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Electron beam lithography using a PMMA/P(MMA 8.5 MAA) bilayer for negative tone lift-off process

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The authors demonstrate a high resolution lift off process for electron beam lithography using a PMMA/P(MMA 8.5 MAA) bilayer as negative tone resists. Fifty-nanometer features were achieved for metal deposition up to 100 nm thick. The process was tested on silicon substrates as well as indium tin oxide on glass transparent substrates in order to prove the applicability of the patterns for extraordinary optical transmission. © 2015 American Vacuum Society.

I. INTRODUCTION

Electron beam lithography has become one of the most widespread nanofabrication tool for both industrial and academic research purposes, the short wavelength of electrons and the availability of great focusing equipment allows for one of the best resolution available, combined with a great flexibility in writing. It is a technique of great interest to study the properties of devices at the nanoscale level and to develop applications such as data storage, nanoelectromechanical systems, plasmonic devices or semiconducting technology components. Because this technique consists in a lithographic process, further steps are required in order to obtain the desired final structures. The patterned resist serves as a mask for etching or as a mask for deposition in a lift-off process. The availability of different resist materials and procedures becomes crucial in order to efficiently achieve any desired structure.

In this paper, we present a lift-off process using a bilayer of poly methylmethacrylate (PMMA) and copolymer P(MMA 8.5 MAA) as negative tone resists. While these commonly available resists are normally used as a high resolution positive-tone resist, overexposing them induces crosslinking of the polymer molecules, leaving only the exposed regions unetched by organic solvents. It has been demonstrated that PMMA can achieve a similar resolution in the negative and the positive tones. Furthermore, using the bilayer, an undercut profile is achieved after development, which is crucial for obtaining a proper removal of the patterned resist and metallic layer on top during the lift-off step. The undercut profiles are highly important in the case of lift-off of isolated features, for which the removal of the material cannot start from the edges and propagate toward the structure. This method represents an additional high resolution process for the negative tone lift-off that compares in resolution to other reported methods that usually use hydrogen silsesquioxane (HSQ) as the top layer such as HSQ/PMMA, HSQ/HPR, and HSQ/novolak bilayers. It is an easy to implement recipe suitable for thick metallic deposition and gives great wall verticality, which is of great interest whenever the deposited material is part of the final structure.

II. EXPERIMENT

The procedure to achieve the lift-off process is schematically presented in Fig. 1. A first layer of P(MMA 8.5 MAA) copolymer (9% in ethyl lactate) was spin-coated on a glass substrate covered with a 100 nm indium tin oxide layer (Sigma-Aldrich) using a Brewer Science 200cbx spin coater and was oven baked at 140 °C for 30 min in order to evaporate any excess solvent in the resist. A second layer of PMMA 950 (2% in anisole) was then spun on top of that layer and soft-baked at 170 °C for 30 min. For the results presented here, the thickness was usually set to 340 nm for the copolymer layer and 75 nm for the PMMA, but different thicknesses could be used depending on the thickness and the resolution desired for the final structure. The bilayer was then patterned using electron beam lithography (Raith eLine Plus system) at an acceleration voltage of 20 kV and a beam current of 230 pA. The development of the resist was achieved by gently manually agitating the sample in acetone for about 240 s. The sample was then placed in a high vacuum chamber inside an Edwards electron beam evaporator where a 100 nm gold layer was deposited on top of the pattern. The electron beam was accelerated at a tension of 7.5 kV at an emission current of 280 mA toward a gold filled crucible to heat the sample at 140 °C for 30 min in order to evaporate any excess solvent in the resist. A second layer of PMMA 950 (2% in anisole) was then spun on top of that layer and soft-baked at 170 °C for 30 min. For the results presented here, the thickness was usually set to 340 nm for the copolymer layer and 75 nm for the PMMA, but different thicknesses could be used depending on the thickness and the resolution desired for the final structure. The bilayer was then patterned using electron beam lithography (Raith eLine Plus system) at an acceleration voltage of 20 kV and a beam current of 230 pA. The development of the resist was achieved by gently manually agitating the sample in acetone for about 240 s. The sample was then placed in a high vacuum chamber inside an Edwards electron beam evaporator where a 100 nm gold layer was deposited on top of the pattern. The electron beam was accelerated at a tension of 7.5 kV at an emission current of 280 mA toward a gold filled crucible to heat the sample at a sufficient temperature for vaporization. Dry etching of the underlying resist was achieved by an O2 plasma at 500 W at a pressure of 200 mTorr for 15 min using a PVA Teplag batch 310 plasma asher. The sample was then rinsed in acetone in an ultrasonic bath for about 5 min to remove any undesirable etching residues.

Crosslinking behavior of 495 and 950 k PMMA resists as well as the P(MMA 8.5 MAA) copolymer resist was characterized by performing the atomic force microscopy (AFM) measurements of exposed patterns for each resists taken separately. Silicon was used as a substrate for those characterization measurements. The layers were soft-baked and then patterned using a voltage of 20 kV and a current of 230 pA, for different doses. The patterns for the characterization were made of circles of 200 nm diameter separated by a 600 nm period. The width and thickness of the developed patterns for the different resists are presented in Fig. 2.

