# [2] Some peculiarities of a new method of microrelief creation by the direct electron-beam etching of resist

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## Abstract

We discuss new results concerning the mechanism, characteristics and application potentialities of a novel method that allows an image to be generated in some positive resists directly during exposure by an electron beam in vacuum. In particular, using the PMMA resist as an example, we show that this method is very convenient for obtaining micro– and nano-reliefs with a rounded cross-section profile. Examples are given of obtaining 3D-structures with good accuracy of image vertical size and low surface roughness. In the authors opinion, the data presented show, on the whole, that the suggested method has application potentialities for the manufacture of diffractive optical elements.

**Keywords:** *electron-beam lithography, new dry method of microrelief creation, optoelectronics, diffractive optical elements, 3D-structures.*

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## Introduction

Methods of photo and electron-beam lithography are now used for the manufacture of diffractive optical elements (DOE) [1-4]. Therefore in order to form images of micron and submicron masks or reliefs the traditional technology of electron-beam lithography (EB lithography) is usually used which involvesexposure by the electron beam in vacuum at a room temperature of polymer resist layer on a solid substrate, and a subsequent non-vacuum stage of image development related to sample processing with lots of organic solvents (see, for example [5]). We will further call it a "wet" technology. The main advantage of the wet technology of electron– beam lithography in applying high-resolution positive resists (polymethylmethacrylate – PMMA, ZEP, etc.) is a possibility to obtain a high-resolution lateral image (approximately 10-20 nm). Main disadvantages of this method as a process of manufacture of diffractive optical elements are as follows: 1) necessity of large exposure doses resulting in relatively lower throughput of the lithography process and its high cost; 2) relative complication for obtaining relief structures with a rounded (spherical, aspherical, sinusoidal, etc.) profile cross-section; 3) relatively low accuracy of vertical sizes (Z-axis) of a resulting 3D-image [6]. The authors of this paper have proposed [7, 8] a new "dry" method of the image formation in some positive resists directly during exposure by the electron beam in vacuum (DEBER – dry electron-beam etching of resist). The method is based on the electron-stimulated chain depolymerization reaction in polymer resist during exposure at temperatures close to a glass transition temperature (or at higher temperatures) with release of volatile products (monomer) removed from resist directly during exposure. The method may be applied to resists capable under the above conditions to efficient monomer depolymerization (PMMA, other polymethacrylates, poly-a-methylstyrene, polymethylisopropenylketone, etc.). The dry electron-beam etching of resist method (DEBER) enables to increase sensitivity of PMMA resist approximately 10–300 times

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in electron-beam lithography process compared with the wet technology of EB lithography. The method also permits to form 3D-structures with good accuracy of vertical sizes (approximately 2 nm) and with lowsurface roughness (up to 1 nm) that is substantially better than when applying the wet method. Disadvantagesof the DEBER method are lowlateral resolution (approximately 100–150 nm) and lower image contrast (0.7–1.5). When solvingproblems with not-too-high requirements to theseparameters, it appears that this method can presentconsiderable practical interest.

For PMMA resist as an example this paper presentssome new results concerning the mechanism, characteristicsand feasibility of the DEBER method. Ithas been shown in particular that this method isvery convenient for obtaining relief micro and nanostructureswith a well-rounded profile includingspherical (aspherical) and sinusoidal ones,which may be used for the manufacture of variouskinds of diffractive optical elements (DOE).

