1<sup>st</sup> place in the Ludwig Erhard Prize competition. We received much public attention and praise, and our joy was shared by both partners and customers. The television station rbb broadcasted two reports covering this success.

On the occasion of the prize awarding, we organised a colloquium "Excursion through the nanocosmos – results from research and customer cooperations" in our company building. In addition to the presentation of our own results (Matthias Schirmer), also Hüseyin Sahin, UMS Ulm; Klaus Dieter Preuß, CiS Erfurt; Dr. Thomas Köpnick, IDM Teltow and Prof. Dr. Georg Schmidt, MLU Halle presented highly interesting details from the joint cooperations.

In particular the talk of Prof. Dr. Schmidt was focused on joint scientific findings which reveal the nanocosmos in all its fascination.

For the official honouring, the State Secretary of the Ministry of Economics Henning Heinemann stepped in for Minister Ralf Christoffers who had to cancel his participation on short notice. Further participants were the president Ulrich Müller and the managing director Gundolf Schülke of the

Chamber of Industry and Commerce (IHK) East Brandenburg, the Mayoress of Strausberg, Elke Staderer and other representatives from politics and industry. The State Secretary recognised the outstanding achievements of the team of Allresist which should be taken as an example for all of Brandenburg. He also emphasized that Allresist has now reached the level of the "big" enterprises Bosch and BMW which were award winner and honoured in the Ludwig Erhard Prize in 2012.



Fig. 1 LEP award ceremony on November 26, 2012 in Berlin

## **2. CSAR 62- the future alternative for the ZEP-PMMA resist**

With the development of our new positive e-beam resist we are now able to meet the requests of many users for a sensitive plasma etch-resistant electron beam resist with highest resolution.

The generally used ZEP resist has similar properties and thus also meets these demands. Since the commercial availability however is limited and prices increased exponentially in the last years, customers approached us with the request for an alternative. We took this as an incentive and now present with CSAR 62 a technically improved resist at considerably more favourable conditions.

Three of the main actors of the above mentioned colloquium were and still are involved in this development (MLU, IDM, Allresist). The laborious research works produced already after only a few months surprisingly positive results.

The successful development was preceded by various polymerisation experiments in the IDM with different halogenated acrylates and aromatic vinyl compounds. These investigations were financially supported by the "Innovation Voucher" of the Land Brandenburg. From the most promising copolymers, resist samples were produced and assessed further in Halle at the MLU.

In these investigations it became evident that an addition of CAR components (Chemical Amplified Resists), in particular of acid generators, improves the sensitometric features of the resist. The new resist is thus referred to as CSAR 62 (Chemical Semi Amplified Resist).

CSAR 62 is the general name for the future type designation AR-P 6200, while the current experimental sample is called SX AR-P 6200/2.

The following results were obtained in investigations conducted so far:

- Sensitivity comparison of CSAR 62 – PMMA 950K

The sensitivity (dose to clear) of sample SX AR-P 6200/2 was compared to the sensitivity of the PMMA 950K resist (AR-P 679.03). Using the standard developer AR 600-56, the sensitivity of the PMMA-resist was  $165 \mu\text{C}/\text{cm}^2$  and increased to  $311 \mu\text{C}/\text{cm}^2$  if the (contrast-enhancing) developer AR 600-60 was used (see Fig. 2). The sensitivity of SX AR-P 6200/2 reached  $55 \mu\text{C}/\text{cm}^2$  and was thus threefold and sixfold higher, respectively.

- Contrast comparison of CSAR 62 - PMMA 950K

The maximum contrast of PMMA resists is generally in the range of 5 – 7. If AR 600-60 (IPA-based) is used as developer, increasing the gradation to up to 10 is possible. This increase is however achieved at the expenses of a certain loss of sensitivity.

The contrast of CSAR 62 in developer X AR 600-54/6 is excellent, reaching a value of  $> 14$  (see Fig. 2), and may increase even more in further optimisation procedures.

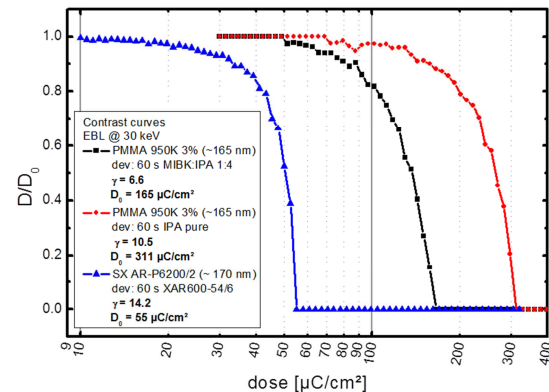


Fig. 2 Comparison of sensitivity and contrast between CSAR 62 and PMMA 950K

- Resolution achieved with CSAR 62 so far

A resolution of 10 nm could be determined for CSAR 62 at a film thickness of 180 nm (see Fig. 3), which corresponds to an aspect ratio of 18. The sensitivity for a maximum resolution like this is in the range of 220 – 270  $\mu\text{C}/\text{cm}^2$ .

