Resolution limits of the dry e-beam etching of resist for nanophotonic structure formation

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Abstract

Micro- and nanostructures formation of special well-rounded shape using an e-beam lithography is a huge task. Usually stair-like profile is used instead that complicates the process immensely. The problem can be solved using the dry method of relief formation in some positive resists during electron-beam exposure in vacuum (DEBER method). DEBER method can be used for formation of wide range of structures for nanophotonics and optoelectronics. The structures obtained by the method are presented. Resolution limits of the method are analyzed and the approaches to resolution enhancement are discussed.

Keywords: DEBER; lithography; e-beam etching; nanophotonics; diffractive optical elements

1. Introduction

Dry electron beam etching of resist (DEBER) proposed by Bruk et. al. [1, 2] could be used for formation of wide range of optoelectronic and photonic structures. The method is based on the chain depolymerization reaction, which takes place in the polymer resists during e-beam exposure at the glass-transition or higher temperatures. The volatile reaction products (monomers) are pumped out during exposure. The method provides quite simple way for formation of well-rounded or 3D structures. In some cases it could be much more flexible than usual methods, in others it could be more productive or convenient.

In this paper structures of diffraction or binary gratings, some diffractive optical elements (DOE), 3D structures or planar photonic crystals obtained by DEBER method are presented. It is difficult to use DEBER method for nanophotonic structure fabrication due to low lateral resolution. It is not clear which physical mechanism leads to the lateral resolution limitation. In the paper different mechanisms that could lead to the broadening of the trenches are analyzed. Also some possible approaches to the resolution enhancement are discussed.

2. Dry e-beam etching of resist

The DEBER method is based on the chain depolymerization reaction which takes place in the polymer resists during e-beam exposure at the glass-transition or higher temperatures. Volatile reaction products (monomers) are pumped out during exposure (fig. 1). Various resists that could be effectively decomposed to monomer under these conditions can be used in the method (poly(methyl methacrylate), poly-α-methylstyrene, polymethyl isopropenyl ketone etc.).

In the DEBER method at a temperature higher than glass-transition temperatures e-beam stimulated chain depolymerization reaction takes place. In this process polymer bonds are broken during e-beam exposure. As a result molecules of terminal macroradicals are formed. These macroradicals at increased temperatures split off monomer molecules one by one with “zipper” mechanism [2, 3]. Lots of monomer molecules are evacuated during exposure. The process is faster at higher temperatures. The relief (trenches or holes) formation is defined by appearance in the exposed region free space due to evacuation of volatile monomers and polymer relaxation as affected by surface tension. Well-rounded shape of the structures is determined by a specific form of the etching kinetic curves (fig. 2) of DEBER method [4]. Similar phenomena was observed in PMMA during ion beam irradiation [5] and UV radiation [6].

PMMA sensitivity to e-beam in the DEBER method is about 100 times higher than that in the standard “wet” e-beam lithography process. Because of high vertical resolution (about 1 nm) the method could be used for high-precision 3D structuring. On the other hand DEBER lateral resolution (about 100 nm) and contrast (0.7 – 1.5) are rather low.

DEBER process could be implemented in some scanning electron microscopes (SEM), e-beam lithography or focused e-beam induced process (FEBIP) systems. Most of the systems require minor modifications for it. It is possible to transfer relief after DEBER process from the resist to the silicon or fused silica substrate or to the metal mask [4].

