AR NEWS

14. Issue

Allresist GmbH

Content:

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1. Allresist with new organisational structure and vision

Valued reader of the AR NEWS, we would like to inform you again about the further development of Allresist and our products:
2006 was an outright successful year for Allresist. We were able to increase our business volume considerably and would like to take the opportunity and thank our customers for the confidence placed in us. Two scientific projects were successfully brought to an end (see below, section 2 and 4), while two new projects "Nano-structures using lift-off-techniques" (see section 3) and "Photo resist for the wet-chemical etching of silica and silica oxide" were initiated.

A big step forward was taken by Allresist with the introduction of a new ERP-software which is almost completely implemented by now. All procedures and workflows were optimised and can now be displayed comprehensively in real time. During this complex project, we were supported professionally by CBS Systems AG, Gelsenkirchen, which offers also attractive software solutions for KMU. This new organisational structure will allow for more efficient research and an even more improved customer service.
Annually, the auditing of our quality management system (ISO 9001 : 2000) certifies the claimed conformity as well as a constantly growing, high level of development of our company. In 2006, we continually improved our corporate philosophy in the scope of the EFQM-model for sustainable excellence together with our staff, thereby setting up an ambitious business plan until 2012. This idea became our now vision to develop permanently into an enterprise of the "Business of Excellence". With our application for the "Quality Award Berlin-Brandenburg" in 2008, our progress will be re-evaluated again.
The following articles will inform you about out latest research news. We wish and hope that these topics will find your interest and might even encourage a stimulating cooperation.

2. CAR 44 – Introduction of the new series CAR 44

The INNO-WATT project "Resists for the LIGA- and micro system technology", a cooperation with the Bessy GmbH, Berlin, was finished according to plan in the middle of the year 2006. Relevant results were presented on the HARMS 2005 in Korea [1] and on the MST-congress 2005 in Freiburg [2]. The results of successive developments will be presented on the GMM-workshop in May 2006 in Karlsruhe and on the HARMST 2007 in July in France.

2.1 CAR 44 – further results with AR-N 4400

Meanwhile, many users have tested CAR 44 with promising results, the main focus placed on applications in the 100 µm-range. If you should be interested in an exchange of experiences with other users, we would be pleased to make the respective contact information available to you.

- For several users, a possible exposure of CAR 44 even in the wave length range of 400 – 450 nm (g-line 436 nm, laser 442 nm) was important. A determination of the sensitivity at the g-line revealed that a threefold higher exposure dose is required under these conditions as compared to the i-line (365 nm). However, since CAR 44 is characterized by an excellent light sensitivity (150 mJ/cm2 at a layer size of 30 µm, i-line) exposure times are even for the g-line in an acceptable range. This allows the application of this resist in an wider operative range.
- In most cases, resist layers of CAR 44 could not be entirely developed after a coating on copper substrates. A residue was observed covering the entire surface, even in unexposed areas of the substrate. In the upper resist layers, the structures were correctly reproduced. Apparently, the copper substrate catalyses an acid regeneration, which induces the complete cross linking of the lowermost layer. A possible solution for this problem offers a tempering performed at low temperatures. If soft bake as well as cross linking bake are conducted in the temperature range between 85 – 90 °C, a "normal" development step may be used. An alternative offers the application of a thin isolation layer of PMMA. The copper substrate is covered with a 0,7 µm-PMMA layer (e.g. AR-P 669.06). Subsequently, CAR 44 is applied using spin coating and processed as usual. Finally, the PMMA can be removed with oxygen plasma.
- For the production of thick layers (> 200 µm) however, it became obvious that structures obtained do not achieve the desired quality, which can be attributed to the drying properties of the solvent mixture used so far. Therefore, further tests are performed currently to allow an application of CAR 44 even for higher thickness layers.

