Selective profile transformation of electron-beam exposed multilevel resist structures based on a molecular weight dependent thermal reflow

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Novel 3D resist structures are generated with both smooth slopes and stepped resist profiles on the same substrate and in very close vicinity. By performing gray-scale electron-beam exposure and development steps twice with different dose ranges, a selective transformation of multilevel structures into continuous slopes upon thermal treatment was enabled. The molecular weight dependence was analyzed and related to the locally different ability of the resist to flow, which enables one to selectively address resist structures which should be altered while others stay unaffected. The technique has large potential for prototyping elements and devices and can be used to fabricate stamps with complex 3D surface patterns for fabrication using nanoimprint. © *2011 American Vacuum Society*. [DOI: 10.1116/1.3634013]

I. INTRODUCTION

Gray-scale electron-beam lithography (EBL) is commonly used to generate stepped 3D structures in a single resist layer either of positive[1–3] or negative[4–7] tone. The process is based on an exposure-dose modulation that leads to a locally nonuniform etch rate for resist solvents (the developer) and thus to the removal of different resist quantities during the development. This can be used to generate lithographically defined multilevel resist profiles with defined steps of various heights. Recently, the capabilities of 3D manufacturing in poly(methyl methacrylate) (PMMA) were improved by combining a dose-modulated EBL with a thermal postprocessing.[8,9] It was shown for PMMA (used as a positive tone resist) that both the solubility to the developer and the glass transition temperature (T_g) depend on the molecular weight, which is reduced upon the exposure to high energy electrons.[10] Due to the reduced T_g of the exposed and developed multilevel structure, a selective melting was enabled or more precisely, a pronounced local decrease in viscosity, if the temperature during reflow was accurately chosen near the initial T_g. The thermally induced local material flow (or reflow) facilitated the transformation of stepped profiles into smooth continuous slopes with an inclination of up to 45°.

This way, a local combination of tilted surfaces with nearly vertical sidewalls was enabled. Moreover, roughness due to digitalization errors usually connected to standard gray-scale exposures was reduced. In previous research the ability to generate multilevel resist pattern and to subsequently transform the stepped profile into a continuous contour was demonstrated for a specific development condition.[9] These investigations also showed that in order to generate stepped profiles, different combinations of exposure doses and development conditions can be chosen. The resulting stepped structures exhibit similar geometrical contours but a different molecular weight range of the remaining polymer. This gives rise to the question of whether a threshold can be defined below which the transformation of multilevel profiles into sloped sidewalls is enabled by a specific molecular weight while unexposed regions and other stepped structures stay unaltered during the reflow. This is particularly important since the thermal treatment is generally applied to the sample in a global way (e.g., using a hot plate or oven). This fundamental consideration leads to the idea of a two-step gray-scale EBL, as depicted in Fig. 1, which allows the fabrication of stepped and sloped profiles in close vicinity to each other.

The aim of this paper is therefore to restrict this transformation to specific patterns by using the fact that structures with similar initial shape, but different molecular weight, can be fabricated. Consequently, they may exhibit significant differences in their ability to flow. Based on further research on the correlation between applied dose and resulting molecular weight, technical limitations were overcome by modified exposure and development conditions.

II. EXPERIMENT

All 3D multilevel structures have been fabricated in 1 μm thick PMMA resist with a molecular weight of 950 k (k means kg/mol), spin-coated on a 100 mm diameter silicon substrate and prebaked for 5 min at 175 °C on a hot plate. The dose-modulated EBL was performed with a high energy electron beam in a commercial pattern generator (Vistec EBPG 5000+ HR at 100 keV and 1 nA). Exposed samples were developed under slight agitation in a temperature-controlled developer bath. For the 1 μm thick PMMA used here, undiluted methyl-isobutyl-ketone (MIBK) was found to be the most suitable developer giving optimized sensitivity and contrast characteristics as well as a minimized pattern surface roughness at 20 °C. After

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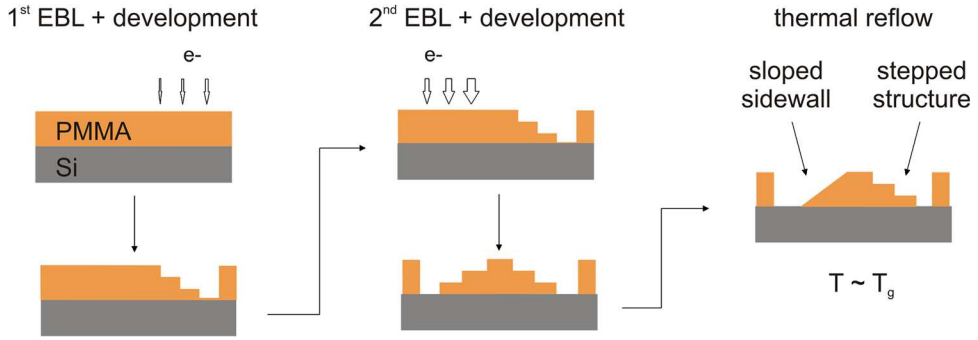

FIG. 1. (Color online) Two consecutive gray-scale EBL steps are applied to a single PMMA layer. The resist is selectively transformed from a stepped structure into a sloped sidewall based on a molecular weight dependent thermal reflow.

development, the samples were rinsed for 30 s in isopropyl alcohol and blow dried using nitrogen.