## 1. The experiment

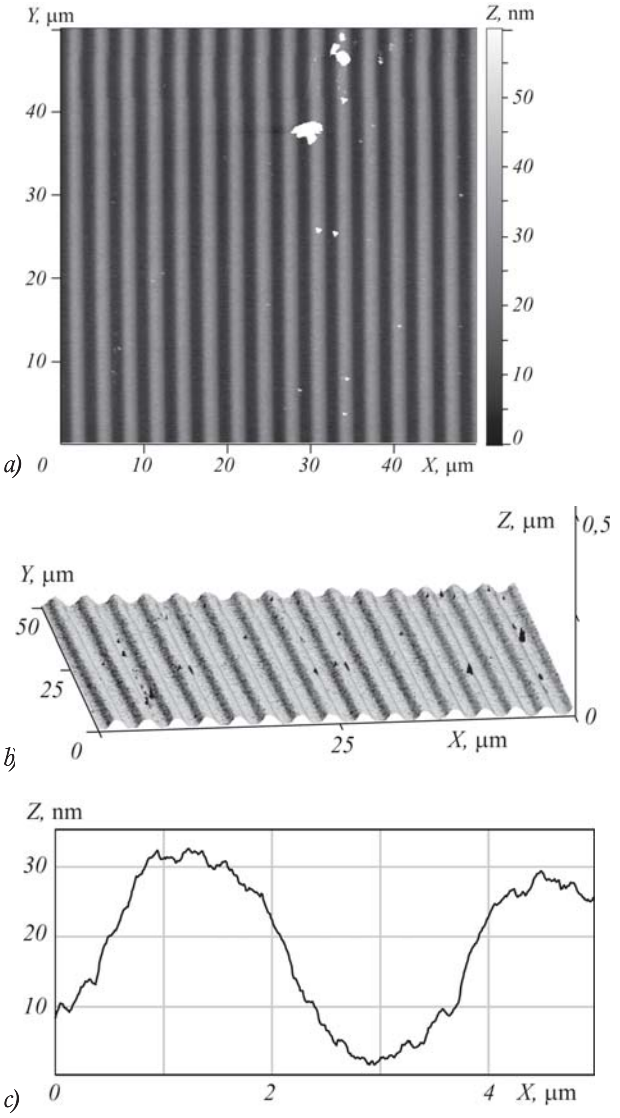
Commercial positive resist 950K PMMA was applied to a silicon wafer using the spin-coating method followed by drying. The resist layer thickness $L_o$ was from 50 to 1000 nm. The obtained sample was placed on a special heater, introduced into a chamber of a scanning electron microscope (SEM) Camscan S4 or Ultra-55, heated to the required temperature, and in vacuum of approximately $10^{-5}$ –$10^{-6}$ mbar it was exposed by electron beam at multiple area-scanning (“in-frame”) or longwise scanning. The image in resist was formed directly during exposure. E-beam cross-section was approximately 0.2 μm in Camscan SEM and 10–15 nm in Ultra SEM.

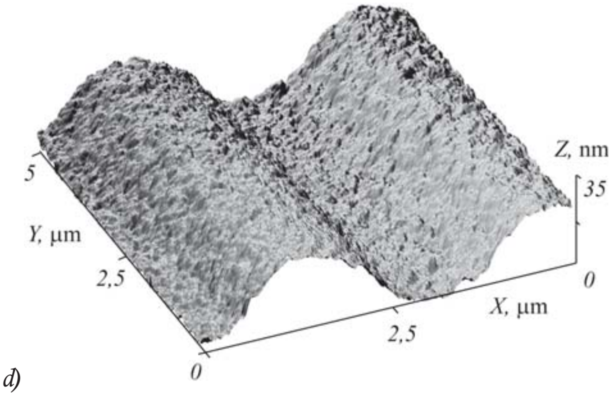
Experiments on formation of a “step-like” 3D-image were carried out in manual mode as follows: several exposures were subsequently performed on a resist plate heated up to the desired temperature at constant positions of the beam and the plate during scanning in various subsequently decreasing areas. Relationships of linear dimensions of scanning areas defined a step width formed on the edge of the exposed area. We did not try to set up a problem of obtaining strictly the same step widths and heights during our experiments. Irradiation doses at each exposure stage were calculated in accordance with a characteristic (contrast) etching curve.

The thickness of resist layer before and after etching as well as a shape of obtained etching figures were defined by atomic force microscope (AFM) Veeco Multimode 8 with Nanoscope V controller in semi-contact mode using a silicon cantilever with the tip radius of 8 nm.

