Study of the new CSAR62 positive tone electron-beam resist at 40 keV electron energy

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Abstract. One of the few “top-down” methods for nano-device fabrication is the electron-beam lithography, which allows flexible patterning of various structures with a nanoscale resolution down to less than 10 nm. Thinner, more etching durable, and more sensitive e-beam resists are required for the better control, linearity, and uniformity of critical dimensions of structures for nano-device fabrication. Within the last decade, researchers have made significant efforts to improve the resolution of the nanoscale e-beam lithography. The resist material properties are an important factor governing the resolution. Only the e-beam resist ZEP 520 of the Japanese manufacturer ZEON is characterized by relatively good properties and thus meets most users’ expectations. This paper deals with the investigation and simulation of the characteristics of the new less-expensive AR-P 6200 (CSAR 62) positive e-beam resist (available since May 2013, manufactured by Allresist GmbH company).

1. Introduction
The SX AR-P 6200/2 electron-beam resist is a positive-tone electron beam resist which provides, depending on the respective developer, a high to a very high sensitivity and allows realizing resolutions down to the sub-10-nm range. The resist is, furthermore, characterized by high process and plasma etch stability and, in addition, is very suitable for lift-off processes up to structure sizes of 10 nm.

Due to the very high contrast of the order of 15, a resolution of 10 nm can be achieved at a film thickness of 180 nm. Realization of an aspect ratio of 18 is thus possible.

By selecting an appropriate developer (X AR 600-54/8), the sensitivity of the resist can be increased to 10 µC/cm². An even higher resolution power is obtained with the X AR 600-54/6 developer.

All customers who employed the good qualities of the popular ZEP 520 can now look forward to an equivalent e-beam resist with a clear price advantage. After an intensive development work, Allresist was able to reach and partly even exceed the application benefits of the ZEP 520, e.g. with respect to the easy fabrication of lift-off structures.

The main components of the resist are poly(α-methylstyrene-co-methyl chloroacrylate), an acid

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generator and the safer solvent anisole. The acronym CSAR is deduced from the mechanism used: Chemical Semi Amplified Resist.

A particularly advantageous feature is the easy fabrication of lift-off structures. The plasma etch resistance of the CSAR62 and ZEP 520 is comparably high and twice as good as the plasma etch resistance of the PMMA resist.

In comparison with the PMMA resists, the CSAR 62 is characterized by a higher sensitivity and a substantially improved plasma etch resistance. The higher sensitivity results from the introduction of halogen atoms into the polymer chain. Generally, chlorine is used for this purpose (as well as for the CSAR 62 – methyl chloroacrylate), but bromine or iodine are also possible alternatives. The chlorine atom supports breaking of the polymer chain during irradiation with electrons. In addition, a halogen-containing acid generator enhances this effect. The introduction of further reactive halogens accelerates the influence on the polymer chain even more. As a result, less energy (a lower dose) is required to break the high-molecular polymer into smaller fragments. These fragments quickly dissolve in the developer, while the unexposed, still high-molecular resist, remains intact.

Due to the temperature-stable acid generator, the fractions of the chain are activated during the process of electron irradiation, and the resist layer does not require any tempering after exposure.

The improved plasma etch resistance results from aromatic substitutions of activating groups, such as e.g. phenyl, naphthyl or anthracyl groups into the polymer. The CSAR furthermore contains α-methylstyrene to provide etch stability. Due to their π-electrons, aromatic compounds are considerably more stable in the presence of different plasmas as compared to aliphatic polymers such as PMMA and thus reach the same level of stability like photoresists composed of novolacs (cresol mixtures condensed with formaldehyde).

2. Experiments and calculations

2.1. Experimental results

The investigations were performed on a 400-nm layer of CSAR 62 positive e-beam resist prepared by a spin coating technique onto a Si substrate for the case of 40 keV electron energy. The contrast and sensitivity characteristics were obtained experimentally for various development times.