For the consecutive gray-scale lithography steps, two different dose–depth correlations (contrast curves) were used as will be discussed later. The corresponding data were obtained from the exposure of 200×200 μm^2 rectangles, which were developed for 30 and 900 s, respectively. Contact profilometry was used to determine the remaining resist heights. The normalized contrast curves are drawn in Fig. 2. Dose-to-clear values (complete removal of PMMA) were found to be 480 and 100 $\mu C/cm^2$ for the 30 and 900 s development, respectively.

The thermal treatment after exposure and development was performed on a hot plate under ambient conditions at different constant temperatures and process times. The reflow step was stopped by instant cooling, when the samples were removed from the heater after the required time was reached.

III. RESULTS AND DISCUSSION

A. Molecular weight dependent thermal reflow

For a detailed examination on specific molecular weight values correlated to the discrete layer thicknesses of a multilevel resist profile at certain development conditions and thus to further investigate the molecular weight dependent reflow behavior, the PMMA was exposed to defined doses (d20, d40, d60, and d80) that were derived from the two contrast curves in Fig. 2. For example, a 30 s long development in MIBK results in a reduced resist thickness of 80% of the initial one, if the PMMA is exposed to $d80 = 250$ $\mu C/cm^2$, whereas the height of 20% is achieved with a dose of $d20 = 450$ $\mu C/cm^2$ (high dose gray-scale EBL). The corresponding dose values for the 900 s development step are $d80 = 27$ $\mu C/cm^2$ and $d20 = 85$ $\mu C/cm^2$ (low dose gray-scale EBL). The exposure on an area of 20×20 mm^2 with a homogeneous dose provided sufficient material quantity (no development step performed) for a subsequent gel permeation chromatography (GPC) of the exposed resist, which was calibrated using PMMA standards. The results of the GPC are depicted in Fig. 3 and illustrate the dependence of the molecular weight of the PMMA on the applied exposure dose.

The chromatogram in a semilogarithmic graphic in Fig. 3(a) shows the influence of the exposure dose on the molecular weight distribution of the PMMA chains. Two groups of the molecular weight are plotted which correlate to d20, d40, d60, and d80 of the high and low dose gray-scale EBL. A graphical evaluation of the *number average molecular weight* (M_n) over the applied dose is given in Fig. 3(b) in a double-logarithmic scale. The indicated linear decay of M_n for increasing dose value shows the reduced probability of an electron to cut an already broken PMMA chain for higher doses. This is most probably due to the onset of additional cross-linking. The GPC measurements are summarized in Table I, which shows the quantitative analysis of M_n, supplemented by the *weight average molecular weight* (M_w) as well as the polydispersity (PD). As can be seen, the initial molecular weight (i.e., 950 k according to resist supplier) is significantly reduced upon the exposure to high energy electrons by approximately 1 order of magnitude for the low dose and by 2 orders of magnitude for the high dose EBL. This is in good agreement with data presented by other groups.[10]

The melting of the stepped profiles into continuous contours was further investigated for the high dose gray-scale exposure correlated to the 30 s development, which was also used in previous work.[9] Table I indicates the M_n reduction below the T_g-relevant value of 10k, which leads to significantly reduced T_g (Refs. 11 and 12) and thus ability to flow.[13] This enabled the transformation of the stepped pattern into a continuous and smooth slope, as illustrated in Fig. 4. A summary of a temperature-duration survey was

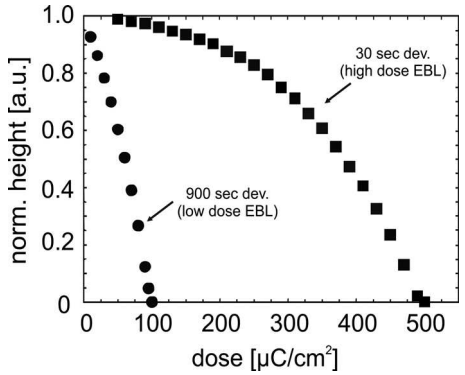

FIG. 2. Contrast curves of 1 μm thick 950 k PMMA resist electron beam exposed at 100 keV/1 nA and subsequently developed in undiluted MIBK at 20 °C for 30 s (standard) and 900 s, respectively.