## 2. Results and discussion

As mentioned above, the DEBER method is very convenient for obtaining micro and nanostructures with a well-rounded profile. Some examples of this type of structures are given in Fig. 1–4. Fig. 1 shows in particular an continuous structure with a well-rounded relief and a close-to-sinusoidal profile obtained directly during exposure. Fig. 2 shows a structure with divided lines. Fig. 3 shows reliefs with different thickness from 190 to 910 nm obtained in resist coating with the initial thickness of about 900 nm. The figure shows in particular how the relief cross-section shape can be changed by changing the trench depth. Attention should be paid to very low exposure doses (0.1-2 mcCoul/cm²) and rather large frame size (3×3.9 mm) that should basically ensure high process efficiency for the manufacture of such structures.





d)

*Fig. 1. The continuous structure with the rounded relief and thes inusoidal cross-section profile. “Inframe” exposure at 125°C in Camscan SEM.*
*Frame size is2×2.6 mm. Electron energy E = 20 keV.*
*The initial thickness ofresist layer $L_0$ = 80 nm. Theby-frame averaged dose is 0.5 $\mu C/cm^2$. a – the topography,b and d – the 3D-image,*
*c – the cross-section profile*

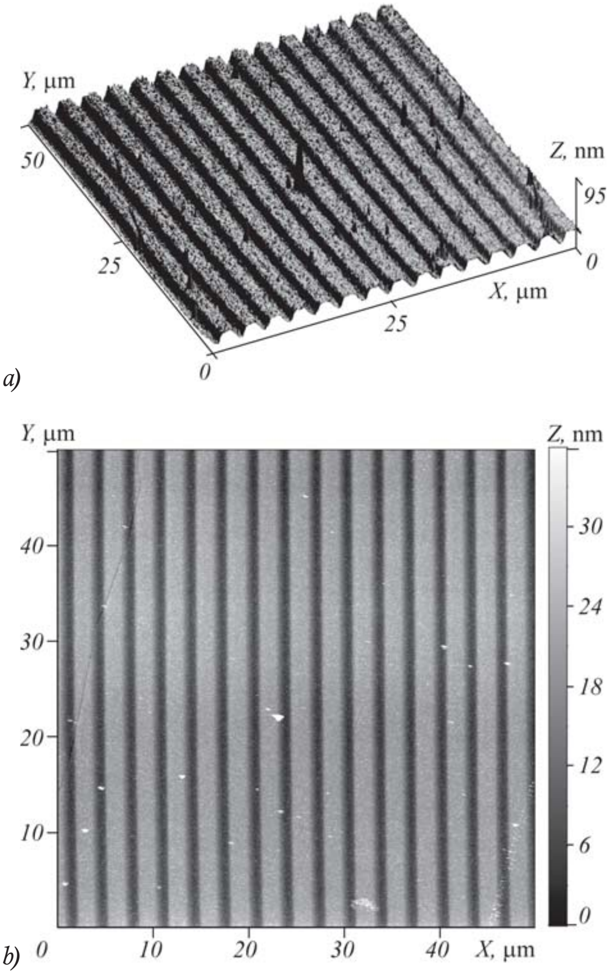
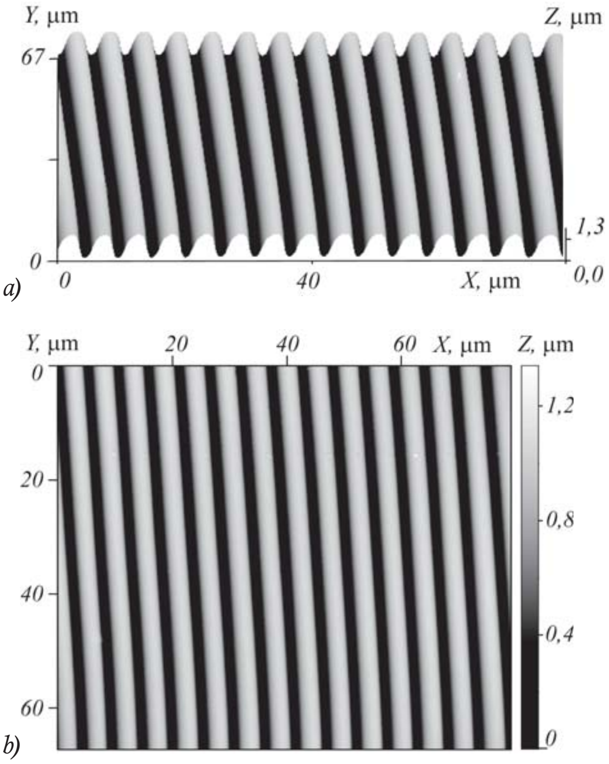