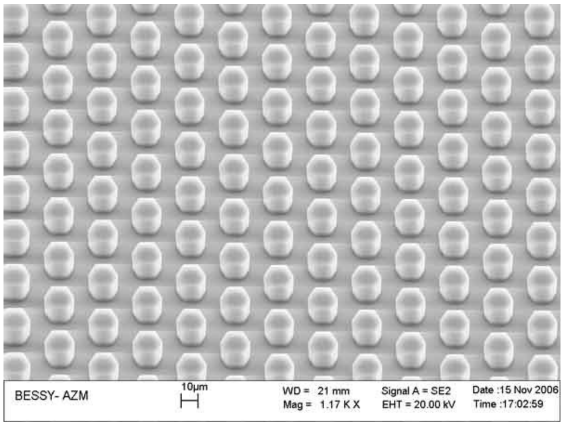
☞ Our research concerning the development of CAR 44 is not yet finished. We would like to encourage all technical requests or dialogues concerning the features of this new resist system.

2.2 CAR 44 – Production of x-ray masks in a two-step process

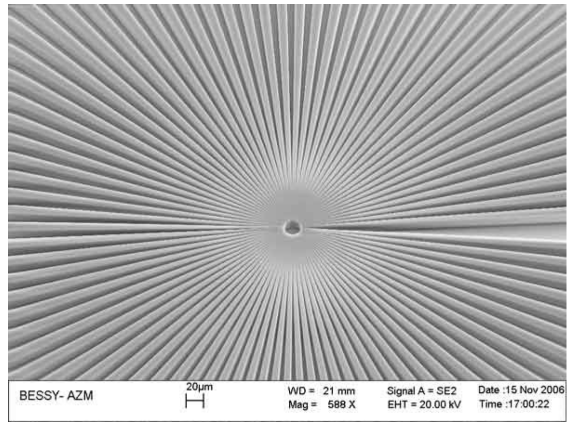
In this section, we present the high-precise production of x-ray masks using CAR 44. In a process involving two steps, at first a 7 µm thick resist mask is generated with UV-lithography. The subsequent gold galvanic process completes the x-ray master mask.

In a second step, this structure with the master mask is transferred via synchrotron radiation into a CAR 44-layer with a thickness of 30 µm. The mask is finished using gold galvanoplating and a final removing step.

X-ray masks produced with this protocol are of an excellent quality. Process parameters and the results of the UV- and synchrotron lithography such as gradation curves, maximal resolution, aspect ratio, surface roughness, and edge steepness will be presented in the GMM-workshop publication. The simple removing step, information concerning the long term stability, and batch uniformity during the manufacturing process will be exemplified. Please ask for this publication after the workshop!



Picture 1: Gold structure for x-ray masks



Picture 2: 10 µm-resist layers AR-N 4400-10

Literature:

[1] M. Schirmer et al., Microsyst. Technol. (2007) 13, 335-338, "A new removable resist for high aspect ratio applications"

[2] M. Schirmer et al., Mikrosystemtechnik-Kongress Freiburg, VDE-Verlag, Berlin, (2005), 531-533, „Wieder entfernbarer Negativresist für die Mikrosystemtechnik"

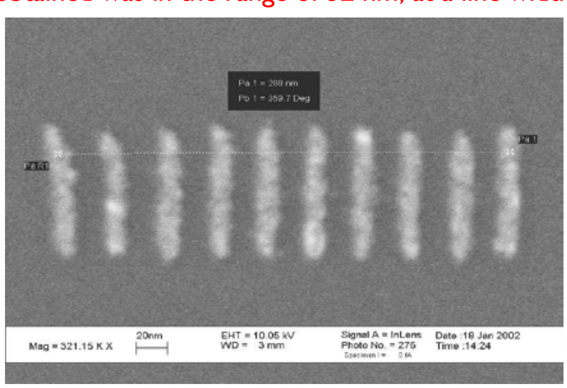
3. Higher resolution for e-beam resists

One main focus of our research activities is the development of new e-beam resist. Here, we continue in the tradition of e-beam lithography of the "Fotochemische Werke Berlin Köpenick" and the Academy of Sciences in Berlin-Adlershof (ZIOC), which started at the beginning of the eighties. Currently, we would like to refer to three projects.

