Success story of the CSAR 62 - or a high-tech resist makes its way

The constant strive for more and more powerful computers is correlated with the demand for increasingly smaller structures in the manufacture of integrated circuits. Electron lithography is a technology which is already today able to realise a resolution of < 10 nm. This however requires high-performance electron beam resists. The company Allresist is specialised in the production of such high-tech resists and was honoured in May 2014 with the Brandenburg Innovation Award for the successful development and marketing of e-beam resist CSAR 62.

Short Profile

Allresist is an independent manufacturer of resist for microelectronics. Established on the market since 1992, the company develops, produces and distributes photo and e-beam resists. Micro- and optoelectronic clients worldwide use Allresist resists to produce a large variety of integrated circuits.

Fig. 1 Team of Allresist

In addition to the standard product range, Allresist also offers customer-specific process-adapted products. These products are developed in close cooperation with customers and according to their requirements. With consistently high quality, fast professional implementation of individual customer requests at reasonable prices and very short delivery times, the company generates high customer benefits. This is impressively demonstrated by high levels of customer satisfaction and longstanding customer loyalty.

Presentation of the Innovation

The new product "CSAR 62" is a high-tech resist for electron beam lithography which allows the implementation of high-end applications in microelectronics, e.g. for aerospace industry or high-performance computers. Even incredibly small structures of < 10 nm for the highly integrated circuits of a microchip can be realised with this resist. For comparison: A hair with a diameter of 30 µm is 3000 x thicker than any of these structures.

CSAR 62 is characterised by an excellent resolution, a good sensitivity, and has a particularly high plasma etching stability. All parameters were adjusted in such a way that the high resolution can not only be achieved under academic laboratory conditions, but also is already suitable for industrial applications with e-beam point writers which focus the electron beam to 2 nm.

Motivation for resist development

Electron beam resists are already in use for more than 30 years for other applications. These resists possess many advantageous properties, but do not reach the specific parameters of CSAR 62. Only e-beam resist ZEP 520 which is produced by a Japanese company is characterised by comparably good properties and thus meets most users' expectations. So far, no competing resist product was available. In the past three years however, the market situation for ZEP users began to deteriorate dramatically. The manufacturer quadrupled the prices within a few years. Costs for one litre have meanwhile reached 9,000 € in Europe, with delivery times in a range of several weeks. Another bottleneck also became increasingly apparent in the production of mask blanks for photolithography. Since 2012, our customers repeatedly asked on fairs, congresses or during visits if Allresist might be able to offer a solution for this problem.

In 2012, the Team of Allresist was thus faced with the challenge to develop a high-resolution etching-stable e-beam resist for the efficient production of integrated circuits with highest resolution and the manufacture of high-quality masks blanks. Based on intensive research in the literature and patents, promising new approaches were detected. After approval of the availability of raw materials and compatibility with Allresist process procedures, the project was incorporated in the strategic research/marketing agenda 2013.

Scientific Implementation

In parallel, both partners required for this project, the Institute for Thin Film and Microsensors Technology e.V. (IDM) and the Martin Luther University of Halle (MLU), were included in the consultative process. The IDM (Teltow) and Allresist share an intense collaboration since meanwhile 18 years which resulted in many innovative product developments. In the CSAR-project, particularly the longstanding competence of the IDM in the synthesis of new polymers was required. Already initial experiments in the first couple of days produced polymers which could easily be processed into resist samples. Only sensitivity and storage stability could still be improved, and recipes and reaction conditions were thus optimized in the IDM. In six weeks of hard work, appropriate new polymers were finally developed (☞ Fig. 2) which met the requirement for high plasma etching stability, sensitivity and storage stability of this resist.