*Fig. 2. The structure with divided lines. The by-frame averaged dose is 0.1$\mu C/cm^2$. Other conditions are the same as in Fig.1.a – the 3D-image, b – the topography.*

Fig. 4 shows the results obtained during exposure in the Ultra-55 system. It is in particular obvious that the line width of the obtained image is much less than during exposure by Camscan SEM that should be associated with a significantly smaller cross-section of the electron beam.

We believe that by selection of conditions to perform dry electron-beam etching of resist (electron-beam parameters, exposure area, resist layer thickness, exposure temperature, etching depth, etc.) well-rounded relief structures of any shape could be obtained. It must be emphasized that the formation of such rounded structures results from a specific shape of kinetic etching curves typical for the DEBER method. This shape (Fig.5a, [8]) enormously differs from the shape of respective curves in the “wet” EB lithography technology (Fig.5b, [9]). These differences could be explained by completely different mechanisms of the image formation in each of the considered methods.

It is known [5] that the image is formed in the “wet” EB lithography due to dissolution rate inequality of exposed and unexposed resist areas caused by destruction (for positive resists) or cross-linking (for negative resists) of resist macromolecules.



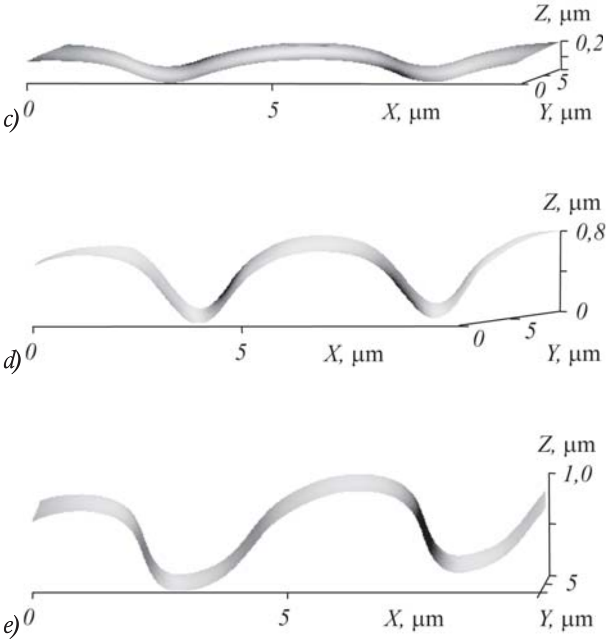


*Fig. 3. The reliefs obtained in resist layer with the initial thickness of about 900 nm. Frame size is 3×3.9 mm. E = 20 keV.a – the relief 3D-image 910 nm in depth, b – the relief topography, c, d, e – the relief profiles of 190, 700 and 910 nm in depth, respectively; exposure doses 0.12, 0.48 and 2.04 μC/cm2, respectively.*

In DEBER during exposure of samples at temperatures higher than the resist glass transition point (for PMMA it is 100°C) in exposed samples, there proceeds the electron-stimulated chain chemical depolymerization reaction accompanied by evolving a large number of monomer molecules being removed from the resist during exposure. The approximate depolymerization mechanism is as follows [10]: during exposure there occurs breaking of polymer resist molecules followed by the formation of macroradicals capable to remove monomer molecules one-by-one at high temperatures by "zipper" mechanism. The in-depth image formation (etching trenches or pits) can therefore be determined by occurrence of an additional free volume in the polymer exposed area resulting from removal of volatile products (monomer) from the polymer and polymer volume relaxation (shrinkage) caused thereby under the action of tension forces, which proceeds quickly enough if compared with the experiment time.