3.1. Production of sub-10 nm lift-off-structures using e-beam lithography

These projects result from a close cooperation with the University of Würzburg, Physical Institute, under the direction of Dr. Georg Schmidt. A PMMA two-layer system is built from polymers which differ only slightly with respect to their molecular mass. The experiments were initially performed with a 50K-PMMA (lower layer, 30 nm thickness) and a 200K-PMMA (upper layer, 40 nm thickness). For the exposure, a conventional "Raith Elphy plus" e-beam lithography system with an acceleration voltage of 30 kV was used. The radiation dose was 800 pC/cm². As developer, isopropanol and as stopper, water was used. Afterwards, an Au-Pd-layer of 3 nm was evaporated and the resist layer subsequently removed in acetone. The smallest width of lines obtained was 5 nm for a single line.

In order to determine the maximum resolution of nano-structures, several lines were placed side by side. The smallest period obtained was in the range of 32 nm, at a line width of 12 nm (see picture 3).



Picture 3: 12 nm-gold-palladium lines, generated with a two-layer PMMA-system

In the following tests, the layer thickness of the two-layer system was varied. Interestingly, it became evident that the highest resolution can be obtained at a total resist thickness between 70 and 120 nm.

Lowest layer 50K (in nm)	Upper layer 200K (in nm)	Minimal width (in nm)
12	30	14
30	30	9
30	40	5
93	30	5
93	40	8

Table 1: Minimal width of lines for two-layer systems with different thickness values

As expected, the resolution decreases constantly with an increase of layer thickness which is due to the aspect ratio that can be obtained for the PMMA-resists. For layers < 70 nm thickness, the well-known interfering influence of the proximity effect becomes evident. Due to the pear-shaped scattering of the electrons, structures are widened. The imaged structure is thus written in an height of approximately 90 nm and reproduced via evaporation of the metal. The evaporation process requires also a couple of technical finesses; more detailed information may be requested from Dr. Georg Schmidt.

3.2. Highest-resolution negative resist with high aspect ratio – AR-N 7500

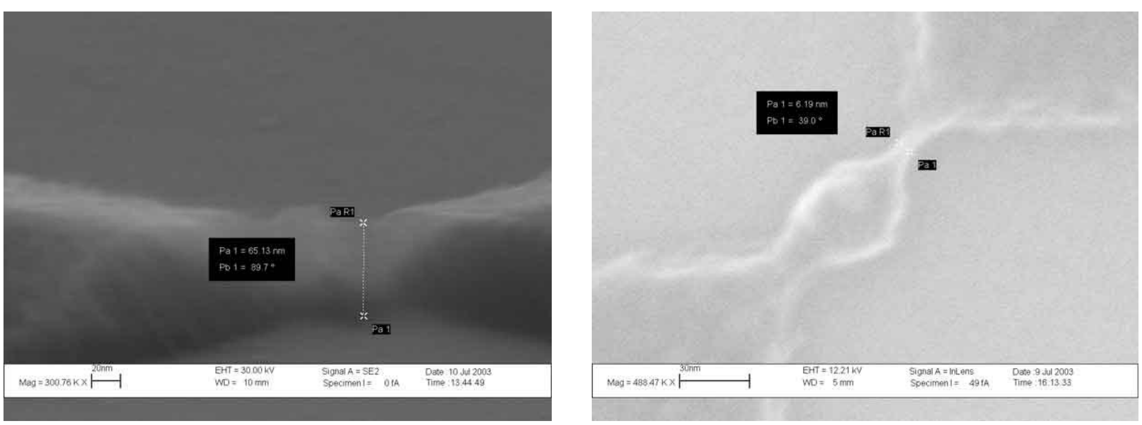
In Würzburg, also AR-N 7500 was investigated with respect to the highest resolution possible. The team led by Dr. Georg Schmidt was able to achieve a resolution of 6 nm in a 60 nm-layer (see picture 4 + 5). The aspect ratio of 10 is remarkable for the highest resolution. All process parameters essentially correspond to the standard recommendations:

Soft Bake: 15 minutes hot plate, 90 °C

Exposure: 30 kV, dose is highly dependent on the structure

Developer: AR 300-47, 45 seconds

Thus, evidence could be provided that AR-N 7500, representing a non-chemically amplified resist, may potentially be used for the sub-10 nm-range. These analyses will be continued with emphasis on the relevancy to practice (shorter writing times).