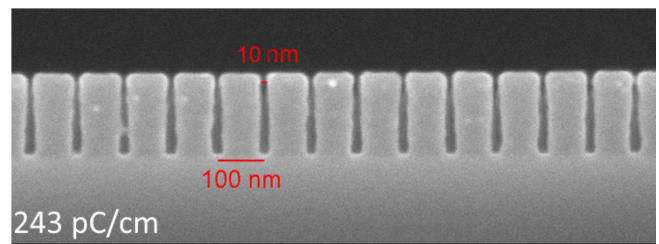


Fig. 3 Fully developed minimum structures of 10 nm

- Generation of extremely small lift-off structures with CSAR 62

Another important possibility which this resist offers is the generation of nano-lift-off structures. If a 1.5-fold higher exposure dose is applied, undercut resist profiles can be produced due to the proximity effect (see Fig. 4).

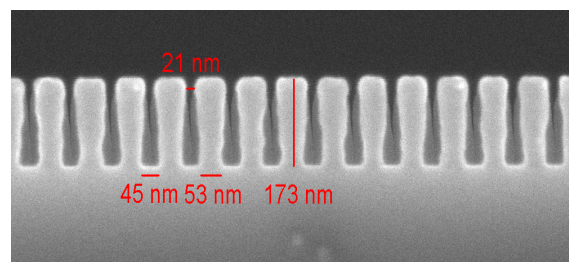


Fig. 4 Undercut resist profiles for the lift-off process with CSAR 62

If these structures are subsequently sputtered or coated with metal, conductive channels are formed with a structural width of up to 10 nm (see Fig. 5).

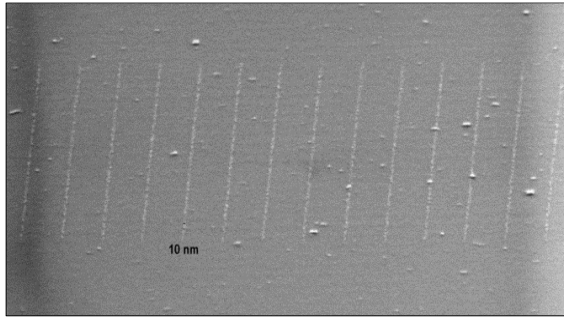


Fig. 5 Vapour-deposited 10-nm AuPd-lines

- **Optimisation of developer**

The sensitivity of the resist system strongly depends on the kind of developer used. In addition to the future “flagship” X AR 600-54/6 intended for a broad process window, also developers for highest sensitivity are designed. In first experiments, dose values of less than  $10 \mu\text{C}/\text{cm}^2$  were measured. The optimisation of developers also includes a strict minimization of possible hazards (safer solvents, flash point  $> 21^\circ\text{C}$ ).

A typical problem arising from an extreme resolution at an aspect ratio of  $> 15$  is the collapse of bar structures. In Fig. 6, 10-nm bars with a pitch of 50 nm are displayed. During the development step, the surface tension of the solvents leads to an undesired “sticking together” of single bars. Currently experiments are carried out to minimize this effect with optimised developers.

In April, we will present the latest results for the first time on the “HARMNST 2013”.

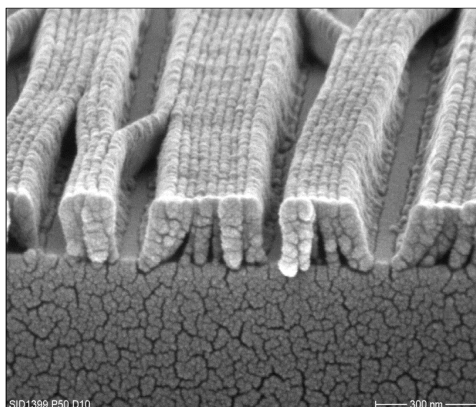


Fig. 6 10-nm bars still partly stick together (pitch 50 nm)

These highly promising results and the well known market situation have prompted us to further improve the properties of CSAR 62 and respective developers with great intensity and to realise the synthesis and resist production quickly and in the highest quality.

**First samples of CSAR 62 will already be available as of May 2013.**

For the interim period, we offer all ZEP resist users the possibility to obtain suitable developers for ZED-500 and ZED-N50 from Allresist quickly and for a explicit lower price.

Please contact us, we will gladly submit you a favourable offer on short notice.

### 3. NIR-resist in the development

Allresist further continued the development of sensitive CAR negative-tone photoresists for laser applications in an exposure wavelength range between 500 and 1100 nm. We reported already last year the first promising results (AR News 23).