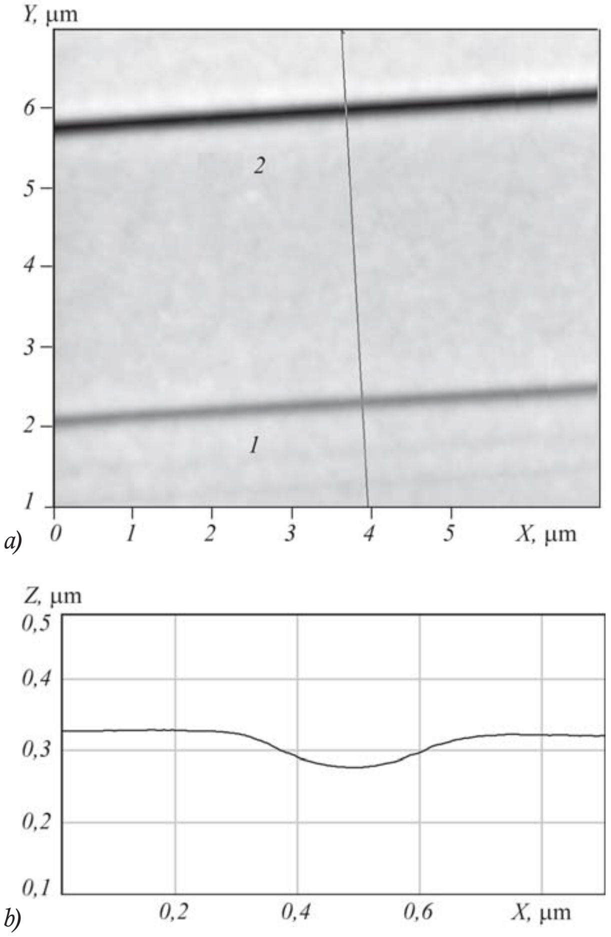


*Fig. 4. Drawing of lines obtained using the DEBER method by means of Ultra-55 SEM at 116°C. Exposure time 1 s (line 1) and 4 s (line 2). The initial thickness of resist coating is 80 nm. a– the topography, б – the cross-section profile of line 2 in real scale (identical both in X and Z directions).*

In the wet EB lithography technology during PMMA exposure performed at the room temperature, there is also the break of resist macromolecules influenced by e-beam exposure followed by the formation of macroradicals. However these macroradicals are practically not capable to remove monomer molecules, since in order to implement this process some additional energy, the so-called "activation energy" is needed for which the room temperature is too low. Thus irradiation effect is reduced to decrease the molecular weight of the resist polymer that shall cause the accelerated resist dissolution in irradiated areas during subsequent wet etching.