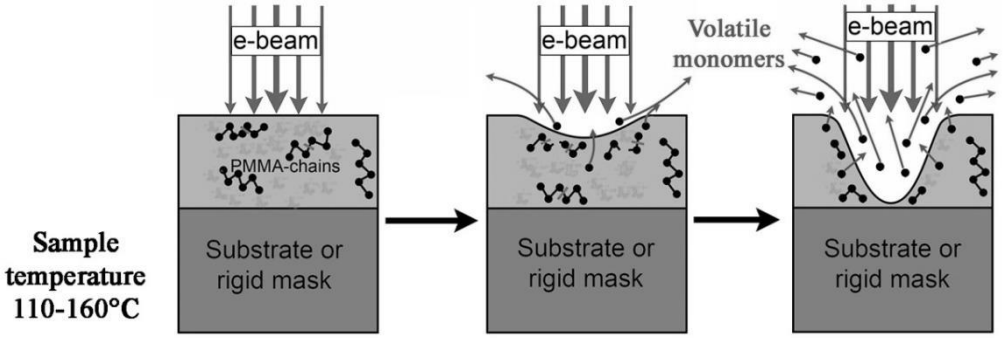

Fig. 1. Dry e-beam etching of resist process scheme.

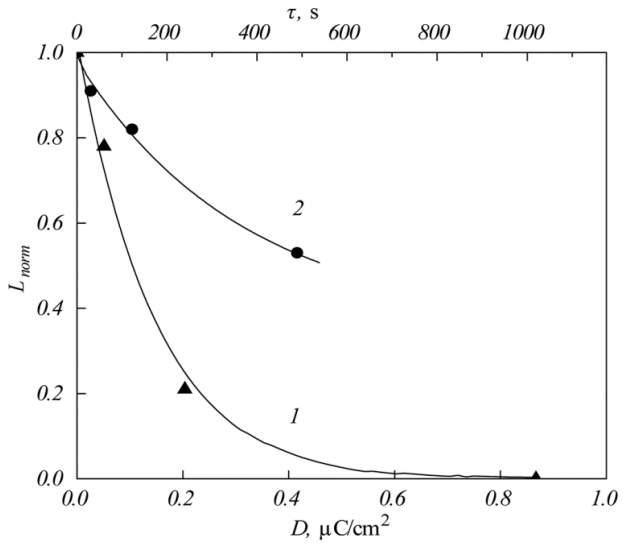

Fig. 2. DEBER kinetic curves for PMMA: normalized "etching depth vs. exposure dose" dependence; initial PMMA thickness are 900 nm (curve *1*) and 340 nm (curve *2*); exposure in Camscan S4 system at 160°C.

3. Optoelectronic and photonic structures obtained by DEBER method

DEBER method could be effective for the formation of diffraction or binary gratings, some diffractive optical elements (DOE), 3D structures or planar photonic crystals [7].

Simple gratings obtained by DEBER method are quite similar to holographic gratings (fig. 3(a)). They also have sinusoidal shape and limited efficiency. Throughput for DEBER method is lower than ruling or holographic method but it is high enough for small gratings production. DEBER exposure time of 3x3.9 mm^2 is about 10-100 s (exposure dose 0.1-1 $\mu C/cm^2$). DEBER method is extremely accurate due to e-beam system exploitation. Moreover the shape of the grating produced by DEBER method could be modified. The shape of the grooves could be skewed, for example. Also complex grating like binary gratings could be produced by DEBER method if e-beam lithography or FEBIP system is used. Large set of positive resists could be used with DEBER method.

Diffractive optical elements (DOE) contain staircase structures. Formation of staircase structures by DEBER process is quite simple (fig. 3(b)). The technique is similar to grayscale e-beam lithography. But due to specific etching mechanism vertical resolution of the DEBER method is 1-2 nm. DEBER is a one-step process and misalignment also does not take place for the method. The method also is comparatively high-productive.

Drawbacks of DEBER method here are edge rounding and low lateral resolution. Edge rounding leads to insignificant efficiency decrease [8]. It appears that if the DEBER method is implemented in the modern e-beam lithography or FEBIP system lateral resolution will be enough for DOE fabrication.

DEBER method could be used not just for simple diffraction grating formation but also for formation of complex binary gratings or planar photonic crystals (fig. 4). In this case DEBER works like standard e-beam lithography with limited lateral resolution. On the other hand it seems that edge rounding could somewhat decrease efficiency of these structures.

