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The new dry method of mask (relief) formation by direct electron-beam etching of resist

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ABSTRACT

The new method of mask or relief formation by the direct electron-beam etching of some type of the positive resists is proposed. It is shown that the exposure of PMMA resist (layer thickness of about 80–85 nm on the Si-wafer) by electrons with an energy of 20 keV in a vacuum at temperatures above the glass transition temperature of PMMA leads to efficient resist etching with the rates which are approximately 10–100 times larger than in the traditional "wet" electron-beam lithography process with the same resist. The mechanism of such etching probably is the radical-chain depolymerization of PMMA resist to the monomer molecules. The high efficiency of the proposed method for the formation the spatial 3D-structures in PMMA resist is established.

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1. Introduction

In the early 80s of the last century the idea of the direct resist etching for the lithographic process was formulated. It's combined the resist exposure and the image development into one stage. However the proposed approaches [1–4] were not sufficiently effective and did not receive the further development later. In this paper we suggest the method of mask or any other relief formation in some type of the positive resists by their direct etching during electron beam exposure. This method is based on the reaction of electron-stimulated depolymerization of the polymer resist to the monomer. Further in this paper we call this process as DEBER method (method of "dry electron-beam etching of resist"). The results of direct etching of poly(methylmethacrylate) (PMMA) are generally discussed in this paper and the data concerning poly(α-methylstyrene) (P-α-MS) etching are presented briefly.

2. Experiment

The commercial resist A2 950K PMMA or 2% solution in anisole of P-α-MS (Fluka, average molecular weight of about 460,000, polydispersity 1.05) were spin-coated on the silicon wafer, followed by drying. The layer thickness was L_0 = 80–85 nm. The specimen was mounted on a special heater and then loaded into the specimen chamber of the scanning electron microscope (SEM CamScan S4 or SEM Ultra-55). After pumping the chamber to working vacuum (10^{-5} to 10^{-6} mbar) the specimen was heated to the desired temperature and then exposed by electron beam with the energy 20 keV. Experiments on the DEBER process in the microscope CamScan were performed in the scanning mode over the area 1×1.3 mm^2, beam size about 100 nm, the incident beam current I = 1 nA. Experiments in the SEM Ultra was performed in the scanning mode over the different areas, beam size 10–15 nm, I = 15 pA.

Experiments on the formation of spatial 3D-images in the form of "steps" were carried out as follows. The wafer with resist was heated to the desired temperature and then exposed by the series of rectangular rasters with sequentially decreasing size. For all experiments the center of all rasters was the same and the wafer position was fixed. The series of the bands on the sides of rectangles changed dose gradually, so each band was etched to the required depth. Step-like structure was obtained. The width of the steps forming at the edge of the exposed area was determined by the ratio of linear dimensions of the scanned rasters. The characteristic (contrast) curve of the etching was obtained. Exposure doses were calculated for each raster in accordance with this curve. For each subsequent exposure we additionally took into account the dose absorbed by the exposed area in the previous irradiation.

The thickness of the resist layer before and after etching as well as the spatial shape of obtained etching figures were determined by atomic force microscope (AFM) Solver P47 (NT–MDT, Russia) in Tapping mode.

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3. Kinetics and mechanism of etching

Data were obtained for the rates of the PMMA DEBER process at different temperatures above the glass transition temperature T_g (for the 100 nm layer of 950 K PMMA resist on Si-wafer $T_g = 118\,°C$ [5]). It was established that with increasing temperature the etching rate of PMMA resist significantly increases (Fig. 1). Dose necessary to etch the layer, equal to half of its initial thickness (half-etching dose) $D_{0.5}$ is about 2.5, 0.8 and 0.3 μC/cm^2 for the temperatures 125, 150 and 170 °C, correspondingly. Dose of the complete etching of resist layer D_1 (dose clean) for the same temperatures is approximately 20, 12 and 6.5 μC/cm^2. We underline that in the DEBER process doses D_1 approximately 10 times, and doses $D_{0.5}$ approximately 100 times smaller than the doses D_1 and $D_{0.5}$, required for the formation of a positive mask or a relief in PMMA resist in the typical "wet" technology.

These data indicate that in these experimental conditions the etching of PMMA is energetically very efficient process and proceeds probably by the mechanism of a chain chemical reaction. In accordance with this mechanism, the radiation energy is necessary only for the formation of initial active centers. The appearance of the one active center leads to the formation of a large number of volatile gaseous products leaving the sample. We suppose that this chain reaction is depolymerization – the process reversed to polymerization reaction. Earlier [6] we determined that PMMA under the similar experiment conditions (thin films, temperatures 120–180 °C, vacuum, gamma-irradiation) depolymerize effectively with monomer formation. The probable mechanism of depolymerization is as follows. Under the electron beam irradiation the main chains of PMMA macromolecules are broken with formation of the so-called terminal macroradicals ∼∼∼$CH_2C\cdot(R_1R_2)$, where R_1 – CH_3 - group, and R_2 – $COOCH_3$ - group. These macroradicals split off the monomer molecules one by one by "zipper" mechanism.