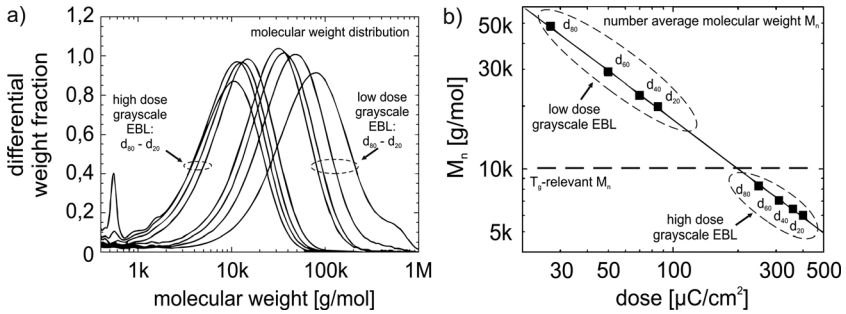

FIG. 3. Molecular weight of 950 k PMMA resist exposed to different doses analyzed by gel permeation chromatography. (a) Two groups of the molecular weight distributions are plotted which correlate to a high and a low dose gray-scale EBL. (b) A graphical evaluation of the number average molecular weight M_n over the applied dose shows a decay of the molecular weight for increasing dose values.

compiled showing different 1 μm high PMMA multilevel structures, which were exposed and developed according to the above-described standard procedure and thermally treated under different reflow conditions. The asymmetric pattern consists of five steps with a width and height of 1 μm and 210 nm, respectively. Different reflow times (5, 20, and 120 min) were applied at two different temperatures (110 and 120 °C) around the original T_g (measured at 122 °C) in order to study the reflow behavior. Interestingly, vertical features remain steeper, if the reflow is performed at lower temperature for considerably longer time. A higher temperature leads to a deformation of unexposed regions, which was reported previously.[9] However, similar sloped patterns are accomplished for a fast (5 min at 120 °C) as well as slow reflow (120 min at 110 °C). This way, processing times can be minimized, if no vertical elements have to be preserved.

B. Selective reflow of patterns with molecular weight threshold

The specific correlations between the applied dose ranges during the gray-scale EBL and resulting molecular weight distribution provided a better understanding of the mechanism behind the molecular weight dependent reflow. In particular, since the low dose gray-scale exposure leads to multilevel resist pattern with a molecular weight well above the T_g-relevant M_n of 10 k,[12] where differences in T_g become significant [see Fig. 3(b) and Table I]. Based on this result, a exposure strategy was implemented which uses a two-step gray-scale EBL at different dose ranges in order to exclude certain patterns from profile transformation during thermal treatment and to create stepped and sloped profiles on the same substrate.

The two consecutive gray-scale EBL steps are based on the (high and low dose) contrast curves shown in Fig. 2. The exposures are performed on the same single PMMA layer, each followed by an appropriate development step. First, a stepped pattern is generated by using the contrast curve for a 900 s development. The low dose range employed for the gray-scale exposure results in a reduction of M_n in the range of 20–50 k (see Table I). Afterwards, an additional stepped structure is created using a second exposure according to the 30 s development, which is performed at higher doses resulting in a reduction of M_n below 10 k. Since the patterned area of the first EBL step is developed two times, the 900 s development is completed in two stages: partially (870 s straight after the first exposure) and finally (additional 30 s) after the second one.

The generated stepped resist profiles exhibit similar geometrical contours but with different molecular weight distributions below and above the T_g-relevant $M_n < 10$ k. Thus different reflow behavior can be expected for the two different multilevel patterns if the thermal reflow is properly applied, i.e., stepped structure exposed to higher doses can be selectively transformed into a sloped profile while other exposed areas maintain their original stepped shape.

TABLE I. Quantitative analysis of the number average M_n and the weight average M_w of the PMMA resist as function of the exposure dose.

Dose (μC/cm^2)	M_n (kg/mol)	M_w (kg/mol)	PD[a]
27	48.3	90.1	1.9
50	29.1	56.8	1.9
70	22.5	42.3	1.9
85	19.8	37.1	1.9
250	8.3	15.8	1.9
310	7.0	13.3	1.9
360	6.4	11.9	1.9
400	6.0	11.0	1.8

[a]PD represents the polydispersity, i.e., the ratio of M_w/M_n.

