Experimental and theoretical study on chemically semi-amplified resist AR-P 6200

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Abstract. Experimental and simulation results are presented and discussed on electron-beam lithography (EBL) nano-structuring using the positive chemically semi-amplified electron-beam resist AR-P 6200 (CSAR 62), which provides high sensitivity and allows achievement of high resolutions (sub-100 nm). The influence of the e-beam lithography process parameters, namely, exposure dose, development process conditions, and proximity effects on the obtained developed images was studied for the case of 40-keV electron energy.

1. Introduction

Since the Novolac resin in photoresists is not transparent to the KrF laser radiation, while diazonaphthoquinone (DNQ) is not sensitive to this laser radiation, chemically-amplified resists (CAR) were developed [1] and the use of the CAR system has been extended to ArF and ArF immersion lithography as well [2, 3]. Recently, a number of advanced resist systems with good combination of sensitivity and resolution have been developed mainly for extreme ultraviolet lithography (EUVL) [4].

CARs exhibit high resolution and high sensitivity, so they are very attractive materials for electron-beam lithography (EBL) as well. In EBL, the resolution capability is not an issue, as the beam size of the focused electron beam is usually small compared to the minimal feature size of the device patterns. However, an important requirement for the electron-beam resist has always been the combination of high resolution, high sensitivity, and line-edge roughness (LER). The first commercialized CAR was the negative-tone electron-beam resist SAL 601 [5]. Subsequently, various kinds of CARs for electron-beam systems have been developed for mask making and direct writing applications.

Aiming to improve the resolution of the nano-dimensioned EBL and to obtain results concerning the critical dimensions of structures for nano-device fabrication in view of nano-lithography applications, further experimental and theoretical studies (simulations) are needed to understand the

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effects of increasing the contrast on the resolution of final resist patterns (profiles). In this paper, we present investigations on the positive chemically semi-amplified electron beam resist AR-P 6200 (CSAR 62 – Chemically Semi-Amplified Resist) (Allresist GmbH) [6].

2. Results and discussion

2.1. Experimental procedure

The investigations were performed on a 600-nm-thick layer of positive e-beam resist CSAR 62 prepared by spin-coating on a silicon substrate. The thickness of 600 nm was chosen as being appropriate for dry etching of silicon for some applications. The resist was prebaked at 150 °C for 1 min on a hot plate. The post-exposure bake performed usually for CARs was not applied because an additional increase in the sensitivity already occurs during the exposure of the CSAR 62 resist due to the halogenated acidifiers [6]. The resist was developed by an AR 600-548 developer, followed by rinsing in an AR 600-60 stopper for 30 s. The exposures were carried out using a ZBA 23 (Vistec Electron Beam GmbH) variably-shaped e-beam equipment at a constant electron energy of 40 keV [7]. The contrast and sensitivity characteristics were obtained by exposure wedge tests (beam cross-section 3000×3000 nm²). The resist AR-P 6200 is characterized by high process and plasma-etch stability; in addition, it is suitable for lift-off processes. The resist profile shape is an important issue in both processes. We conducted resist profile studies on test structures consisting of long single lines with various linewidths and on periodical gratings with various line/space (L/S) dimensions. The length of the e-beam cross-section was 3000 nm, with the width varying from 50 nm to 1000 nm. After development, the sample was broken perpendicularly to the lines and gratings. All dimension measurements were carried out using a Quanta 3D (FEI) high-resolution scanning electron microscope (SEM) with a field-emission cathode.

2.2. Experimental results and discussion

Series of line test structures were exposed with the aim to follow the dependence of the resist profile shape on the exposure dose and find the conditions for producing a vertical sidewall shape and Line = Space. Typical results of the tests inspection are demonstrated in figures 1 and 2. The dependence of the resist profile dimensions and the image shape on the exposure dose for a single-line pattern is shown in figure 1. The e-beam cross-section was 100×3000 nm². The exposure dose was increased from 120 μC/cm² to 340 μC/cm². As seen, the shape of the profile in the resist changed as the exposure dose was raised. The optimal (vertical) side wall shape was formed at the exposure dose of 310 μC/cm² (figure 1c).

![Figure 1. Single line, linewidth 200 nm.](image)

The linewidth was measured at different levels along the resist depth – at the resist top (T), at the middle resist depth (M), near the resist bottom (B1/8) and at the resist bottom (B). The corresponding measured values of the linewidth in the case of a 340 μC/cm² exposure dose were: T = 638.4 nm, M = 652.8 nm, B1/8 = 715.1 nm, and B = 813.9 nm.