When the sample is exposed above the glass transition temperature of the resist the etching process occurs apparently over the whole thickness of the layer. The forming a depth pattern is due to the bulk polymer relaxation, which runs quite rapidly compare with the experiment time [7].

We also suppose that the etching process rate in our experiments is approximately the same through the whole thickness of the layer. In other words, the diffusion of monomer released into vacuum proceeds rapidly through the whole thickness of the layer and does not limits the rate of etching. For that reason the etching rate is proportional to the layer thickness and decreases during the process with the decreasing of thickness.

We tried to evaluate the average number of monomer molecules, formed by the one terminal macroradical R_t during the time from its formation to its disactivation, using the data of Fig. 1 and the literature data on the dependence of the 950 K PMMA resist molecular weight from a dose of electron irradiation (see [8]). We exclude here the details of this evaluation and present the result. At the stage corresponding to the etching about 30% of the initial resist layer thickness (L_{norm} about 0.7) under our experimental conditions the formation of one radical R_t leads to about 10^3 acts of splitting off the monomer molecules which go away to the vacuum. That is the reason of the high rates of the etching process.

Using the data of Fig. 1 we obtained the characteristic (contrast) curve of PMMA DEBER process at 125 °C. Shape of this curve indicates the low contrast of the image (approximately 0.7). The main reason of low contrast is the corresponding shape of the kinetic curve of etching process. The image contrast improves with decreasing of the etching depth. At the etching depth 0.3 L_{norm} the image contrast is about 1.5. The low image contrast is also confirmed by the shape of the cross section of the lines, obtained by "in-line" scanning (Fig. 2).

The preliminary results on etching rates of PMMA 950 K resist layers of about 200 nm and 340 nm thickness at 150 °C in experimental conditions similar to those for the data in Fig. 1 were obtained. The average etching rate in absolute terms of the 200 nm

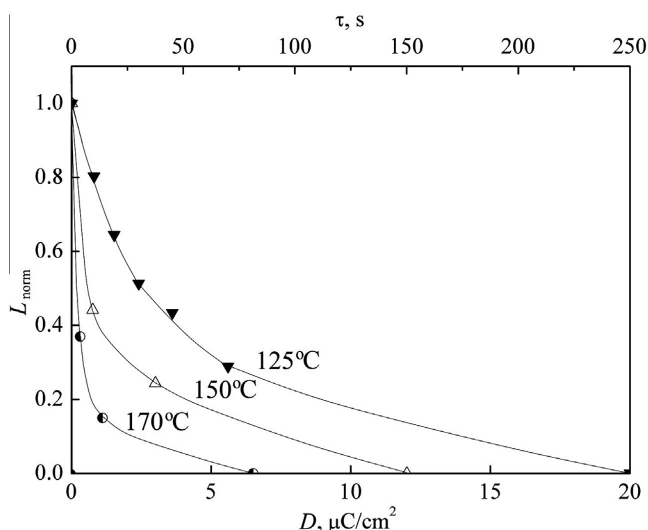

Fig. 1. Kinetic curves of DEBER process of PMMA in the SEM CamScan at temperatures 170 °C, 150 °C and 125 °C. The initial thickness of the resist layer is 80 nm. L_{norm} – normalized layer thickness, τ – the time of exposure, D – the dose of exposure.

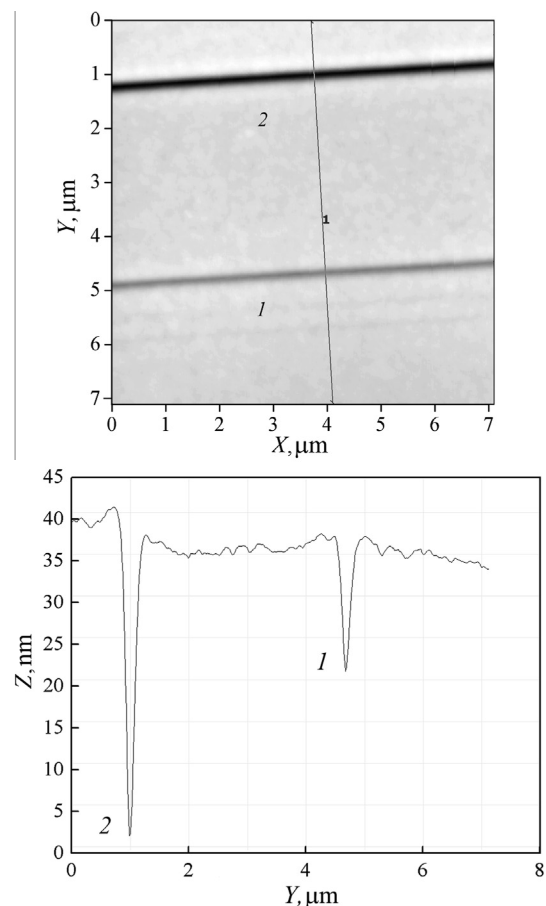

Fig. 2. AFM image of topography and profile of the cross section of lines, obtained by DEBER method in the SEM Ultra at temperature 116 °C. The times of exposure are 1 s (line 1) and 4 s (line 2).

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