Our new, very sensitive negative laser resists are suitable for a use in the wavelength range between 200 – 500 nm (cw and pulse operation). In addition, these resists are also sensitive beyond the generally applied exposure wavelength range of  $> 480$  nm up to the NIR-range if a pulsed mode is used. In the range of extremely high energy densities which occur in the pulsed laser mode, two-photon absorption is observed. A cross-linking can therefore also be induced by longer wavelength (and thus lower energy) light and leads to a complete build-up of the layer. The sensitivity can drastically be increased by addition of dyes which absorb in the range of the laser wavelength used. This increase in sensitivity is due to thermal effects since the dyes heat up as a result of the intensive irradiation.

Among a large variety of influential factors, the writing speed of the laser beam is of particular importance. The faster the writing speed, the lower is the local energy input. Below a certain energy input, no cross-linking of the photoresist is possible. The resist is however quickly destroyed if the irradiation is too intensive.

In a new series of experiments, a novel CAR photoresist with considerably high temperature stability up to approximately  $300^\circ\text{C}$  was processed at a wavelength of 532 nm. Even in the case of a very low writing speed  $< 0.5 \text{ mm/s}$  and the consequently high energy input, no destruction of resist layers could be observed. The development of these resist films with a thickness of  $1.5 \mu\text{m}$  was performed in conventionally used aqueous-alkaline developers. Even without addition of dyes, sharp lines with a width of approximately  $35 \mu\text{m}$  were produced with high sensitivity. The width of these lines thus roughly corresponds to the beam diameter of  $30 \mu\text{m}$  (see Fig. 7).



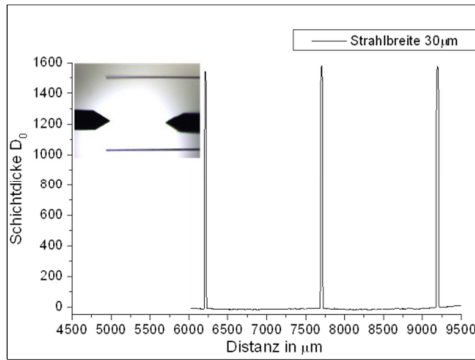


Fig. 7 Line structures generated with ultra-short pulse laser

Even after tempering at 300 °C, no signs of melting or rounding of lines occurred. Observed is only a gradual reduction of the film thickness which is caused by sintering processes.

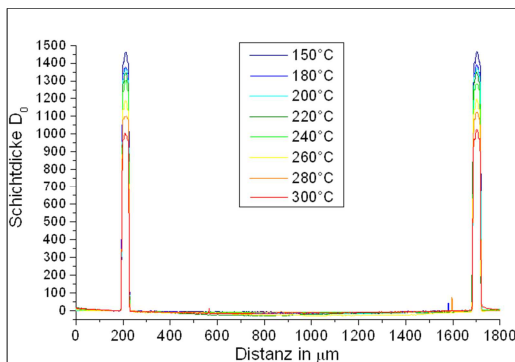


Fig. 8 High thermal stability of 30µm lines generated with laser, film thickness in nm

Experiments were also performed with our new negative CAR polyimide resist. Again, we were

able to produce sharp lines with a diameter of approximately 35 µm which were characterised by excellent thermal stability > 400°C. In this case, the aqueous-alkaline developer was replaced by a MLK-based developer. We thus recommend the polyimide negative resists for all users who process moisture-sensitive substrates.

Due to the utilisation of temperature-stable photoresists, the process window for laser applications could be expanded considerably.

These resists are also suitable for the usual photolithography (i-line, g-line).

In addition to the generation of temperature-stable line structures, also planar and undulating surfaces with defined periodicity are possible (Fig. 9).

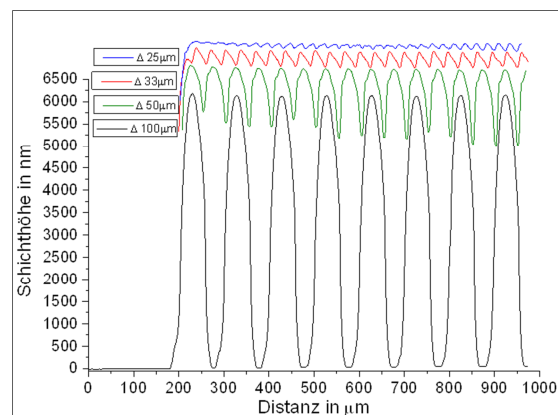


Fig. 9 Single bars (black line) up to closed surfaces (blue) can be generated by varying the distance of the lines.

We hope to have offered a few interesting suggestions also for you and strongly encouraged our interested customers to communicate your desires and requests.

The next issue of our AR NEWS will again be presented in October 2013.

Successful times until then!



Strausberg, 26.02.2013  
Matthias & Brigitte Schirmer  
Team of Allresist