Picture 4 + 5: 6 nm-lines with an aspect ratio of 10, written in AR-N 7500

3.3. E-beam resist for the production of masks - SX AR-N 7700/37

One problem occurring during the manufacturing of masks with negative e-beam resists is the instability of the process. The parameters change with long writing times as well as during long storage times of the coated blanks. Problematical is also the sensitivity of resists to traces of amines in the climate-controlled environment. In close cooperation with Phototronics MZD, Dresden, we developed an e-beam resist without these disadvantages.

Experimental samples of SX AR-N 7700/37, a chemically amplified resist, are characterised by a high process stability. According to our results to date, blanks may be stored for three month without loss of quality; long-term experiments are still ongoing.

Between the single process steps (exposure, cross linking, development), the process can be interrupted for several days each. A sensitivity to amine compounds is excluded, since the resist contains amine components. For the process on silica blanks, the sensitivity is in the range of 1 μC/cm².

This extremely high sensitivity is however so far associated with a resolution of only 300 nm, which is too low. Therefore, tests for an optimisation were started in order to achieve a resolution of less than 100 nm at a sufficiently high sensitivity (dose approx. 5 1 μC/cm²).

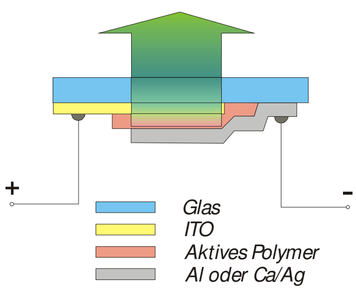
Customers who are interested are invited to participate in the optimising process.

4. Patterning of OLED-polymers with photo resists

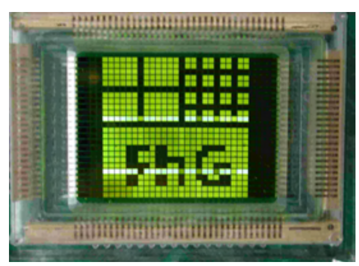
In cooperation with the Fraunhofer Institute for Applied Polymer Research (IAP), Golm, the patterning of active polymers for the production of OLEDs with photo resists was investigated. The manufacturing process used so far is technologically difficult and allows only a pixel resolution in the range of 100 μm.

4.1. Functionality of OLED

The general structure of organic light-emitting diodes is shown in picture 6.



Picture 6: Schematic structure of a polymer-OLED



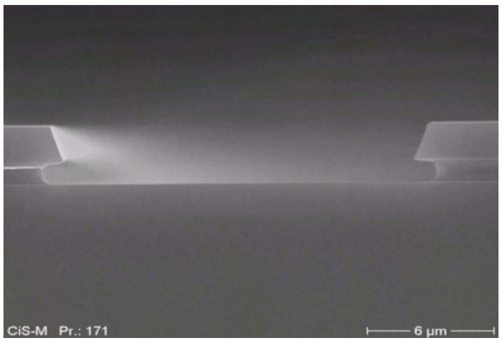
Picture 7: Passive matrix display

At first, a transparent electrode is deposited on glass, generally indium tin oxide (ITO) is used for this process. The active polymer layer is applied onto this electrode using spin coating or special printing procedures. Subsequently, the counter electrode (e.g. Al) is evaporated using vacuum deposition. For the production of passive matrix displays from these OLEDs, the display requires pixels. For this purpose it is state of the art to arrange both electrodes in lines. Thus, the transparent ITO-electrode can be structured using a photolithographic process even before the active polymer layer is applied. The patterning of the counter electrode can be carried out after the application of the active polymer layer by using shadow masks. With this method, a pixel is only produced at the intersection of patterned ITO and metal electrode (see picture 7).

