Patterning of structures by e-beam lithography and ion etching for gas sensor applications

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Abstract. This work deals with a method of preparation of nanometer structures for a gas detector based on e-beam lithography and ion etching of a thin TiO\textsubscript{2} film. The aim was the fabrication of a gas sensor with meander or comb structures of nanometer dimensions. This is of importance since both the size of the contacts and the layer thickness affect the sensor’s sensitivity.

1. Introduction
In the past decade, the size of the features in ultra-large-scale integration has been continuously decreasing, leading to fabrication of nanostructures. Among all fabrication methods, the resist-based electron-beam lithography seems to be a suitable and flexible technique when preparation of nanostructures is desired, including in the development of sensors. The achievement of sub-100 nm structures using e-beam lithography is a very sensitive process determined by various factors, starting with the choice of a resist material and ending with the development process. The accurate definition of patterned structures is limited mainly by electron scattering, i.e., the well-known proximity effect \cite{1}. To correct pattern distortions caused by electron scattering in the resist/substrate material, estimation of the lithographic parameters is required. The main factor influencing the accurate definition of patterned structures in the resist is backscattering of electrons from the substrate in the case of a low (30 keV) accelerating voltage.

Although electron backscattering can be simulated by the Monte Carlo method \cite{2,3} or analytically \cite{4}, neither of these two methods considers the influence of the development process and equipment-related characteristics; experimental studies are, therefore, important concerning sub-100 nm structures.

2. Experimental
All experiments were conducted using the scanning electron microscope VEGA II SBH (TESCAN) equipped with a control system for nanolithography (TESCAN, Brno, Czech Republic). VEGA II

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SBH is equipped with a thermal emission cathode, the accelerating voltage is in the range of 1 – 30 keV; the minimal probe size can be around 7 nm at a beam current of 10 pA. An accelerating voltage of 30 keV and a working distance of 5 mm were used to achieve the highest resolution. In most experiments, a spot size of 18 nm at a beam current of 40 pA was used due to the lower noise.

The other crucial factor in e-beam nanopatterning is the choice of materials sensitive to electron irradiation. Over the past decades, various types of resist materials have been investigated. Poly(methyl methacrylate) (PMMA) has been most widely used for high resolution e-beam lithography ever since the first report [5]. In brief, PMMA can be used to obtain reproducibly patterns with nm sizes. The resolution can be improved by optimizing various steps of the lithographic process, such as the writing strategy or the development process. The fabrication of very small structures (< 5 nm) utilizing this resist were reported in [6, 7].

Positive resist PMMA A2 (Microchem) with a molecular weight of 950 000 was chosen for nanostructure pattern transfer due to its high resolution, high contrast for EBL exposures, uniform resist coating, long shelf life, and good adhesion to most substrates. A thin layer of PMMA A2 resist with a thickness of 70 nm was prepared by spin coating at 3700 rpm on an Al₂O₃ substrate with a photolithographically pre-patterned platinum layer with a thickness of 20 nm. Subsequently, the resist was baked on a hot plate at 180 °C for 90 s. The exposure was carried out at 30-keV accelerating voltage and 40-pA beam current. After exposure, the resist was developed in MIBK:IPA (1:3) at 23 °C and served as a mask for ion etching of meander structures with sub-100 micrometers dimensions in a Pt layer.

Several exposure tests were performed in view of optimizing the exposure of PMMA A2 on a Pt layer. The contrast and sensitivity test consisted of large rectangles with the exposure doses being varied in the range from 10 μC/cm² to 120 μC/cm². The resist thickness in rectangles at various doses after development was measured using an Alphastep Stylus Profilometer.

The line tests allowed us to monitor the impact of the exposure dose on the linewidth of the exposed structures, to determine the optimal exposure dose needed for precise patterning and to identify the dimension limits of the patterned structures.

To determine the resistance of the PMMA resist to ion etching of the Pt layer, etch rate and etch selectivity tests were conducted. The ion etching was performed by argon ions from a PLATAR (KLAN-53M) ion source with ion energy \( E = 500 \text{ eV} \), ion current \( I = 20 \text{ mA} \), pressure of \( 10^{-2} \text{ Pa} \) and 5 sccm; the etching time was 6.5 min for a 20-nm thick Pt layer.

### 3. Results

The sensitivity and contrast curve is shown in figure 1. The dose-to-clear \( D_0 \) was 100 μC/cm², the contrast value \( \gamma \) being 4. The etch rate of PMMA A2 for etching with Ar ions is shown in figure 2.

![Figure 1.](image1.png) **Figure 1.** The sensitivity and contrast curve of the positive resist PMMA A2.

![Figure 2.](image2.png) **Figure 2.** Etch rate of the positive resist PMMA A2 for ion etching.
The influence of the backscattered electrons in the case of a PMMA A2 positive resist is demonstrated in figure 3. The linewidth in the middle of periodical stripes is significantly narrower compared to that at the borders. In view of performing precise measurements, the stripes were made using the lift-off method in a 20-nm thick Pt layer using a PMMA A2 positive resist. The area of noticeable influence of the backscattered electrons is around 3 µm. The ends of the stripes are narrower by 20% than in the middle.

![Figure 3](image_url)

**Figure 3.** Influence of backscattered electrons on the linewidth of stripe structures; a) the linewidth in the middle of periodical stripes is significantly narrower compared to that at the borders; b) stripes made using the lift-off method with a 20-nm thick Pt layer using a PMMA A2 positive resist.