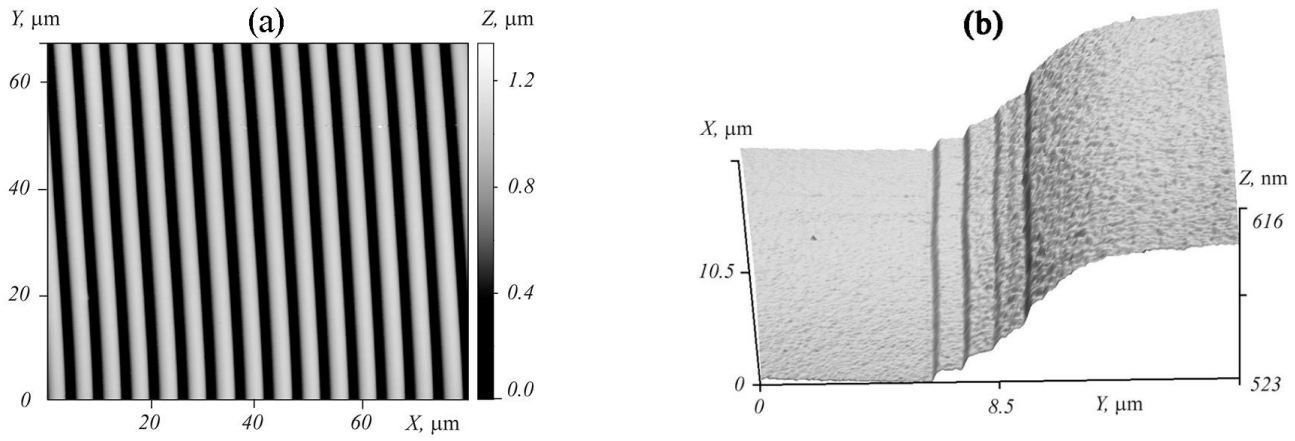

Fig. 3. AFM images of the (a) diffraction grating and (b) staircase structure obtained by DEBER method.

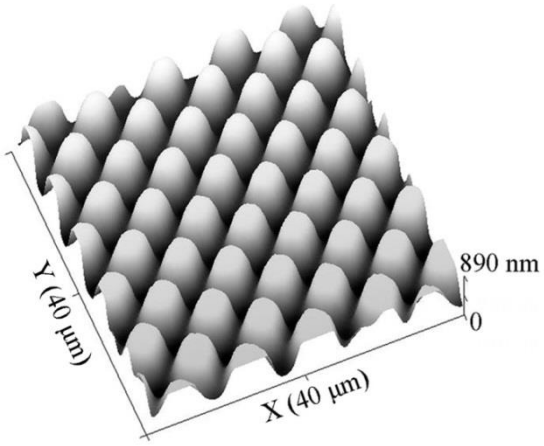

Fig. 4. 3D AFM image of structure obtained by DEBER method during exposure of two sets of lines.

4. Origins of the DEBER resolution limit

It is difficult to use DEBER method for nanostructure fabrication due to low lateral resolution. It is not clear which physical mechanism leads to the lateral resolution limitation. We used two scanning electron microscopes in our study: Camscan S4 with 200 nm e-beam diameter and Zeiss Ultra-55 with 10 nm e-beam diameter. Dry e-beam etching of PMMA in the first system provided 2000 nm wide trenches. In the second system 200 nm wide trenches were obtained at the same process parameters.

There are several possible mechanisms of the line broadening. We split them into four groups: products of the e-beam interaction events; chemical mechanisms; mechanical processes and thermal mechanisms.

4.1. Products of the e-beam interaction events

In this group we placed e-beam scattering and particle generation due to scattering events. In the DEBER process the sensitivity of the resist at low doses is extremely high. As a result tails of the electron distributions could play essential role into the broadening of the line.