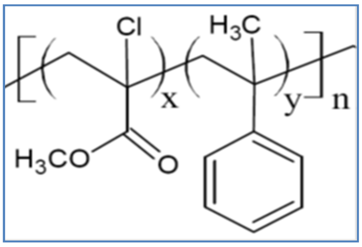

Fig. 2
Structural formula: Copolymer of chloro methyl methacrylate and methylstyrene

First resist samples based on these polymers were synthesised by Allresist and characterised in detail. This innovation could be further improved by addition of an acid generator which utilises an entirely new mechanism of action to enhance the sensitivity. The acronym CSAR is deducted from this mechanism: **C**hemical **S**emi **A**mplified **R**esist.

The Martin Luther University of Halle has also been a reliable partner for Allresist for many years. In particular in the field of electron beam lithography, the university possesses extraordinary know-how and vast experience, and is a pioneer in the field of electron beam lithography, which is evidenced by a large number of scientific publications. The Department of Nanophysics is particularly interested in e-beam resist CSAR 62, since finest structures of up to 10 nm can be written with high sensitivity (☞ Case Study MLU).

The samples studied at the University produced sensationally good results: Almost immediately, a resolution of 10 nm with good sensitivity was achieved (☞ Fig. 3).

The resolution of a 173 nm thick CSAR-layer is 10 nm with a sensitivity of 65 µC/cm².

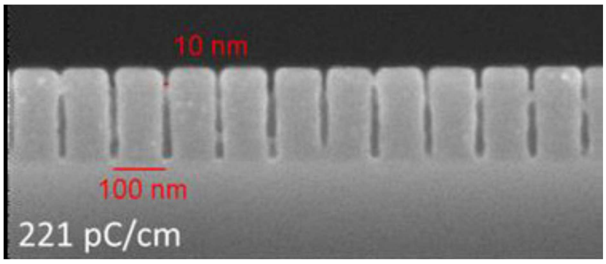

Fig. 3 CSAR 62 structures with AR-P 6200.09: resolution 10 nm; process parameters: Si 4" wafer, layer thickness 173 nm, 150 °C, 60 s, hot plate; Raith Pioneer, 30 kV; dose 65 µC/cm², developer AR 600-546, 60 s, 22 °C

The first experimental samples could be provided to long-lasting customers for additional testing in May 2013. Surveys conducted thereafter provided an extremely positive feedback and resulted in repeated orders of larger quantities. Properties currently available on the market have been fully met and partially even exceeded significantly.

Synthesis and resist production at Allresist

In anticipation of a constantly growing demand, the synthesis of CSAR-raw materials was quickly transferred to production scale. Since Allresist produces many strategic raw materials for resist production itself, existing equipment and know-how could be used appropriately. After polymerisation and precipitation, the polymer is dried and subjected to intensive quality controls. CSAR resists are then produced by dissolving the polymer in a solvent and subsequent ultrafiltration.

Conquest of the market

As of June 2013, sufficient amounts of CSAR 62 together with developers were available, so that the regular sale could be launched. Delivery to customers without delay could be arranged within a few days, since production capacities could be adapted at short notice.

By the end of the year, Allresist processed 67 CSAR orders from 34 countries, including 19 new customers, and turnover went up by 11 % with the new product line. In the first half of 2014, sales figures doubled again.

Many customers expressed approval concerning the excellent coating properties, the availability of small samples as well as the fast availability. Account managers also recognised customer requirements for other applications and forwarded these directly to the development department.

Technical development

Following the demands of our customers, Allresist in 2014 continued with the development and adjusted CSAR62 for the "production of connective paths in the nanometre range."

The manufacture of these extremely thin metal lines requires lift-off techniques which generate undercut structures that are narrower at the bottom than the top.

