PMMA resist profile and proximity effect dependence on the electron-beam lithography process parameters

I Kostic1, K Vutova2,4, E Koleva2,3 and A Bencurova1

1Institute of Informatics, Slovak Academy of Sciences,
9 Dubravská Cesta, 845 07 Bratislava, Slovak Republic
2Acad. E. Djakov Institute of Electronics, Bulgarian Academy of Sciences,
72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
3University of Chemical Technology and Metallurgy,
8 Kliment Ohridski Blvd., 1756 Sofia, Bulgaria
E-mail: katia@van-computers.com, ivan.kostic@savba.sk

Abstract. The study reveals the influence of the electron-beam lithography parameters (such as the exposure dose, resist thickness, depth) on the resist profile shape in the case of the PMMA (polymethyl-methacrylate) positive resist. The experiments are performed using an Elphy Quantum (Raith) e-beam lithography control system installed on an Inspect F50 (FEI) scanning electron microscope with a field emission cathode and a Gaussian intensity distribution. Profiles developed in the PMMA using the MIBK:IPA 1:3 developer and simulation results based on measurements along the resist profile depth for the case of 30-keV electron energy are presented and discussed. The results contribute to the knowledge on electron scattering in the resist/substrate in electron-beam lithography and assist in the development and approval of simulation tools for prediction and control of resist profiles in thick PMMA layers for lift-off nanopatterning.

1. Introduction
Electron-beam lithography (EBL) is among the most important and widely used top-down technological research and development (R&D) methods in nanotechnology. It is widely used in academic and research institutes for R&D of applications, such as nano-electro-mechanical systems, opto-electronic and quantum devices, nanofluidics, molecular electronics, surface science applications, and even in leading life-science research [1]. The EBL process is affected by a large number of parameters in a complex, interconnected fashion. The precise control of these parameters requires a systematic understanding of the limiting factors involved in the processes of both the electron-resist material interaction and in the polymer resist dissolution (development), as well as the corresponding interplay between the numerous process control parameters, including the accelerating voltage, exposure dose, materials, and development conditions.

The PMMA (polymethyl-methacrylate) resist is one of the most widely used positive tone resists with important applications in nanolithography due to, e.g., its good adhesion to different substrates coupled with the possibility of achieving high resolution and high contrast [2, 3]. PMMA is suitable

4 To whom any correspondence should be addressed.
for three-dimensional, dense and high-aspect-ratio nanoscale structuring for such applications as photonic crystals, plasmonic devices, metamaterials, X-ray lithography masks and diffractive X-ray optics. In [4], a fabrication method is described that utilizes electron-beam lithography in 1.1-μm thick layers of PMMA for electroplating. The use of the PMMA is also important in the lift-off technique where EBL plays an important role [5]. For a defect-free process, the resist thickness should be three times as high as the thickness of the final structures resulting after a lift-off process. Thus, the main goal in using thick PMMA in lift-off applications is attempting to push the working limits towards achieving a high-aspect-ratio, in order to have just a single layer of positive resist. Therefore, further investigations are needed to understand the effects of the EBL parameters on the profiles (images) obtained in the resist. In this paper, we present a study on using PMMA as a thick positive e-beam lithography resist, as usually required in the lift-off technique.

2. Results and discussion
2.1. Experiments
The goal of the profile measurements carried out in this work was to obtain a set of experimental data on exposing a PMMA resist to the electron beam with a Gaussian electron energy distribution and a nanometer diameter produced by the field-emission cathode of a high-resolution scanning electron microscope (SEM). The experimental data were used in the development and optimization of simulation tools concerning the profiles developed in the resist. The experiments were conducted on an 1800-nm-thick layer of PMMA resist on a silicon (Si) substrate using the Elphy Quantum (Raith) e-beam lithography control system installed on an Inspet F50 (FEI) SEM [6]. The electron energy of 30 keV was used at a beam current of 42.5 pA. The exposures were performed in a single-pixel line mode (the linewidth is set to zero, i.e., the beam diameter) with a line step size of 20 nm. In a single-pixel line mode, the line exposure dose is expressed in nC/cm. The resist was developed by means of MIBK:IPA 1:3 developer for 60 s. A Quanta 3D (FEI) high-resolution SEM was used to measure the PMMA resist profiles dimensions at magnifications of 100 000× and 200 000×.