The process conditions for the CSAR 62 (AR-P 6200.13) e-beam resist are summarized in table 1.

| Table 1. Process conditions for the positive e-beam resist CSAR 62 (AR-P 6200.13). |
|----|----|
| Coating | AR-P 6200.13, 4000 rpm, 0.4 μm film thickness |
| Pre-bake (± 1 °C) | 150 °C, 1 min hot plate or 150 °C, 30 min convection oven |
| E-beam exposure | 40 keV Dose-to-clear $E_0$: 30 μC/cm² |
| Development (21-23 °C ± 0.5 °C) puddle | AR 600-548, 60 sec |
| Stopping / Rinse | AR 600-60, 30 s / DI-H₂O, 30 s |
| Post-bake (optional) | 130 °C, 1 min hot plate or 130 °C, 25 min convection oven for slightly enhanced plasma etching resistance |
| Customer-specific technologies | Generation of semiconductor properties |
| Removal | AR 600-71 or O₂ plasma ashing |
A comparison between the contrast curves for the CSAR62 and PMMA is shown in figure 1. The advantages of the sensitivity and the contrast of the CSAR62 resist in comparison with the PMMA resist are clearly seen. A higher sensitivity and a better contrast for the CSAR62 resist are observed.

2.2. Simulation of the characteristics of the CSAR and PMMA resists

The proximity effect parameters were simulated for 400-nm thicknesses of the CSAR resist and of the PMMA resist layer on Si substrates. All exposures were performed at 40-keV e-beam energy (point or Gaussian sources). Discrete data for the energy deposition function (EDF) at the interface (at a depth of 400 nm) and near the resist surface (at a depth of 10 nm) were obtained by Monte Carlo simulation [1,2] using a point source for 10 000 particles (figures 2 and 3). An analytical approximation of the discrete data obtained for the EDF was performed using a sum of two Gaussians. Afterwards, the proximity effect parameters ($\beta_f$, $\beta_b$, $\eta_E$) along the resist depth were investigated and their variations were evaluated by the Monte Carlo methodology [1,2]. Tables 2 and 3 represent values of the parameters ($\beta_f$, $\beta_b$, $\eta_E$) at two resist depths – at the resists surface and at the resists/substrate interface for the CSAR and PMMA, respectively, for a point e-beam source. The values obtained of the proximity effect parameters are similar for both CSAR and PMMA resists.

The results of the Monte Carlo simulation and comparisons between the obtained EDF discrete data (●) and the corresponding analytical fit (solid curves) at different resist depths are presented in figures 2 and 3. Figure 2 represents the discrete data and analytical fits for the EDF at the resist/substrate interface, while figure 3 shows the results at the resist surface (at a depth of 10 nm) for a point source.
(10,000 particles) for both resists. A comparison between the EDF obtained at the interface for both investigated positive resists CSAR and PMMA is shown in figure 4.

2.3. Modeling and calculation of dissolution rates for the CSAR and PMMA resists

Table 4 shows estimated regression models for the dissolution rates ($V$, nm/s) depending on the change of the exposure dose ($D$, $\mu$C/cm$^2$) for the investigated positive CSAR and PMMA resists.

Figure 2. Comparison between the discrete data obtained (•) and the analytical fit (solid curve) at the resist/substrate interface in the case of: (a) CSAR/Si; (b) PMMA/Si.

Figure 3. Comparison between the discrete data obtained (•) and the analytical fit (solid curve) at the resist surface ($d = 100$ Å) for: (a) CSAR/Si; (b) PMMA/Si.

Figure 4. Obtained EDF discrete data (•) and an analytical fit (solid curves) at the interface for the PMMA/Si (• and black line, respectively) and for the CSAR/Si (• and pink line).

Figure 5. Dissolution rates vs. the exposure dose for different e-beam resists and development times: 1 - CSAR 62 resist, 60 s; 2 - CSAR 62 resist, 30 s; 3 – PMMA resist, 60 s.
The values of the squared multiple correlation coefficient, which is a measure for the models accuracy (the closer the coefficient $R^2$ value is to 100%, the better is the model) are also presented in table 4. The root mean square prediction error RSME is calculated by:

$$RSME = \left( \frac{1}{n} \sum_{i=1}^{n} (V_i - \hat{V}_i)^2 \right)^{1/2}$$

where $n$ is the number of experimental data for the dissolution rates $V_i, \hat{V}_i$ represent the dissolution rates estimated by the equations in table 4. As can be seen, the estimated models are adequate and good enough for prediction of the dissolution rates for the investigated e-beam resists.