With CSAR 62, Allresist succeeded in developing a resist which allows to produce lift-off structures with 10-nm lines. In order to manufacture such fine conductor paths with this e-beam resist, a wafer is coated with a 100 nm thin resist film and dried. Subsequently, lines are written with an extra high-dose electron beam. Due to the high energy dose, more back scatter from the substrate occurs (proximity effect). As a result, lower areas of the resist layer are additionally irradiated. During development, the resist is not only removed from the bottom, but also laterally, while in the upper layer the original width of lines is preserved (21 nm) and an undercut is formed in the resist structure. If the substrate is now coated with metal, the metal is deposited both on developed areas and the residual resist structures. In the following step, the resist patterns coated with metal before are lifted (removed) with a solvent. After lift-off, the desired fine 10 nm conductor paths remain on the wafer.

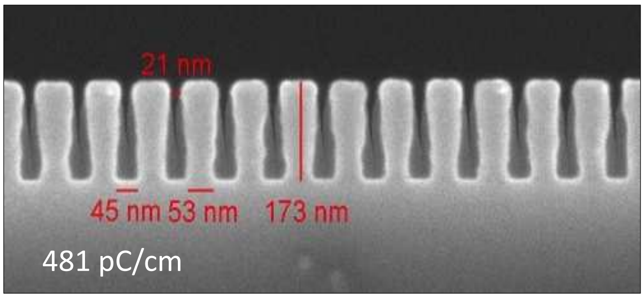

Fig. 4 Undercut structures by lift-off

A resolution of conductor paths like this has never been achieved before! And there are other foreseeable applications of CSAR 62: The smaller the structures on a microchip, the higher the integration density and performance. The industrial production of circuits currently allows for structures as small as 80 nm. According to Moore's Law, the integration density doubles every 18 months. In this respect, e-beam lithography with the optimised e-beam resist CSAR 62 is a future-oriented technology which will meet the high requirements of microelectronics for decades.

With CSAR 62, circuits for the 5 GHz range will be produced in the future which are primarily required for wireless Bluetooth or Wi-Fi technology. E-beam lithography is also needed for research on nanomaterials like graphene, for three-dimensional integrated circuits as well as for optical and quantum computers. With all these technologies, computing power or memory density is increased. The most sophisticated computing requirements (supercomputers), e.g. in computational fluid dynamics or in space applications, call for microchips with highest integration density.

On the following pages, we present user opinions and two detailed user reports on our CSAR 62, which were supplied to us by satisfied customers together with a few pictures:

Comments of satisfied users on CSAR 62

Fraunhofer Heinrich Hertz Institute (HHI) Berlin

Dr. Ralf Steingrüber, a renowned electron beam resist expert working in the HHI, tested the CSAR 62 on mask blanks: "I immediately achieved a resolution of 50 nm, which is an excellent value for masks. Currently, masks with a minimum of 200 nm lines are offered on the market. As soon as masks with CSAR 62 are available, I will definitely use them. "

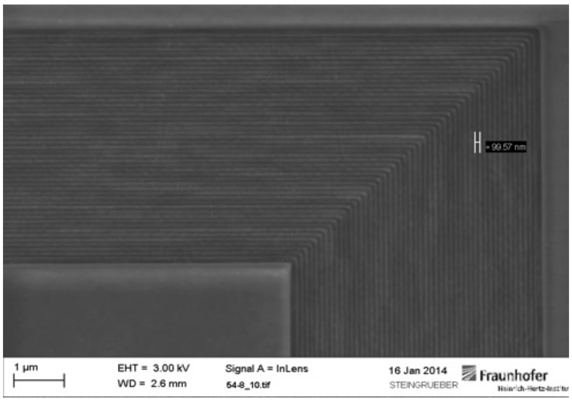

Fig. 5 CSAR 62 test structure on mask blank with 50 nm lines and 50 nm trenches, pitch line & space 99.57 nm

Leibniz-Institute of Photonic Technology (IPHT) Jena

Dr. Uwe Hübner, working group leader for quantum detection, has successfully driven electron beam projects for nanostructuring in the IPHT for many years. He particularly points out the high process stability of CSAR 62 as compared to ZEP 520 (☞ Fig. 6): "With CSAR 62, small process variations can be compensated and the required high resolution is still guaranteed. Furthermore, the new Allresist resist reached contrast values that are 1.5 times higher in comparative measurements with the ZEP."