Figure 2 shows the profile shape and image dimension variations vs. the dose of electron exposure for a periodical line grating with the L/S exposed being 100/700 nm. The optimal profile shape with vertical side walls and Line = Space = 400 nm was formed at the dose of 130 μC/cm² (figure 2c).
2.3. Simulation and estimation of the AR-P 6200 e-beam resist characteristics

Using CSAR 62 allows one to achieve high resolutions (sub-100 nm); its etch stability is comparable to that of ZEP520A resist, while it is reasonably priced [8, 9]. The profile in the resist (relief formed in the resist layer after the development process) and the image dimensions are the most important factors in deciding whether the development conditions (developer, time of development, etc.) are suitable for forming fine patterns. An original nonlinear development model was reported in [10], where the calculation of the developed relief (images) was based on the 3-dimensional absorbed-energy distribution in the resist layer [11] and on the local dissolution rates.

Achieving high EBL resolution requires accurate knowledge of the absorbed-energy distribution in the resist – in lateral direction (r) and along the resist depth (z). At a given resist depth, the energy deposition function (EDF(r,z)) is defined by a sum of two Gaussians; a Monte Carlo approach is used [11] to model the electron scattering process and calculate the proximity effect parameters (βr, βz, ηr) along the resist depth. Figure 3 presents a comparison between the energy deposition functions calculated at two characteristic depths in CSAR 62 – at the resist surface (at a 30-nm depth) and at the resist/Si substrate interface (at a 600-nm depth).

The results for the absorbed energy variation in the resist depth showed a linear dependence of the proximity effect parameters values along the CSAR resist depth concerning the 3D distribution of the EDF. The values for two resist depths were used – for the resist surface and for the resist-substrate interface. For 600-nm-thick CSAR 62 on Si at 40-keV beam energy, the values obtained of (βr, βz, ηr) were (0.0467 μm, 4.038 μm, 0.197) at the resist surface and (0.0541 μm, 5.307 μm, 0.321) at the interface, respectively. Based on these simulation results, one should expect nearly vertical side walls of the profiles in the resist.

We further studied the behavior of the CSAR 62 resist developed in AR 600-548 for different times to obtain the dissolution rates at different doses of electron exposure needed for the simulation.

Figure 4a presents experimental contrast curves for a 600-nm-thick CSAR 62 resist on a Si substrate for three development times, namely, 60 s, 180 s and 240 s. The electron energy was 40 keV and the beam spot size, 3×3 μm². As seen, the CSAR 62 positive-tone resist studied shows a nonlinear development behavior. Based on the residual resist thickness as a function of the time of development, we calculated the solubility rates for the AR 600-548 developer at different times of development when the exposure dose varied from 0.5 μm/cm² to 14.5 μm/cm² (figure 4b). One can see a low solubility rate at low exposure doses and a sharp increase of the resist removal at higher exposure doses. The development rates thus evaluated as functions of the exposure dose can be applied to
simulate the profiles developed in the resist taking into account the peculiarities of the CSAR 62 resist (due to the complicated mechanism of the resist removal from the soluble resist areas) and the variation of the energy deposition function $EDF(r,z)$ in radial and in depth directions (its 3D distribution in the resist layer).

![Figure 4a. Thickness of remaining CSAR 62 positive resist in the range of exposure doses 0.5 $\div$ 14.5 $\mu$C/cm$^2$.]

![Figure 4b. Solubility rates at various electron exposure doses for AR 600-548 developer; development time 60 s, 180 s, 240 s.]

2.4. Application
The simulation tools employed and the evaluation of the important resist characteristics (solubility rate, proximity parameters along the resist depth) are convenient to use to predict and control the image dimensions when the AR-P 6200 chemically semi-amplified resist is applied to nano-patterning. Figure 5 shows details of large-area line gratings for optoelectronics application. The exposed Line/Space ratio was 100/400 nm, 100/500 nm and 100/700 nm. After exposure and development, this ratio was found to be 250 nm for an exposure dose of 60 $\mu$C/cm$^2$ (figure 5a), 300 nm for 90 $\mu$C/cm$^2$ (figure 5b), and 400 nm for 130 $\mu$C/cm$^2$ (figure 5c). Also, the sidewalls were vertical in all cases.

![Figure 5. Gratings in a resist with various L/S: a) L/S = 250/250 nm, Q = 60 $\mu$C/cm$^2$, b) L/S = 300/300 nm, Q = 90 $\mu$C/cm$^2$, c) L/S = 400/400 nm, Q = 130 $\mu$C/cm$^2$. Exposed linewidth is 100 nm in all cases.]

3. Conclusions
The results presented of experimental and theoretical studies of the characteristics of the AR-P 6200 (CSAR 62) positive e-beam resist and of the various process parameters (exposure dose, development time, line width etc.) determining the accuracy of the developed resist profiles and critical structural dimensions can be used to improve the resolution of the nano-dimensional EBL in nano-lithography
applications for fabrication of nano-devices. The study of the AR-P 6200 (CSAR 62) resist profiles was performed using variably-shaped electron-beam lithography with electron energy of 40 keV. The solubility rate at different e-beam exposure doses was investigated and evaluated. The AR-P 6200 (CSAR 62) resist exhibited a nonlinear development behavior with the AR 600-548 developer. Profiles with nearly vertical side walls were obtained; possible applications of variably-shaped e-beam processing are also presented.

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