Four different types of events of the interaction between primary electrons and the matter can be separated [9]. They are elastic scattering and three types of inelastic scattering - generation of secondary electrons, plasmons or excitation (which lead to generation of high energy photons or Auger electrons). These events determine the ways of energy transfer from fast electrons to the photoresist. It should be mentioned that the contribution of plasmon generation mechanism to the electron energy loss is very high but plasmon appearance results only in the heat generation but not any molecular transitions.

Because of elastic scattering of the primary electrons fast electrons can find way to the distant regions of the resist layer. We calculated primary electron trajectories using CASINO program [10] in the PMMA/Si structures (fig. 5) and found that primary electrons can be easily found in 6 μm wide region around the position of e-beam. In the DEBER process resist is extremely sensitive to low doses (it can be seen from the fig. 2) and energy of electrons can be as low as 10 eV. Potentially elastic scattering could lead to the lines broadening. But elastic scattering cannot be the reason of the trench width difference for 15 nm and 200 nm wide e-beams.

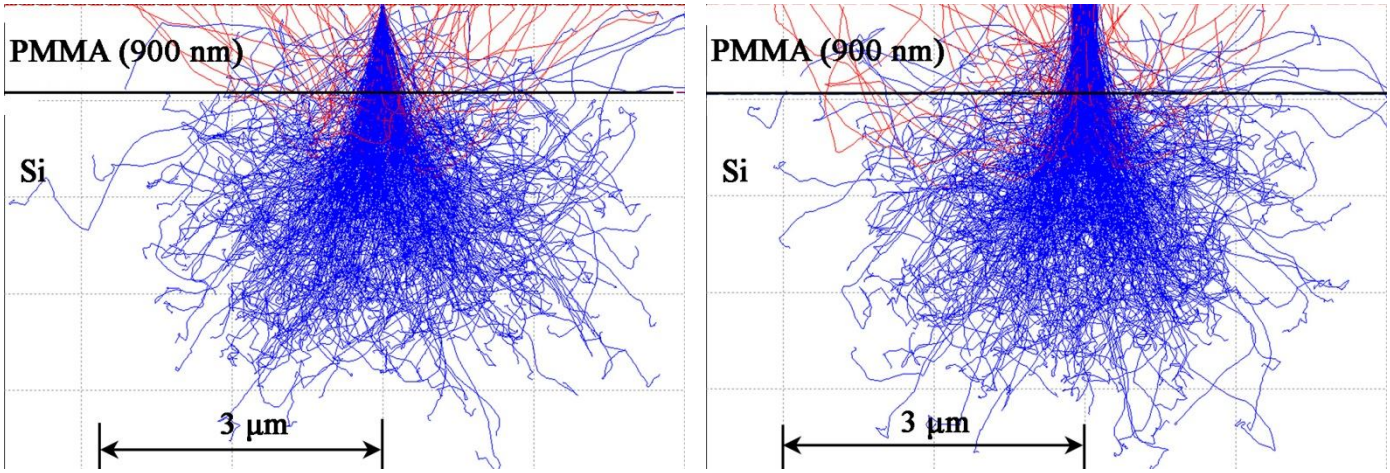

Fig. 5. Trajectories of 500 electrons during e-beam irradiation of the PMMA (900 nm)/Si structure calculated in the CASINO program. E-beam diameters are 15 nm (left) and 200 nm (right). Electron energy is 20 keV.

The secondary electrons have the largest contribution to the distribution of electron energy deposition in the photoresist [9]. To carefully analyze the contribution of the secondary electrons in the line broadening their distributions should be calculated. It is not a simple task and it requires lots of time. In this work we only estimated it using data from the literature. Energy distribution of secondary electrons is somehow described in [11, 12]. The mean energy of "fast" secondary electrons (energy higher than 100 eV) is about 400 eV for primary electron energy of 20 keV [13]. It seems that the amount of secondary electrons with energy higher than 1 keV is negligible. So in the worst case the generation of secondary electrons can results in 30-40 nm broadening of trench.

