Simulation and experimental study on developed profiles in the positive polymer resist PMMA

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Abstract. Theoretical and experimental study on developed profiles in the positive tone PMMA (polymethyl-methacrylate) resist and e-beam lithography process parameters was performed. E-beam lithography control system Elphy Quantum (Raith) installed on Scanning Electron Microscope Quanta FEG (FEI) with a field emission cathode and Gaussian intensity distribution has been used for the conducted experiments. Simulation results obtained by different models concerning the geometry of the developed resist profiles in PMMA were compared and verified with experimental data for improvement characterization of PMMA resist. The estimated models presented are useful for prediction and optimization of the developed resist profiles at electron beam lithography.

1. Introduction

Electron beam lithography (EBL) is one of the most popular technological methods in R&D for device prototyping, where defining and obtaining fine patterns are needed. This top-down technique is one of the most important for nanofabrication that enables reliable patterning with high resolution (down to the nm scale) for production of many devices such as nanowires, quantum devices, high-frequency electronics, etc. This method is based on the physical-chemical changes in the resist layer, and the commonly used resists are polymers that are dissolved in a liquid solvent in order to enhance the lithography performance of the material. The main advantages of the widely used positive tone PMMA (polymethyl-methacrylate) resist, which has important applications in nanolithography, are ultimate resolution (less than 10 nm), high contrast, good adhesion to most substrates, etc. In this paper, theoretical and experimental study on developed profiles in PMMA resist is presented. Simulation results for developed profile geometry at different exposure doses were obtained and compared with experimental data obtained in order to improve characterization of PMMA resist.

In many computer codes, the penetration of irradiating electrons in the polymer layer is calculated utilizing Monte Carlo method [1-3]. Here the prediction models for the developed resist profiles...
widths were estimated by implementation of Response Surface Methodology and regression analysis [4, 5].

2. Experimental investigation
The experiments were conducted using e-beam lithography control system Elphy Quantum (Raith) installed on Scanning Electron Microscope (SEM) Quanta FEG (FEI) with a field emission cathode and Gaussian intensity distribution.

The investigation was carried out for PMMA resist thickness of 1300 nm on Si substrate at 30 keV electron energy. The development was performed by using MIBK:IPA 1:3 developer for development time of 60 s.

The data for the measured widths of the developed resist profiles presented in table 1 was obtained for different values of the line exposure doses (d). The widths of the developed profile were measured at 5 levels along the PMMA resist depth (figure 1): at the top of the resist layer (resist surface) – $y_1$, at 100 nm in the resist depth (below the resist surface) – $y_2$, at the middle level in the resist depth – $y_3$, at 100 nm above the resist/substrate interface (bottom 2) – $y_4$, at the resist/substrate interface (bottom 1) – $y_5$). The data for the wall slope angle ($y_6$) of the resist developed profile, measured at a height of 200 nm above the resist/substrate interface is also given in table 1.

![Figure 1. Measurement details concerning the dimensions of the developed profiles in PMMA resist at single pixel lines exposure.](image)

| Line Dose D (pC/cm) | Width at top (nm) | Width at 100 nm below top (nm) | Width at middle (nm) | Width at bottom 2 (nm) | Width at bottom 1 (nm) | Angle (degrees) |
|---------------------|------------------|--------------------------------|----------------------|-----------------------|-----------------------|-----------------|
| 1.627               | 56.7             | 65.0                           | -                    | -                     | -                     | -               |
| 4.067               | 81.1             | 107.9                          | 172.7                | 91.3                  | 515.3                 | 90.0**          |
| 8.134               | 128.0            | 164.9                          | 267.1                | 399.3                 | 515.3                 | 87.9            |
| 16.268              | 137.6            | 192.0                          | 420.0                | 609.8                 | 798.6                 | 81.0            |
| 32.536              | 154.0            | 250.0                          | 640.0                | 898.4                 | 1000.0                | 77.6            |
| 40.670              | 183.6            | 288.7                          | 690.0                | 1000.0                | 1200.0                | 75.7            |
| 48.804              | 194.3            | 313.1                          | 744.2                | 1106.0                | 1280.0                | 72.0            |
| 65.072              | 240.5            | 330.0                          | 822.9                | 1230.0                | 1320.0                | 65.7            |
| 81.340              | 245.7            | 390.0                          | 879.7                | 1320.0                | 1384.0                | -               |