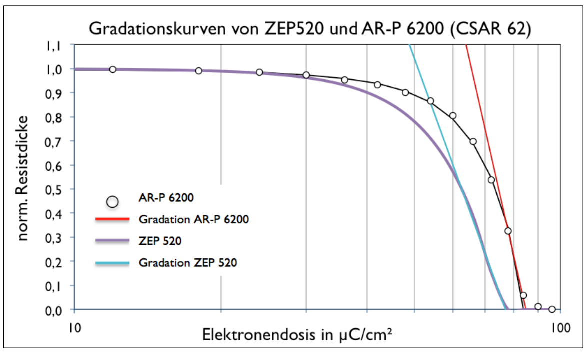

Fig. 6 Contrast curves AR-P 6200 and ZEP 520, 50kV, substrate: Si; ZEP 520, film thickness 220 nm, 60 s developer ZED N-50, contrast 6; AR-P 6200, film thickness 260 nm, 60 s developer AR 600-546, contrast 9

Case study by Prof. Dr. Georg Schmidt, Managing Director of the Institute at the Martin-Luther-University of Halle

The Section "Nanostructured Materials" at the University mainly uses CSAR 62 for highest-resolution lithography for the lift-off and as an etching mask for dry chemical etching processes. The new resist offers several specific advantages. It achieves the high resolution of PMMA, but at much lower dose. For the following reason this is highly desirable: Due to the proximity effect, the required exposure dose for high-resolution structures strongly increases. This must be compensated by longer exposure times or a higher beam current, which both are not desirable for economic reasons. CSAR 62 however can compensate this effect due to its higher sensitivity, and in combination with the more favourable contrast curve it is possible to achieve a slight undercut even in thin layers. This allows an even lift-off in the sub-100 nm range (☞ Fig 7.):

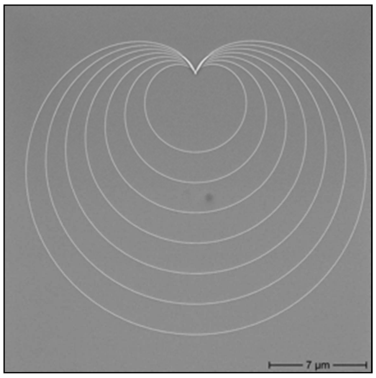

Fig. 7 Chrome structures with 20 nm lines after lift-off

The goal in the lift-off of metal structures is however not always to break the limits of resolution. Typical applications, for example in the contacting of nanowires, rather require dimensions in a range of 30-50 nm. These are indeed also feasible with other resists, but the "resolution reserve" of CSAR 62 allows for a significantly improved structure accuracy and faster design with less iteration (☞ Figure 8):

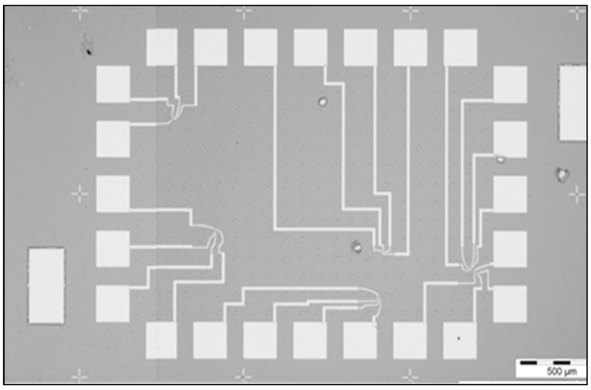

Fig. 8 Typical structure for contacting nanowires. Large areas are mixed with small details

During dry chemical etching, for example in the structuring of silicon nitride, CSAR combines the best of two worlds: First, it allows the use as a high resolution positive resist similar to PMMA, and on the other hand it offers a stability which is similar to novolacs. This facilitates the production of masks with sharp edges that provide the necessary etch stability without the frequently occurring disturbing faceted edges.