Estimation of the contribution of high energy photons into trench broadening is a large task. The lowest possible wavelength of characteristic radiation for 20 keV e-beam is about 0.06 nm. The peak of intensity is somewhere between 0.09 and 0.12 nm. PMMA absorption of this radiation is very low (fig. 6). On the other hand characteristic radiation with wavelength of 2-8 nm (corresponds to energy of secondary electrons) could provide trench broadening observed in the experiments. In any case influence of the characteristic radiation should be accurately calculated. Doping of the PMMA could soften the characteristic radiation influence.

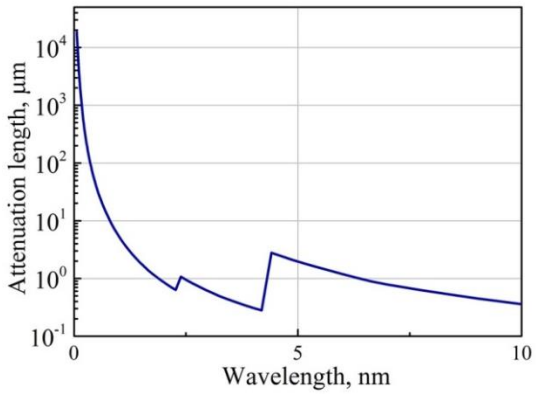

Fig. 6. Attenuation length of X-ray in PMMA vs. wavelength (data from [13]).

4.2. Chemical mechanisms

The second group of processes contains different chemical mechanisms. Two most probable are chain transfer and diffusion of the reaction products along the resist layer.

Chain transfer is the chemical reaction leading to transfer of the depolymerization process from one PMMA chain to another. Usually the process takes place by hydrogen abstraction [7]. In this case interacting chains should not be far from each other. It appears that the distance between them should be less than 1-5 nm. If the size of PMMA chain is about 15-20 nm (for 950K PMMA), 40-50 chain transfer processes are required for 1 μm trench broadening. It appears that the probability of this event is not high enough.

The diffusion of the reaction products can also spread depolymerization process in the distant regions of PMMA. Some products are too heavy for the diffusion (for example, long chain parts and large radicals) but monomer molecules and short

chain fragments could be mobile enough. In concert with chain transfer diffusion could provide substantial trench broadening. These mechanism requires detailed analysis and calculations.

Polymer chemistry is rather complex and embarrassed. It is possible that there are some other chemical mechanisms of depolymerization spreading. Additional experiments and chemical analysis are necessary for understanding of these mechanisms.

Chemical mechanisms could be partially blocked by use of PMMA with lower molecular weight. Also the process parameters like temperature play significant role in chemical mechanisms.

4.3. Mechanical processes

In this group there is a phenomenon connected with low viscosity of PMMA at the process temperatures. At the temperature higher than glass transition one the viscosity of the polymer drops dramatically. This process makes outdiffusion of monomer possible. So it is important for the DEBER process. On the other hand at these temperatures liquidity can lead to redistribution of the PMMA and as a result trench broadening. Some additional experiments are required to analyze this phenomenon. Lowering of temperature could soften the influence of the resist liquidity. It seems that the process of the resist redistribution is quite slow. So it is not very important for short processes.

4.4. Thermal mechanisms

Thermal mechanism is connected with possible lack of temperature uniformity in PMMA and warming up of the sample during exposure. It is not clear if this mechanism is important. Additional research is required.

5. Conclusion

DEBER method could be used for formation of wide range of optoelectronic and photonic structures. In this paper structures of diffraction or binary gratings, some diffractive optical elements (DOE), 3D structures or planar photonic crystals obtained by DEBER method are presented.

It is difficult to use DEBER method for nanophotonic structure fabrication due to low lateral resolution. It is not clear which physical mechanism leads to the lateral resolution limitation. In the paper different mechanisms that could lead to the broadening of the trenches are analyzed. Possible influence of e-beam scattering, generation of secondary electrons and high energy phonos, chemical mechanisms and fluidity of PMMA are discussed. Some possible approaches to the resolution enhancement are suggested.

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