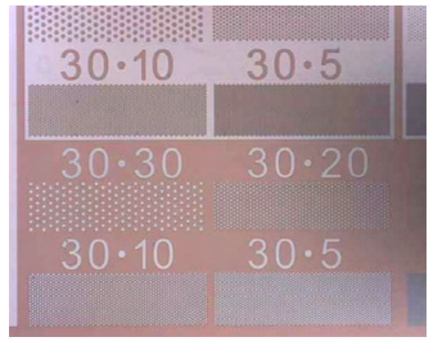
A direct patterning of the active polymer layer offers technological advantages. For passive matrix displays, the size of the single pixels could be further reduced, which is so far limited to approx. 100 μm by the manufacturing technology for shadow masks.

4.2. Results of photo patterning

The direct patterning could be implemented using a two-layer technique. An accordingly optimised photo resist was spin-coated onto an OLED-layer, dried and exposed. As usual, the photo resist layer was developed under aqueous-alkaline conditions with developer AR 300-35, without causing damage to the OLED-polymer (MEH-PPV). The mask with underlying polymer which was generated in this procedure was then treated with a solvent mixture containing chlorobenzene and nonan. Photo resist layers will not be affected, whereas the freely accessible active polymer layer will be removed. Thus, patterns are produced in the OLED-layer which result in the formation of the following characteristic lift-off-structures (see picture 8).



Picture 8: Two-layer system MEH-PPV M 1 / SX AR-P 3500/17



Picture 9: Testing the resolution of MEH-PPV

Thereafter, the photo resist was selectively removed with the aqueous-alkaline remover AR 300-73, leaving only the OLED-patterns behind. The best resolution obtained for the OLED-pattern was in the range of 5 µm (see picture 9).

The polymer properties remained largely preserved, and a smooth surface resulted. The characterization of electroluminescence was conducted in the IAP in Golm and resulted in a luminance of 100 cd/m² for MEH-PPV after photo patterning. However, a reduction in efficiency and required voltage for in order to achieve a certain luminance has to be accepted when applying the photo resist technology. In summary it should nevertheless be noted that the basic experiments of this project were performed successfully, even though further effort is required to investigate the interactions between electroluminescent polymer and photo resist layers. Customers who are interested are cordially invited to participate in this process.

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5. Polyimide resist for high-temperature applications

In cooperation with the Institute for Thin Film Technology and Microsensors e.V., Teltow, we were able to develop a polymer which can be used as photo resist (SX AR-P 5000/82), as sensor (SX AR-P 5000/80), and also as insulating layer.

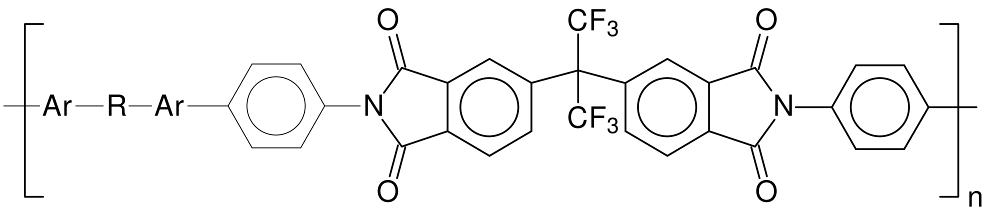


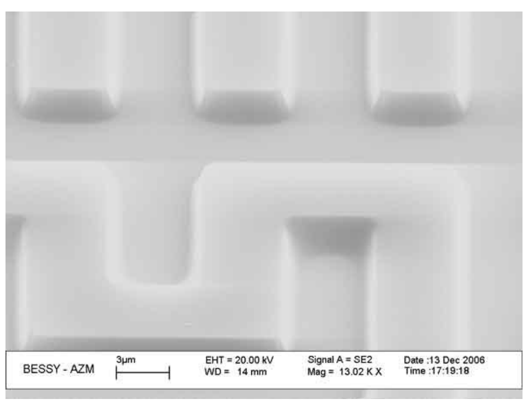
Fig. 1 Chemical structure of the polyimide, OH-groups are bound to the residue –R

For conventional PI-resists, the final properties (e.g. high temperature-resistance) are only attained after a bake of the structures at high temperatures (300 – 400 °C). However, the shrinking which occurs during this process is perturbing. We were able to synthesise a polyimide which is soluble in organic solvents.