* at 80 nm above the substrate
** in the middle along the resist depth
3. Modelling of developed resist profile parameters

Based on the experimental data (table 1) models were estimated. The obtained dependencies of the profile dimensions in PMMA resist on the used line exposure dose \( d \) (coded values \( x \)) are displayed in table 2. The values of the corresponding squared multiple correlation coefficients (determination coefficient) \( R^2 \) (in percent) are also given (table 2). The coded values \( x \) of the line exposure dose \( d \) in the region \([-1+1]\) can be found by using the maximum \( d_{\text{max}} \) and the minimum \( d_{\text{min}} \) values of the line doses \( d_{\text{max}} = 81.340 \text{ pC/cm} \) and \( d_{\text{min}} = 1.627 \text{ pC/cm} \) in the equation:

\[
x = \frac{2d - d_{\text{max}} - d_{\text{min}}}{d_{\text{max}} - d_{\text{min}}}
\]

These determination coefficients are tested for significance and their values are measures of the accuracy of the estimated models. The closer to 1 (to 100%) the value of \( R^2 \) is, the better the model describes the variations of the quality characteristics as a function of the process parameters. All models obtained in the present study have high enough and significant values of their multiple correlation coefficients and consequently these models are good for prediction and optimization of the considered developed profile geometry characteristics.

| Model | \( R^2 \), % |
|-------|-------------|
| \( \hat{y}_1 = 187.78977 + 84.856627 x - 24.744282 x^2 \) | 94.502 |
| \( \hat{y}_2 = 283.71812 + 141.92075 x - 52.17353 x^4 \) | 97.201 |
| \( \hat{y}_3 = 689.25247 + 387.79648 x - 235.98274 x^4 \) | 98.264 |
| \( \hat{y}_4 = 1004.7231 + 387.44436 x + 295.72021 x^3 - 371.06035 x^4 \) | 98.951 |
| \( \hat{y}_5 = 1134.1826 + 476.98608 x - 498.56278 x^6 + 265.82384 x^7 \) | 97.523 |
| \( \hat{y}_6 = 89.195 - 0.35591345 d \) | 96.729 |

Results for the dependencies of the experimental data and the estimated profile widths \( y_2 \), based on the corresponding model, at 100 nm in PMMA resist depth (below the resist surface – figure 1) on the applied line dose \( d \) are presented and compared (figure 2). Figure 3 shows data about the changes concerning the experimentally measured and model estimated values of the wall slope angles \( (y_6) \) of the developed resist profile, measured at a height of 200 nm above the resist/substrate interface, according to the variation of the applied line dose \( d \).
Figure 3. Experimental and estimated values of the wall slope angle ($\gamma_6$) of developed profiles in the resist, measured at a height of 200 nm above the resist/substrate interface, depending on the exposure line dose $d$.

It can be seen, that the developed PMMA resist profile side-walls that are closer to vertical side-walls (the wall slope angle is closer to 90 degrees) were obtained when small values of the exposure line doses are used.

Instead of using five regression models along the PMMA resist depth ($\hat{y}_1 - \hat{y}_5$, table 2) another variable $\tilde{z}$ can be used, describing the depth in the resist layer considered from the resist surface to the resist/substrate interface (figure 1) and varying from 0 to 1300 nm, correspondingly. It also should be coded in the region [-1+1]:

$$z = (2\tilde{z} - 1300)/1300$$

The estimated overall regression equation for the developed profile width $\hat{y}$, depending on the exposure line dose $x$ and on the resist depth $z$ is:

$$\hat{y} = 676.59446 + 263.9929x + 435.87419z - 240.44412x^4 + 287.7237xz - 214.31975x^6z + 48.278013z^7 + 155.05354x^5$$

The squared multiple correlation coefficients (determination coefficient) $R^2$ for this model is $R^2 = 98.431\%$. It is significant and consequently the model is good and can be used for prediction and optimization of the developed profiles obtained in PMMA resist.