The test measurements of the resist profile were performed on a set of long lines separated by 10 μm. The line exposure dose was increased from a minimal value (when the resist was completely developed up to the substrate) up to a significantly higher value (by a factor of about 10) with an appropriate increment thus preparing a set of various profiles. After the development, the sample was cleaved perpendicularly to the pattern. A thin platinum film was sputtered on the PMMA resist using a high-resolution sputter coater SC7640 (Quorum Technologies) in order to avoid charging during the SEM profile measurements. A detail of a single line test for PMMA image dimension measurements is demonstrated in figure 1.

![Figure 1. Detail of a single line test for developed resist profile measurements.](image)

Series of test line structures were formed in thick layers of PMMA resist (1800 nm and 1300 nm) for the case of 30-keV electron energy aiming to follow the influence of the dose on the profile geometry and find the conditions of obtaining vertical profile sidewalls. The results of inspecting the tests in the 1800-nm and 1300-nm PMMA layers for various line exposure doses \((D)\) are shown in figures 2-3. The values measured of the linewidth at the top of the PMMA resist and at the resist/substrate interface are summarized in table 1.

The line exposure dose \((D)\) was in the range 24.92 – 284.69 nC/cm in the case of resist thickness of 1800 nm. The best resist profile in PMMA (figure 2c, table 1) was formed at 41.5 nC/cm line exposure dose (optimal dose). However, the profile sidewalls were slightly rounded. In the case of 1300-nm PMMA resist layer, the minimal line exposure dose was 4.07 nC/cm (figure 3a) and the optimal (nearly vertical) side-wall shape was formed at 8.13 nC/cm (figure 3b).
**Table 1.** Linewidth at the top of the resist and at the substrate for various line exposure doses for resist thicknesses of 1800 nm and 1300 nm.

| Resist thickness (nm) | Line exposure dose (nC/cm) | Linewidth at the resist top (nm) | Linewidth at the substrate (nm) |
|----------------------|-----------------------------|----------------------------------|---------------------------------|
| 1800                 | 2 a) 24.9                   | 35.0                             | remaining resist               |
|                      | 2 b) 33.2                   | 41.0                             | 10                              |
|                      | 2 c) 41.5                   | 57.0                             | 70.0                            |
|                      | 2 d) 49.8                   | 60.0                             | 216.0                           |
|                      | 2 e) 62.3                   | 65.0                             | 642.0                           |
|                      | 2 f) 74.6                   | 70.0                             | 815.0                           |
|                      | 2 g) 136.6                  | 86.0                             | 1519.0                          |
|                      | 2 h) 227.8                  | 170.0                            | 1780.0                          |
| 1300                 | 3 a) 4.07                   | 81.0                             | remaining resist               |
|                      | 3 b) 8.13                   | 128.0                            | 515.0                           |
|                      | 3 c) 40.67                  | 184.0                            | 1200.0                          |

**Figure 2.** Developed resist profiles at various line exposure doses $D$: a) 24.9 nC/cm, b) 33.2 nC/cm, c) 41.5 nC/cm, d) 49.8 nC/cm, e) 62.3 nC/cm, f) 136.6 nC/cm, g) 227.8 nC/cm.

**Figure 3.** Developed single-line profiles at doses $D$: a) 4.07 nC/cm, b) 8.13 nC/cm, c) 40.67 nC/cm.

**Figure 4.** PMMA thickness 1800 nm, $D = 24.8$ nC.

### 2.2. Profile parameters modeling

The linewidths of the developed profiles ($\gamma$) were measured at five levels along the PMMA resist depth, as it is shown in figure 4: at the top of the resist layer (resist surface) – LT; at 100 nm in the resist depth (below the resist surface) – LT1; at the middle level in the resist depth – LM; at 100 nm above the resist/substrate interface (bottom 2) – LB2; at the resist/substrate interface (bottom 1) – LB. The experimental variation intervals of the investigated parameters – exposure line dose ($z_1$) and resist depth ($z_2$) in the case of 1800-nm PMMA resist thickness are presented in table 2.
The measured linewidth data was used to assess a regression model describing the dependence of the profile dimensions on the line exposure dose used. The assessed regression model relating the developed resist line widths ($y$) to the varying line dose ($x_1$) and resist depth ($x_2$) is:

$$
\hat{y} = 720.02704 + 391.84188x_1 - 600.06928x_2 - 182.69547x_1^2 + 454.39483x_1x_2 + 130.59362x_1^5 + 233.8796x_1^6x_2.
$$

### Table 2. Experimental parameter regions.

| Parameter          | Denoted | Coded | Lower level ($z_{\text{min,}i}$) | Upper level ($z_{\text{max,}i}$) |
|--------------------|---------|-------|----------------------------------|----------------------------------|
| Line dose, nC/cm   | $z_1$   | $x_1$ | 24.92                            | 284.69                           |
| Resist depth, nm   | $z_2$   | $x_2$ | 0                                | 1800                             |