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The cross-linking sensitivity for all three resists can be retrieved from Fig. 2(a) which plots the thickness of the features as a function of exposure dose. The exposure gave significant structures starting at a dose of 80 mC/cm² for both PMMA resists and at 65 mC/cm² for the copolymer, identified as the gel dose of the resist. It then reached a plateau at doses of 100 or 120 mC/cm², respectively, which corresponds to full cross-linking of the polymer molecules. No significant differences were observed for the two PMMA resists of different molecular weight (495 and 950 K). According to Greeneich’s equation which describes the average molecular weight of polymer molecules upon exposure, with a relatively small exposure, most of the PMMA molecules in both resists should be cleaved into smaller fragments of similar low molecular weight. This dose corresponds to the positive tone resist sensitivity and represents 1%–10% of the total dose used for crosslinking. The crosslinking events thus begin with the same state of the polymer molecules, and so, the initial molecular weight of the material has a little effect on the final size. A significant difference was observed for the P(MMA 8.5 MAA) copolymer, probably due to the different nature of the material. As can be observed from the data in Fig. 2(b), the cross-linked state of the molecule starts at a lower dosage, but the width of the features remains always smaller than the PMMA resist for high enough doses, making it an ideal undercut layer for the bilayer system. This difference in size can be attributed to the significantly different chain lengths of the cross-linked polymer molecules as well as the different three-dimensional organization of the polymer after cross-linking.

The diameters of the developed structures are wider than what is implemented in the e-beam lithography software for doses that corresponds to a narrower diameter of the underlying copolymer resist. A small adjustment thus needs to be made to obtain correct dimensions of the features, which depends on many factors such as the beam current, the acceleration voltage, and the nature of the substrate. We also observe in Fig. 2(a) that the polymer is reduced to about 60% of its initial thickness for the PMMA resists after exposure and development when fully cross-linked. The degree of swelling for the cross-link molecules is less compared to the linear molecule, and this reduction in thickness can thus be associated with solvent evaporation in the material. This reduction was 90% for the copolymer case, which involved a different solvent (ethyl lactate) as well as a different density of cross-links. It is to be noted that different development times were tested and had no effect on the final size of the features, as long as it was sufficiently long to assure that the unexposed regions were fully etched.

### III. RESULTS AND DISCUSSION

In order to demonstrate the advantage of the bilayer, scanning electron microscope images of the structures were taken after the deposition of gold and after stripping of the resist.
The larger PMMA layer on top of the P(MMA 8.5 MAA) layer creates an undercut profile that will allow the etching molecules to reach the underlying resist during the lift-off [Figs. 4(a), 4(c) and 4(e)]. Negative photoresist exhibit strong positive slopes [see Figs. 3 and 4(e)] upon exposure due to forward electron scattering which renders any stripping of the deposited material difficult since material can be deposited on the sides of the features, forming a continuous layer. In the case of the bilayer, the material was easily lifted using O₂ plasma dry etching. Note that residues of the lift-off are cleaned using ultrasonic agitation in acetone.

Usage of the cross-linked material gives great advantages compared to other conventional electron beam resist. The cross-linked PMMA is a very robust and resistant material, making it a versatile material for MEMS fabrication either as a sacrificial layer or as a component of the MEMS itself. It can also reach high aspect ratio pillars (around six for the case considered here) without collapsing upon manipulation. A very good regularity of the individual patterns was found on patterned windows of 100 μm. As shown in Fig. 5, a lift-off process of 50 nm features was achieved using this material for a gold layer thickness of 100 nm, yielding an aspect ratio of 2 for the structured deposited material.

This technique thus represents an easy fabrication process in order to achieve great resolution with a high aspect ratio for the pattern transfer through lift-off. Although a larger...
exposure dose is required compared to other reported methods, notably one using a HSQ/PMMA bilayer,\textsuperscript{15,22} no optimization steps other than the exposure are required since the development is noncritical and the bottom layer naturally develops into a narrower structure. The resist used, PMMA, is a commonly available and low-cost electron beam resist. Stripping is made through O\textsubscript{2} plasma, making the technique compatible with most substrates. The recipe implemented in this study was optimized for thicker deposited material (100 nm). While the resolution achieved of 50 nm is larger than other reported resolutions,\textsuperscript{22} it is comparable when the aspect ratio is taken into consideration. The presented method thus represents a viable alternative with similar fabrication capabilities than the other commonly used negative-tone processes.

In Fig. 6, we show the transmission spectrum of a 475 nm period nanohole array of 190 nm diameter holes in a 100 nm thin gold film that exhibits extraordinary optical transmission.\textsuperscript{23} These structures were obtained using a 340/75 nm bilayer of P(MMA-MAA)/PMMA bilayer at an exposure dose of 130 mC/cm\textsuperscript{2}. The resonant peaks can be identified, which are related to coupling of light with surface waves of the highly conductive metal. A good agreement is found for the experimental results compared with the simulation of the ideal case using COMSOL finite-element method, which shows the quality of the fabrication process. A slight increase in the full width at the half maximum for the resonance peaks is attributable to the surface aspect of the metallic structures, which was considered perfectly flat in the simulations.

**IV. SUMMARY AND CONCLUSIONS**

The process suggested in this paper represents an easy to implement nanofabrication method of great resolution for thick lift-off of a negative tone resist. The bilayer of widely available PMMA/P(MMA 8.5 MAA) resists helps to achieve an undercut profile without any other steps than the development itself. A resolution of 50 nm was presented for closely stacked structures of 100 nm thicknesses. Other resolution and/or thickness of the deposited material could be achieved using different thicknesses of the resists. This method is of great interest for many applications involving nanoscale features, as was demonstrated for the extraordinary transmission of nanohole arrays.

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