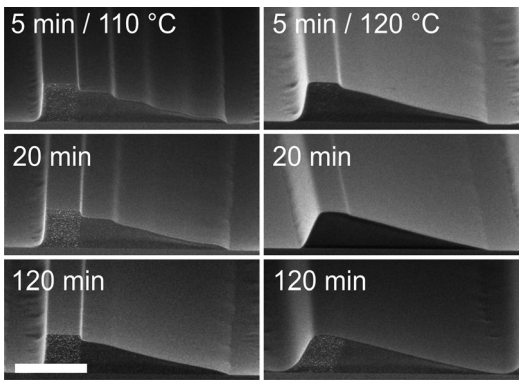

FIG. 4. Summary of a reflow survey: a 1 μm high five-level PMMA pattern was exposed to different temperatures for various durations. Vertical features remain steeper if 110 °C is applied for a considerably increased time of 120 min (scale bar: 2 μm).

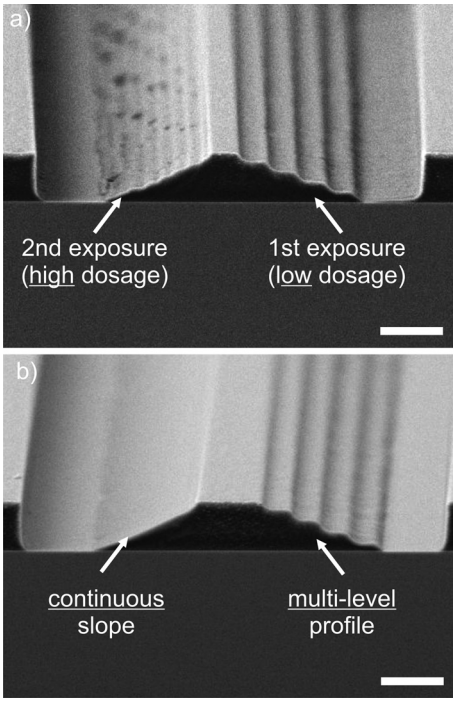

FIG. 5. Sloped and stepped resist profiles in 1 μm PMMA is accomplished by combining two consecutive gray-scale exposures based on different contrast curves (a) and a thermal postexposure treatment (b). Only a high dose gray-scale exposure to PMMA leads to a M_n reduction below the T_g-relevant value of 10 k, which allows the selective melting due to a significant but locally defined shift in the T_g. For the two examples shown, the (unexposed) center levels unintentionally have different widths due to a misalignment during EBL exposure (scale bar: 2 μm).

The described procedure was used for the profile refinement for a 1 μm high PMMA pattern shown in Fig. 5. A five-level pattern with a step width of 500 nm (low dosage) and a nine-level structure with a step width of 250 nm (high dosage) were generated using dose ranges derived from the specified contrast curves. The subsequent reflow at 110 °C for 120 min results in a continuous slope (smaller increments improve slope quality[9]) and a multilevel profile due to the difference in the molecular weight and thus reflow behavior. AFM measurements were used to characterize selectively reflowed profiles. It was found that the slope exhibits a smooth surface (surface roughness $R_q \sim 4$–7 nm) with an inclination of approximately 22°, while the nontransformed steps were still clearly distinguishable. Due to a minor etching of unexposed PMMA with an etch rate of around 5 nm/min, the resulting maximum pattern height was found to be lowered by roughly 7% compared to the initial resist thickness.

IV. CONCLUSION AND OUTLOOK

The presented two-step gray-scale exposure in conjunction with the molecular weight dependent reflow process opens up new possibilities for the manufacture of 3D resist profiles, which were not achieved or not easy to achieve until now. Bringing together sloped, stepped, and vertical sidewalls with suitable surface properties in a single resist on the same substrate is a major advancement toward 3D manufacturing capabilities based on high energy EBL. Currently, the process can be reproducibly controlled to a maximum resist height of 2 μm and structure heights of up to 4 μm and higher seem to be feasible. We envisage this selective transformation to be employed for any kind of 3D resist structure as long as a significant local reduction of the molecular weight can be achieved. The use of a local homogeneous (flood) exposure to x-ray or electron beams on previously patterned 3D resist structures may lead to further process simplification.

The developed technique has large potential for prototyping of optical devices and elements, e.g., as a functional optical 3D structure needed for improved light emitting diode, or LED, backlighting in display industry,[14] since it allows the generation of a complex 3D pattern such as prisms and gratings on the same substrate. In order to make such patterns also available for other materials the resist structures can be transferred into the silicon substrate by proportional RIE or by casting with UV curable materials.[15,16] This way, 3D stamps can be fabricated for the replication by nanoimprinting, injection molding, or roll-to-roll processing.[17] This is a mandatory requirement for the successful implementation of these structures in the applications envisioned.

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