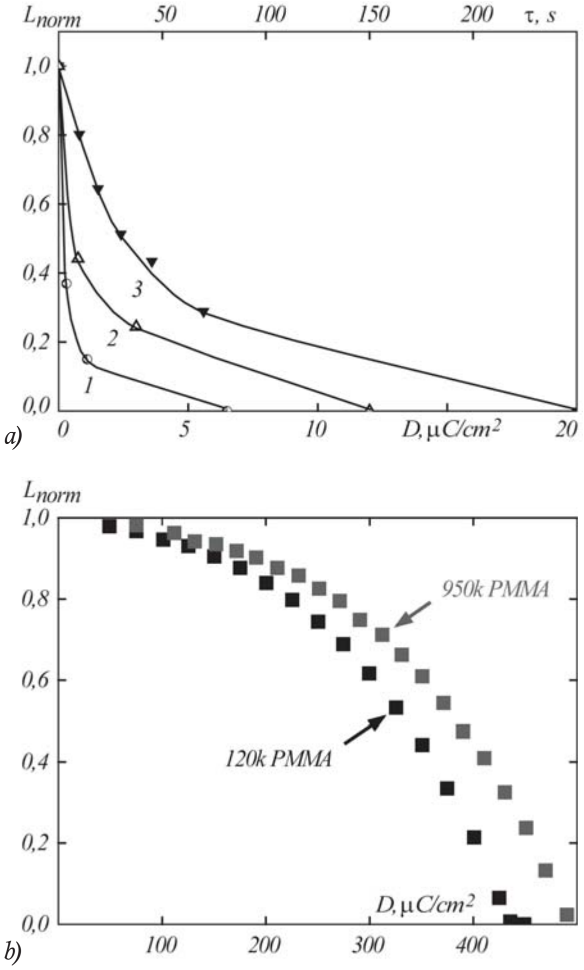


*Fig. 5. Normalized "layer thickness - dose" curves when forming PMMA resist image using the dry electron-beam etching of resist (a) and the wet method (b). Fundamental differences in curve shapes are illustrating the differences in image-forming mechanisms. The curves 1, 2 and 3 in Fig.5a have been obtained at exposure temperatures of 170, 150 and 125°C, respectively. Fig.5a and 5b have been taken from papers [8] and [9], respectively*

In DEBER during the sample exposure, when the electron stopping length in the resist Le is much higher than the initial layer thickness Lo( if the electron energy is 10 keV and more, this condition is mostly filled), the etching process is simultaneously performed throughout the resist layer . Some data have been obtained from which it was concluded that for small initial thicknesses of resist layer Lo (up to 100–150 nm) the etching rate is approximately the same throughout the layer thickness. Otherwise speaking, diffusion of the gas-phase evolved monomer proceeds rather quickly across the whole layer thickness, and it does not limit the etching rate. Accordingly, the etching rate is proportional to the current resist layer thickness and can be decreased as the process progressed with the decrease of this thickness that defines in particular the specific shape of kinetic etching curves in Fig. 5a.

The shape of kinetic etching curves also determines the dependence of the line width on the etching depth. The lines are broadened with depth increase.

As mentioned above, the DEBER method is characterized by rather high energetic efficiency of the etching process. It could be explained by a chain-type depolymerization reaction of etching, in accordance with which the formation of an active centre (a macroradical), which requires irradiation energy to be spent, will cause spontaneous removal of hundreds and thousands of molecules flying into a gas phase from the macroradical. As applied to PMMA resist, this mechanism enables to improve resist sensitivity in EB lithography approximately 10–300 times compared to the wet technology. This opens possibilities to considerably increase throughput of the lithography process and to decrease its cost.

In this work a problem of influence of the resist layer thickness Lo (under otherwise equal conditions) on the etching rate has been reviewed. It has been established that when Lo is less than 100–150 nm, the initial etching rate in absolute units is proportional to Lo. This proportion is violated in large layer thicknesses. Fig. 6 shows that when Lo = 340 nm, the initial etching rate in absolute units is 1.5–2 times greater, whereas on a per-unit basis (in a fraction of the initial thickness) it is 2–2.5 times less than the initial rate when Lo = 80 nm. These data seem to indicate that in the coating 340 nm thick during the etching process there occur substantial diffusion delays in monomer removal from deep layers of a resist film that slows down the whole etching process (if there were no such diffusion delays, the absolute etching rate at 340 nm should be approximately four times higher than when Lo = 80 nm).

As noted above, the DEBER method is also very convenient for obtaining 3D-structures. Some examples of such staircase-type structures are shown in Fig. 7 and 8. A set of obtained data allows us to conclude that the DEBER method enables to form 3D-structures with very high vertical resolution (about 2 nm) and low surface roughness (about 1 nm) that is substantially better than when using the wet method [6].