The dependencies obtained of the dissolution rates on the exposure doses for both CSAR and PMMA resists at different development conditions are presented in figure 5. It can be seen (figure 5) that for 60 s development time the dissolution rate for the CSAR 62 resist (curve 1) reaches the same values as for the PMMA (curve 3), but at much smaller doses. At one and the same exposure dose the dissolution rate in the case of the CSAR 62 resist is much higher than the one for the PMMA resist. The increase of the development time for the CSAR 62 resist leads to a decrease of both the dissolution rate and the dose needed to clear the resist (figures 1 and 5).

### Table 4. Regression models for the dissolution rates $V$ depending on the exposure dose $D$.

| Resist and conditions | Regression equations                                                                 | $R^2$  | RSME  |
|----------------------|--------------------------------------------------------------------------------------|--------|-------|
| AR-P6200.13_4 (CSAR 62), development time - 60 s, resist thickness - 393 nm, exposure dose range is 2 - 27 $\mu$C/cm$^2$. | $V = 0.006034*D^2 + 0.07813*D + 0.02899$                                           | 99.94% | 0.0491 |
| AR-P6200.13_1 (CSAR 62), development time - 30 s, resist thickness - 397 nm, exposure dose range is 2 - 38 $\mu$C/cm$^2$. | $V = 0.001701*D^3 - 0.001539*D^2 + 0.1604*D - 0.1668$                               | 99.90% | 0.1190 |
| PMMA, development time - 60 s, resist thickness - 404 nm, exposure dose range is 10 - 230 $\mu$C/cm$^2$. | $V = 5.871*10^{-9}*D^4 - 1.524*10^{-6}*D^3 + 0.0001972*D^2 - 0.007249*D + 0.09337$ | 99.98% | 0.0248 |

### 3. Application
The Strausberg-based company Allresist won the Brandenburg Innovation Award 2014 for the development of the innovative product CSAR 62, which we consider as an appropriate replacement for the very expensive ZEP520A resist. The performance of the CSAR 62 being similar to that of ZEP520A in resolution, speed, and etch resistance, is confirmed in references [3,4].

A difference in the dependencies of the relative resist thickness (and solubility rates) vs. the doses of exposure at two development durations – 30 s and 60 s, respectively, can be seen on the experimental contrast curves obtained by us and shown in figure 1. Similar nonlinear behavior has been observed for the CAR CAMP6 resist [5-8]. In these references, the multiplicated functions for the solubility rates provide different development kinetics behavior of the images developed, which can be predicted by the new computer algorithm. For the CSAR 62 resist, the equations in table 4 are implemented in the numerical code to be used for simulation of the profiles developed in this new positive-tone chemical self-amplified resist.

In the current R&D of nanoscale devices, patterning in various combinations of thin films and substrates is required, e.g. in the III-V semiconductors (GaN, GaInN, AlGaN, AlGaN, GaInN, GaInN), SOI wafers (Silicon on Insulator), photonic crystals, etc. The simulation methodology of the characteristics
of e-beam resists, described in this paper, is suitable for an effective and precise control of structure dimensions in an e-beam resist applied as a masking layer for patterning onto various thin films. As an example of such applications, we present a dimension control of photonic crystals structures. In this case, hexagonal gratings are required with various diameters and periods of the holes. Exposures were performed with a Gaussian beam to obtain optimal circular shapes of the holes. Thin film of CSAR 62 positive resist was prepared by spin coating onto 220 nm silicon nitride/1900 nm silicon dioxide thin films on a silicon substrate. The thickness of 600 nm was chosen as appropriate for dry etching of 220 nm thin silicon nitride. The diameter of the holes was controlled by varying the dose. In figure 6, hexagonal gratings with hole diameters of 80 nm (figure 6a), 130 nm (figure 6b) and 200 nm (figure 6c) are demonstrated. The distance between the holes forming a hexagonal pattern was 380 nm for all the cases.

4. Conclusions
In this paper, we present and discuss the results of an investigation of the characteristics of a new positive tone chemical self-amplified resist, namely, CSAR 62. It is shown that they are appropriate for various nano-lithography applications. Additionally, this resist is a cheaper alternative to the ZEP type nano resist. It was also observed that its development rate exhibited a nonlinear behavior, i.e. it depended on the time and/or the resist depth. Simulations were carried out in order to study the development of the CSAR 62 resist for hexagonal gratings with different hole diameters. The results demonstrated an efficient dimension control of photonic crystals structures.

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