Several users already tested the sensor and insulator capacities successfully. However, the main focus of our work was the production of resist structures. For that purpose, two solutions were found so far:

5.1. Two-layer resist for patterning processes

With an introduction of OH-groups during the synthesis, we were able to make the polyimide alkaline soluble. With the addition of light sensitive components on the basis of diazonaphthoquinones, a resist (SX AR-P 5000/82) is generated which can be patterned under the usual conditions of UV-lithography. At a layer thickness of 1,8 µm, the sensitivity amounts to approx. 100 mJ/cm² (developer AR 300-26, 3 : 2 dilution, see picture 9). The soft bake was performed at 95 °C. If the structures are not heated above 150 °C, a removal is possible without difficulties. At 170 °C and above, a chemical conversion sets in which makes the patterns resistant against solvents. In this case, a removal is no longer possible, which is however generally not necessary in high temperature applications. The patterns remain stable up to temperatures of 400 °C.



Picture 9: Patterns of the light sensitive polyimide, layer thickness 1,8 µm

5.2. Two-layer-system for the application in sensor technology

For certain applications it would be desirable to keep the properties of a polymer unaltered, i.e. without an addition of light sensitive components, as for example for an application as wet sensor.

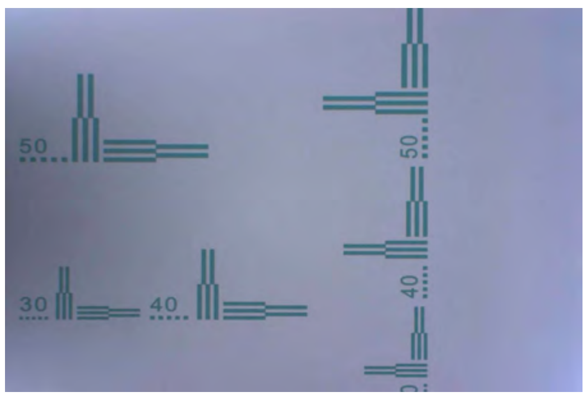
A patterning of the pure polyimide resist (SX AR-P 5000/80) is in this case performed with a two-layer system, in analogy to AR-P 5400 / AR-P 3500.

For this, we found a surprisingly simple procedure:

Process steps	**Parameter**
Coating 2.000 rpm with SX AR-P 5000/80	0,5 µm layer thickness
Soft Bake	95 °C, 25 min., convections oven
Coating 4.000 rpm with SX AR-P 3540	1,4 µm layer thickness
Soft Bake	95 °C, 25 min., convections oven
Exposition	35 mJ/cm²
Development with AR 300-46 (0,24 n)	40 sec.
Flood exposure	70 mJ/cm²
Development with AR 300-47 (0,20 n)	20 sec.
Drying	2 min.

Table 2: Process parameters of two-layer technology

The double-layer coating is unproblematic. After exposure, the development of the photo resist and the polyimide are performed in one step. The removal of the now dispensable photo resist is implemented simply by flood exposure and a further development step with a weaker developer.



Picture 10: Structure of the pure polyimide after removal of the photo resist, 600 nm layer thickness

The new resists are now available for application tests, please ask us.

Valued user, we hope that we were able to provide interesting information and suggestions. The next issue of the AR NEWS will be presented on our 15-year jubilee in October 2007.

We hope that you and we will have a successful time until then.

Strausberg, 02.05.2007

Matthias & Brigitte Schirmer