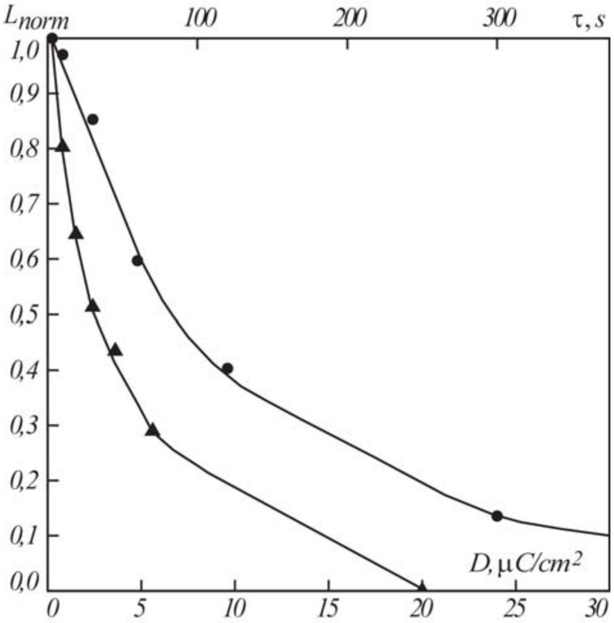


Fig. 6. Normalized “layer thickness – dose” curves in the process of etching PMMA resist coatings using the DEBER method with a different initial thickness layers $L_o$ = 80 nm (the lower curve) and 340 nm (the upper curve). The exposure temperature is 125°C.

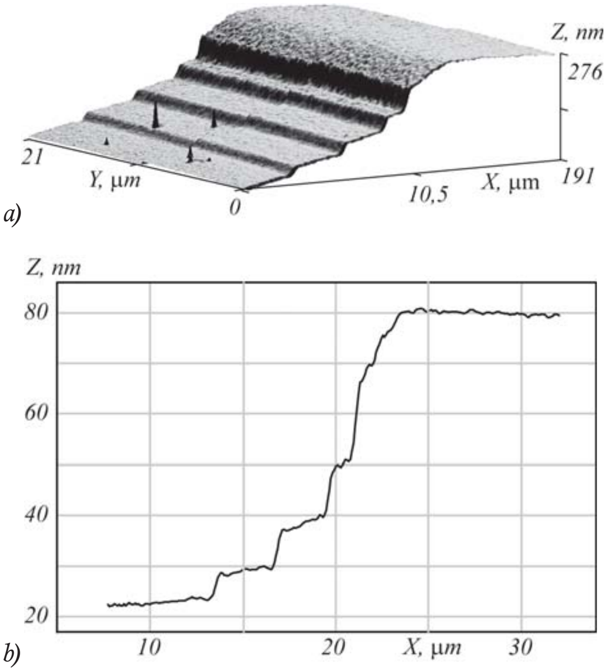


Fig. 7. The image of the ladder-type structure obtained using the DEBER method by means of Ultra-55 SEM at 125°C and $L_o$ = 80 nm. a – the 3D-image, b – the cross-section profile.

## Conclusion

It could be concluded that the DEBER method has a great potential in some applications. For example the method could be used for the manufacture of components of optoelectronics products (diffraction gratings, microlens and their sets, focusers, optical waveguides, etc.). Micro and nanostructures in resists obtained by the proposed method may be used either directly as target products made of the resist material, or as a mask to transfer the relief into the substrate material and obtain products made of this material, or as a preform to produce replicas, stamps and matrices. Typical dimensions of the structure elements obtained in resists are approximately 0.005-2 μm in vertical direction and 0.2-10 μm in lateral plane. When transferring images on the substrate, in some cases there is a fundamental possibility of a significant increase (up to 5-10 times) in vertical sizes of elements.