The proximity effect parameters were simulated for the case of a gas sensor fabrication [8]: the thickness of the PMMA A2 resist and of the thin Pt layer on an Al₂O₃ substrate were 70 nm and 20 nm, respectively. All exposures were performed at 30-keV e-beam energy (point or Gaussian sources). Discrete data for the energy deposition function (EDF) at the interface (at a depth of 70 nm) were obtained by Monte Carlo simulation [2,3] using a point source for 10,000 particles. Analytical approximation of the discrete data obtained for the EDF was performed using a sum of two Gaussians. Afterwards, the proximity effect parameters (βᵣ, βₜ, ηₑ) were determined at the interface for the point e-beam source, and for the Gaussian e-beam with δₑ=18 nm, by Monte Carlo methodology [2].

Results of the Monte Carlo simulation are presented in figure 4; the proximity effect parameters’ data are summarized in table 1. A comparison of the EDF discrete data obtained (•) and its analytical fit (the curve) is shown in figure 4.

A proximity effect correction using these simulated parameters was applied to optimize the stripe and meander structures patterning in view of gas sensor development [8,9]. The minimal linewidth achieved of stripes exposed and developed in a PMMA resist was 77 nm with a space of 173 nm (figure 5a) and a 83-nm PMMA gap with a space of 177 nm at 30-keV electron energy and 18-nm probe size (figure 5b).

![Figure 4](image_url)

**Figure 4.** Comparison between the discrete data obtained (•) and its analytical fit (the curve).
Table 1. Proximity effect parameters’ values.

| Parameter | Point e-beam source | Gaussian e-beam source, \( \delta_b = 18 \text{ nm} \) |
|-----------|---------------------|-------------------------------------------------|
| \( \beta_f \) | 0.4216950000E-01 [\( \mu \text{m} \)] | 0.4585048000E-01 [\( \mu \text{m} \)] |
| \( \beta_b \) | 0.1577453000E+01 [\( \mu \text{m} \)] | 0.1577556000E+01 [\( \mu \text{m} \)] |
| \( \eta_E \) | 0.5816625000E+00 | 0.5816625000E+00 |

Figure 5. a) Stripes with line/space 77 nm/173 nm in a PMMA A2 resist b) Stripes with line/space 167 nm/83 nm in a PMMA A2 resist. Exposure at 30-keV electron energy and 18-nm probe size, thermal emission.

Finally, the optimized e-beam lithography process was applied to fabricating the meander structure needed for the development of gas sensors. Meander structures of various dimension and configurations were etched into a Pt layer on an Al₂O₃ substrate. The platinum layer with a thickness of 20 nm was prepared by magnetron sputtering. Platinum bridge and contacts were prepared using photolithography and the lift-off method. The minimal linewidth of 85 nm achieved using thermal emission is shown in figure 6. The results of the measurements of the gas sensor characteristics were published in [8,9].

4. Conclusions

The limitations of e-beam nanostructure patterning were investigated for a Gaussian e-beam at an electron energy of 30 keV in the case of thermal emission. The influence was evaluated of the backscattered electrons on the accurate definition of patterned structures in an e-beam resist. The proximity parameters (\( \beta_f, \beta_b, \eta_E \)) were simulated for a PMMA A2 positive e-beam resist on a Pt layer with a thickness of 20 nm. The smallest line/space achieved was 77 nm/173 nm.

Figure 6. Meander structure patterned in thin platinum layer by electron beam lithography and ion etching using PMMA A2 (Microchem) positive resist. The channel width in platinum layer was 85 nm. The Pt layer thickness was 20 nm, prepared using magnetron sputtering.
The results of optimizing the e-beam lithography process were applied to the patterning of structures with a minimal linewidth of 85 nm in view of the development of gas sensors.

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References
[1] Parikh M 1980 Proximity effects in electron lithography: magnitude and correction techniques IBM J. Res. Develop. 24 530
[2] Vutova K and Mladenov G 1994 Modeling of exposure and development processes in electron and ion lithography Modelling and Simulation in Mater. Sci. Engin. 2 239-54
[3] Vutova K and Mladenov G 2010 Computer simulation of processes at electron and ion beam lithography Lithography ed M. Wang (Vukovar InTech) part 1 chapter 17 319-50
[4] Raptis I, Glezos N, Valamontes N, Zervas E and Argitis P 2001 Electron beam lithography simulation for high resolution and high density patterns Vacuum 62 263
[5] Haller I, Hatzakis M and Shrinivasan R 1968 High-resolution positive resists for electron-beam exposure IBM J. Res. Develop. 12 251
[6] Wei C and Haroon A 1993 Fabrication of sub-100 nm structures by lift-off and by etching after electron-beam exposure of poly (methylmethacrylate) resist on solid substrates J. Vac. Sci. Technol. B 11 2519
[7] Yasin S, Hasko D G and Ahmed H 2001 Fabrication of <5 nm width lines in polymethylmethacrylate resist using a water:isopropyl alcohol developer and ultrasonically-assisted development Appl. Phys. Lett. 78 2760
[8] Owen G. 1990 Methods for proximity effect correction in electron lithography J. Vac. Sci. Technol. B 8 1889-1892
[9] Durina P, Stefecka M, Roch T, Noskovic J, Trgala M, Pidik A, Kostic I, Konencikova A, Matay L, Kus P and Plecenik A 2010 Patterning of nanometer structures by using direct-write e-beam lithography for the sensor development ASDAM 2010 Proc. 8th Int. Conf. Advanced Semiconductor Devices and Microsystems eds J. Breza, D. Donoval, E. Vavrinsky (Piscataway: IEEE) 89-92
[10] Durina P 2012 Thesis FMFI UK Bratislava