Moreover, a new variant of CSAR 62 with an extremely high layer thickness (1 µm) was assessed. In this case, a strong undercut can be produced with only one layer, which is perfectly suitable for lift-off (☞ Fig. 9). This process is designed for larger surfaces in the micrometer range, which should however clearly be defined since the pronounced undercut (as demonstrated in Figure 9) limits the minimum distance between different structures.

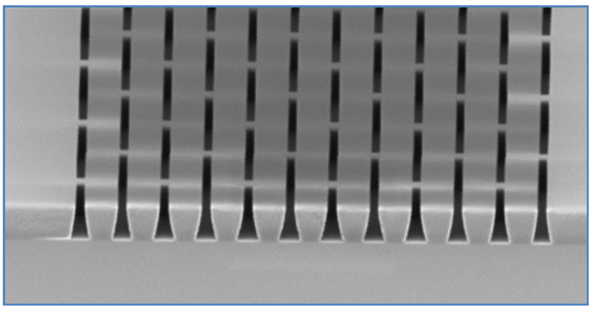

Fig. 9 Particularly thick CSAR with pronounced undercut for extreme lift-off applications

The very good resist properties in combination with the large variability of this new resist make CSAR 62 an attractive product for both research and industry.

User report of Monika Boettcher, Director of Application-Laboratory at the Vistec Electron Beam GmbH

The company Vistec is one of the leading manufacturers for electron beam devices. As a specialist in development and sales of these devices, Mrs. Böttcher tests electron beam resists that are available on the market to provide resist recommendations together with processing guidelines to her customers.

Using the current e-beam system SB 250, three comparative studies of CSAR 62 (AR-P 6200.09) and ZEP 520A were carried out, analysing structure resolution, contrast and sensitivity each in their corresponding developers:

1) Structure resolution: A comparison of 90 nm lines of both resists (☞ Figure 10 and 11) in the centre of a silicon wafer with a film thickness of 200 nm shows that both CSAR and ZEP are characterised by excellent structural resolution (trench width of 91 nm, pitch 202 nm) and comparable process windows:

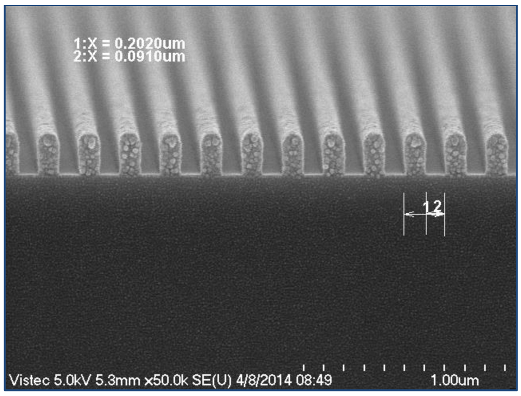

Fig. 10 ZEP 520A, 200 nm, ZED-N50, 50 kV, 80 µC/cm²

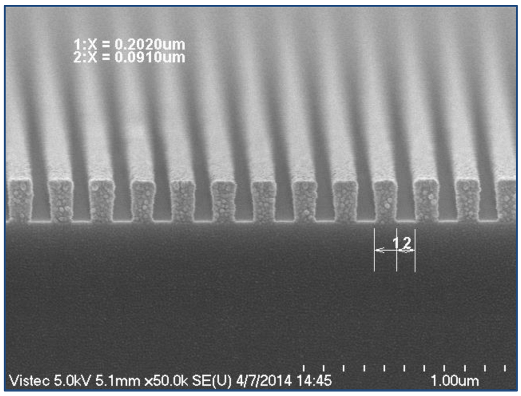

Fig. 11 AR-P 6200.09, 200 nm, AR 600-546, 50 kV, 85 µC/cm²

2) Contrast: The diagram illustrates a comparison of the contrast of ZEP 520 in the corresponding developer ZED-N50 and CSAR in developers AR 600-546 and 600-549. While the contrast for the systems ZEP-ZED-N50 and CSAR-AR 600-549 is almost equally good, the contrast of CSAR in developer AR 600-546 (which was optimised for this purpose) is almost twice as high, which makes it ideal for high-resolution applications:

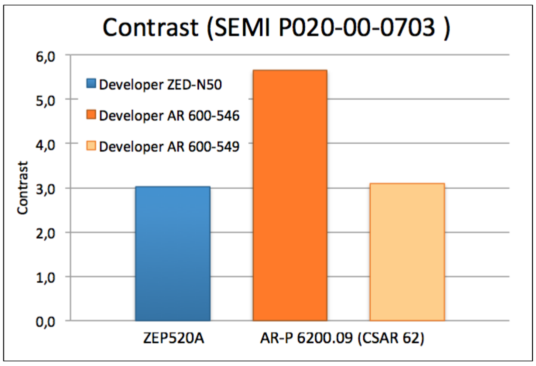

Fig. 12 Contrast ZEP 520A, 200 nm, ZED-N50 and AR-P 6200.09, 200 nm, AR 600-546 and AR 600-549

3) Sensitivity (Dose to Clear): The diagram shows that the required dose is at a good level for both resists. However, the CSAR resist-developer system with AR 600-546 is twice as sensitive as compared to the ZEP resist-developer system:

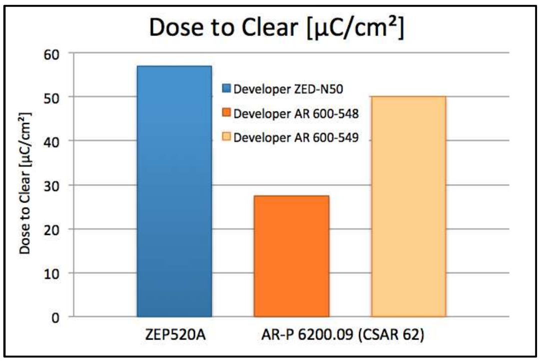

Fig. 13 Sensitivity ZEP 520 A, 200 nm, ZED-N50 and AR-P 6200.09, 200 nm, AR 600-548 and 600-549

All three studies came to the conclusion that both ZEP 520A and CSAR 62 have very good properties. This makes CSAR 62 an adequate alternative with partly even more favourable parameters. Advantages also arise from the variety of developers offered by Allresist, i.e. AR 600-546, 600-548 and 600-549. With these three different developers, exposure dose and developing time and consequently also resist contrast can be adjusted optimally over a very wide range and tailored to the particular application.

Conclusion

A very intense year of collaborative research between Allresist in Strausberg, the Institute of Thin Film Technology and Microsensors in Teltow, and the Martin-Luther-University in Halle has paid off: CSAR production on an industrial scale is meanwhile implemented and Allresist's customer needs are more than satisfied in terms of quality, versatility, price, and delivery time. The former unfavourable supply situation now belongs to the past, since with Allresist, a German resist manufacturer is now one step ahead on the market.

Users confirm that CSAR 62 exceeds ZEP 520 in its characteristics and acts as "all-rounder" for many interesting applications: Lift-off structures with 10 nm resolution and defined undercut can be generated. In addition, CSAR 62 can successfully be used in two-layer systems and for the production of mask blanks and T-gates. Another advantage is its price: currently, the CSAR is 4 times cheaper and immediately available.

In order to meet rising sales figures, Allresist expands the company building since June 2014 and creates new, modern production capacities as well as additional jobs. For the successfully marketed product innovation, Allresist received the Brandenburg Innovation Award 2014. Thus, the highest resolution high-tech resist CSAR 62 now is a striking hallmark of Brandenburg and Germany.

As of Aug. 2014