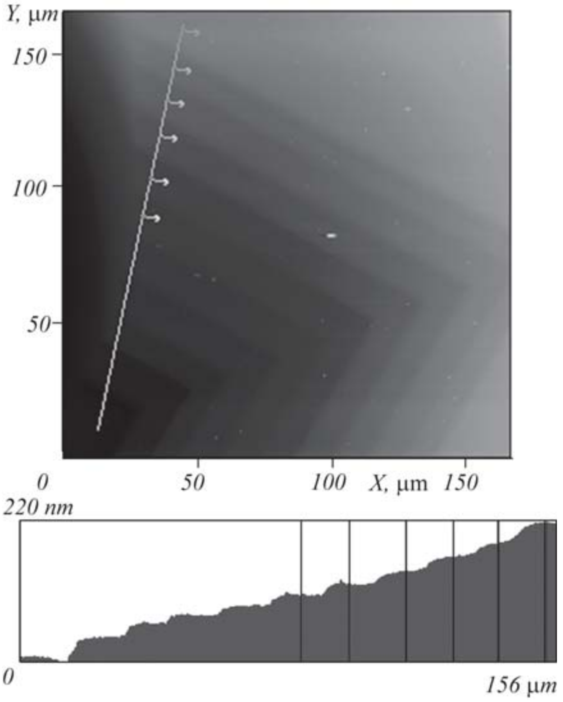


Fig. 8. The image of the 10-step-ladder-type structure obtained using the DEBER method by means of Camscan SEM at 125°C and $L_o$ = 340 nm

To perform dry electron-beam etching of resist we may use conventional electron-beam lithographers or electron microscopes equipped with some additional options such as, particularly, a sample-heating attachment to be used during exposure.

Please also note that additional research is necessary for practical implementation of the suggested by the authors new method of EB lithography.

## References

**1.** Gavrilov, A.V., Golovashkin, D.L., Doskolovich, L.L., Dyachenko, P.N., Kovalev, A.A., Kotlyar, V.V., Nalimov, A.G., Nesterenko, D.V., Pavelyev, V.S., Skidanov, R.V., Soifer, V.A., Khonina, S.N., Shuyupova, Y.O. Diffractive Nanophotonics. BocaRaton (USA): CRC Press, 2014; 704 P. Chapters 8.7.1, 8.7.2.

**2.** Di Fabrizio, E., Grella, L., Baciocchi, M., Gentili, M. Fabrication of Diffractive Optical Elements by Electron Beam Lithography. In Book “Diffractive Optics and Optical Microsystems”. Ed. S. Martellucci, Arthur N. Chester. Plenum Press, New York, 1997; P. 149-160.

**3.** Volkov, A.V., Skidanov, R.V. The formation of DOE microrelief using the achievements in microelectronics. Computer Optics, 2001; 22: 65-71. (in Russian).

**4.** Nesterenko, D.V., Poletaev, S.D., Moiseev, O.Y., Yakunenkova, D.M., Volkov, A.V., Skidanov, R.V. The fabrication of the curved diffraction gratings for UV. Izvestiya SNC RAS, 2011; 13 (4): 66-71. (in Russian).

**5.** Valiev, K.A. The Physics of Submicron Lithography. Plenum Press, New York, 1992; pp. 493.

**6.** Murali, R. Metrology for Grayscale Lithography. AIP Conf. Proc., 2007; 931: 419-422.

**7.** Bruk, M.A., Zhikharev, E.N., Kalnov, V.A., Spirin, A.V., Streltsov, D.R. Method of forming masking image in positive electron resists. Patent RF of Invention N2478226 of September 06, 2011, Russian Bulletin of Inventions N9, 2013. (in Russian).

**8.** Bruk, M.A., Zhikharev, E.N., Streltsov, D.R., Kalnov, V.A., Spirin, A.V. The new dry method of mask (relief) formation by direct electron-beam etching of resist. Microelectronic Engineering, 2013; 112: 1-4.

**9.** Schleunitz, A., Spreu, Ch., Vogler, M., Atasoy, H., Schift, H. Combining nanoimprint lithography and a molecular weight selective thermal reflow for the generation of mixed 3D structures. J. Vac. Sci. Technol. B, 2011; 29: 06FC01.

**10.** Bruk, M.A., Kondrat’eva, M.V., Baranov, A.A., Pebalk, K.V., Sergeev, A.M., Kozlova, N.V. Radiation-Induced Depolymerization of PMMA Adsorbed on Silochrome. Polymer science. Series A, 1999; 41 (2): 159-164.