Figure 4 presents the obtained contour plots for the developed profile line width $\hat{y}$ in PMMA resist depending on the exposure dose $d$ and on the resist depth $\tilde{z}$. The results show that at lower values of the exposure dose, where wall slope angle ($\gamma_6$) of the developed profile is about $90^\circ$, the width of the developed profile does not change much along the resist depth. If the value of the used line dose of exposure is too low, the developed profile does not reach the resist/substrate interface.

Figure 4. Width $\hat{y}$ of the developed profile in PMMA resist, depending on the exposure line dose $d$ and on the resist depth $\tilde{z}$. 
4. Verification of the models for the developed resist profile parameters

The verification of the estimated models obtained can be done by comparing model estimated and experimentally obtained developed profiles in PMMA resist. In figure 5 the cross-validation, based on the estimated values for the developed profile width $\hat{y}$, obtained by the model (1), and the experimentally observed widths $y$, is presented.

The prediction line $\hat{y} = f(y)$ almost coincides with the line, giving equal values of estimated and predicted values (when $y = \hat{y}$ - the dashed line in figure 5). The corresponding line model determination coefficient is $R^2 = 98.4\%$.

Comparison between calculated (by the estimated models in table 2) geometry parameters of the developed profile in PMMA resist (signed by *) and the experimentally measured values for the resist profile width (signed by *) at single pixel line exposure with a dose of 16.268 pC/cm is presented in figure 6. The results in figures 7 - 8 show comparisons between calculated (by model equation (1)) developed profile geometry in PMMA and experimentally measured developed profile widths (*) at single pixel line exposure with doses of 8.314 pC/cm and 48.804 pC/cm, correspondingly.

Both approaches show very good coincidence between calculated results (using different models) and experimental data.
5. Conclusions
A study on developed profiles and e-beam lithography process parameters in the positive tone PMMA resist was performed. The resist thickness of 1300 nm is used for many applications, e.g. in lift-off process of thick films. Models for the dependence of the developed profile line-width on the exposure dose in thick PMMA resists were estimated. Simulation results for the developed profile geometry at different exposure doses were obtained. Comparisons between experimentally measured data and calculated data for the geometry and the dimensions of the developed profiles in PMMA resist were made and good coincidence was observed. The models can be used for prediction and optimization of the developed resist profiles and for choosing appropriate process conditions.

Acknowledgements
The work has been supported by the Bulgarian National Science Fund under contracts DNTS/Slovakia 01/1 and DN17/9, and by the Scientific Grant Agency of the MESRS and SAS under contract No. VEGA 2/0119/18.

References
[1] Cvetkov K, Gerasimov V, Kostic I, Koleva E, Vutova K and Asparuhova B 2018 International journal for science, technics and innovations for the industry Machines Technologies Materials MTM year XII 3 124–127
[2] Mladenov G and Vutova K 2002 Computer simulation of exposure and development in electron and ion lithography Proceedings of St.Petersburg Electrotechnical University (Solid State Physics and Electronics) ed B. Kalinikos (SPbGETU LETI St.-Petersburg Russia) 1 pp 133–173
[3] Urbánek M, Kolařík V, Krátký S, Matějka M, Horáček M and Chlumská J 2013 Monte Carlo simulation of proximity effect in e-beam lithography Proc. Int. conf NANOCON 16 (Brno, Czech Republic, EU)
[4] Koleva E and Mladenov G 2005 Vacuum 77(4) 361–370
[5] Ŏrina P, Kostić I, Vutova K, Konečníková A, Benčurová A, Koleva E, Mladenov G, Kůš P and Pleceník A 2017 Journal of Physics: Conference Series 1742-6596 514 012037