The values of the corresponding squared multiple correlation coefficients (determination coefficients) are: $R^2 = 94.152\%$ and $R^2_{\text{adj}} = 93.778\%$, which define a good prediction accuracy of using the assessed model and its usability for the optimization of the developed resist profiles. Figure 5 shows a comparison between the experimentally obtained resist profile and the calculated profile geometry at $D = 49.8$ nC/cm; a good agreement is seen. Figure 6 presents contour plots of the developed resist line widths ($\hat{y}$) vs. the line exposure dose ($z_1$) and the resist depth ($z_2$).

![Figure 5. Resist profile in 1800 nm PMMA and calculated image geometry at $D = 49.8$ nC/cm, 30 keV.](image)

![Figure 6. Contour plot of the developed linewidth ($\hat{y}$).](image)

The resist profile geometry can be optimized in terms of obtaining vertical sidewalls. Two performance characteristics were considered: (i) the sidewall slope angle ($a$) of the developed profile measured at a height of 100 nm above the interface (LB2) and at the middle level in the resist depth (LM); (ii) the standard deviation ($s$) of the developed linewidth ($y$) at different resist depths ($z_2$). Two regression models are assessed for the sidewall slope angle ($a$) and for the standard deviation ($s$) depending on the line exposure dose ($d$). They are presented in table 3 for realistic values of the line dose, together with the values of the multiple correlation coefficients $R^2$ and $R^2_{\text{adj}}$, which are high and thus define the good prediction accuracy.

### Table 3. Regression models for the sidewall slope angle ($a$) of the developed resist profiles and the standard deviation ($s$) of the developed linewidths.

| Regression model | $R^2$ | $R^2_{\text{adj}}$ |
|------------------|-------|-------------------|
| $\hat{a} = 107.4413374506 - 0.4640851279d + 0.0019608319d^2 - 0.0000269034d^3$ | 88.5% | 86.2% |
| $\hat{s} = -274.1045425 + 10.73010118d - 0.041552557d^2 + 0.0000610282d^3$ | 94.6% | 93.5% |
The assessed models are used for a multi-parameter optimization aiming to achieve vertical sidewalls by implementing the following requirements: a maximal sidewall angle ($\alpha \leq 90^\circ$) and a minimal standard deviation. The optimal solution is obtained at the line exposure dose of 45.9371 nC/cm, where the estimated sidewall angle is $\hat{\alpha} = 90^\circ$ and the corresponding estimated standard deviation is $\hat{s} = 137.0366$ nm.

3. Conclusions
In this paper, we present a study on the positive e-beam lithography resist PMMA for 30-keV electron energy. The influence of the exposure dose and the resist thickness on the shape of the developed profiles in thick PMMA resist layers are studied experimentally and theoretically in order to achieve a high-aspect-ratio of the structures. Models are assessed for predicting and optimizing the geometry of the developed resist profiles in the PMMA resist. Corresponding experiments and simulations for different EBL process parameters are carried out and comparisons are made. The results presented contribute to the knowledge on electron scattering in the resist/substrate in e-beam lithography for the case of a field-emission cathode and a Gaussian intensity distribution, as well as to the development and approval of simulation tools for prediction and precise control of the resist profiles obtained in PMMA for lift-off nanopatterning.

Acknowledgements
The work was supported by the Bulgarian National Science Fund under contracts DN17/9 and KP-06-N27/18, and by the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences under contract VEGA 1/0828/16 and 2/0119/18. The use of the SEM facilities at the Institute of Electrical Engineering SAS is gratefully acknowledged.

References
[1] Yifang Chen 2015 Microelectronic Eng. 135 57
[2] Kostic I, Vutova K, Koleva E, Andok R, Bencurova A, Konecnikova A and Mladenov G 2016 Polymer science research advances, practical applications and educational aspects Polymer Science Book Serie 1 (Eds) A Méndez-Vilas and A Solano-Martín (Spain Formatex Research Center), pp 488-97
[3] Tiwari P, Srivastava AK, Khattak BQ, Verma S, Upadhyay A, Sinha AK, Ganguli T, Lodha GS and Deb SK 2014 Measurement 51 1
[4] Gorelick S, Guzenko V A, Vila-Comamala J and David C 2010 Nanotechnol. 21 295303
[5] Yaghmaie F, Fleck J, Gusman A and Prohaska R 2010 Microelectronic Eng. 87 2629
[6] www.raith.com