3D Nanostructuring of hydrogen silsesquioxane resist by 100 keV electron beam lithography

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The authors investigated the three-dimensional nanostructuring of hydrogen silsesquioxane (HSQ) resist by multiple-step 100 keV electron beam lithography. Consecutive overlay exposures were used to create two- and three-levels in high aspect ratio HSQ structures with lateral dimensions down to 30 nm and resist thicknesses of about 1 μm . The HSQ resist was developed by a high contrast solution and supercritically dried in a carbon dioxide environment after each exposure step. The three-dimensional HSQ patterning has potential applications in the fabrication of performance enhanced devices such as photonic crystals, nanoelectromechanical systems, and diffractive X-ray lenses. © 2011 American Vacuum Society. [DOI: 10.1116/1.3629811]

I. INTRODUCTION

Electron beam lithography (EBL) is a very accurate technique for creating patterns in a layer of material with lateral dimensions down to a few nanometers.¹ To date, hydrogen silsesquioxane (HSQ) has been proven as an excellent negative tone resist for high resolution² and high aspect ratio³ EBL. Sub-10 nm features have been patterned in thin layers (< 20 nm) of HSQ resist by state-of-the-art EBL tools and using high contrast development processes.^{4,5} Nevertheless, the structuring is usually limited to two-dimensional, i.e., binary, patterns; three-dimensional (3D) patterning has not been yet fully exploited and is mostly restricted to much larger feature sizes^{6–8} (> 200 nm) than those reported for two-dimensional patterns (< 20 nm).

Here, we investigate the 3D nanostructuring of HSQ resist by multiple-step 100 keV EBL. Taking advantage of the excellent gap filling and planarization performance^{2,9,10} of HSQ resist, up to three consecutive overlay exposures were used to produce two- and three-level high aspect ratio patterns. Hydrogen silsesquioxane multiple-step structures with lateral dimensions down to 30 nm were fabricated in resist thicknesses of up to 1 μm . The potential applications of the 3D HSQ patterning are in the fabrication of devices with enhanced performance such as photonic crystals,^{11,12} nanoelectromechanical systems¹³ or diffractive X-ray optical devices,¹⁴ i.e., Fresnel zone plates (FZP). Here, we demonstrate the flexibility of the method by reproducibly fabricating a variety of multiple-step 3D nanostructures. In particular, a two-level FZP made of HSQ resist with an effective outermost zone width of 150 nm is shown.

II. EXPERIMENTAL METHODS

Figure 1 illustrates the fabrication steps to create a two-level HSQ pattern by two consecutive overlay EBL exposures. The fabrication procedure was divided in three main

parts: the preparation of the alignment markers (steps 1–3) and the two consecutive separate EBL exposures on two independently spin-coated HSQ resist layers (steps 4–9).

For the nanostructuring results shown in this work, 200 nm-thick silicon nitride (Si_3N_4) membranes were used as a substrate and all EBL exposures were performed using a Vistec EBPG5000 plus EBL tool at 100 keV electron energy. The Si_3N_4 membranes are a mandatory requirement for the fabrication of diffractive X-ray lenses to reduce photon beam absorption of the substrate. Moreover, HSQ resist demonstrates a good adhesion on Si_3N_4 surfaces such that no additional adhesion promoting fabrication step was required. From the technical point of view, the use of Si_3N_4 membranes spared us the need for proximity correction during the EBL exposures as the high energy electron beam is completely transmitted through the thin membranes with negligible back scattering.

The fabrication method started with the preparation of alignment markers made of gold (Au) (steps 1–3). They consisted of several arrays of $15 \times 15 \mu\text{m}^2$ squares placed around the Si_3N_4 membranes. This type of alignment marker geometry is embedded in the standard alignment routines of the Vistec EBL tool. In detail, the EBL exposure of the alignment marker pattern was performed on a 500 nm-thick 600 K polymethyl methacrylate (PMMA) resist layer using a beam current of 40 nA and doses of $1000 \mu\text{C}\cdot\text{cm}^{-2}$. The samples were developed in a solution made of 7:3 isopropyl alcohol (IPA) and water for 30 s, rinsed in water and blow dried with nitrogen (N_2). Next, a thermal evaporation was used to deposit an Au with a thickness of 70 nm which was sufficient for a successful recognition of the alignment marker during the subsequent EBL exposures. Finally, the Au alignment marker fabrication was completed by a lift-off step in hot acetone (50 °C) followed by a rinse in room temperature IPA.

After the PMMA resist removal but before spin-coating the first HSQ resist layer (steps 4–6 in Fig. 1), the samples were exposed to a high pressure (> 200 mTorr) oxygen plasma for one min to ensure a clean surface and a good adhesion of the HSQ resist. The resist layers were prepared from a commercial HSQ solution (FOx 16 Flowable Oxide,

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FIG 1. (Color online) Fabrication method for 3D nanostructuring of hydrogen silsesquioxane (HSQ) resist. A two-level HSQ pattern is created by two consecutive overlay electron beam lithography (EBL) exposures. The fabrication steps are divided in the preparation of gold alignment markers (steps 1–3) and the two consecutive but separate EBL exposures on two independently spin-coated HSQ resist layers (steps 4–9).

Dow Corning). Prior to the spin-coating step, the samples were baked for 5 min at 180 °C, to remove any residual moisture. For the first EBL exposure, the samples were spin-coated at 4000–6000 rpm for 60 s to obtain a resist thickness of 500–400 nm. The HSQ resist layers were not baked to ensure the highest contrast during the EBL exposure and development. The EBL exposure were performed using a beam

current of 500 pA and an estimated Gaussian electron beam spot size of 10 nm. The standard alignment routines of the Vistec EBL tool were used to locate the Au alignment markers and to accurately position patterns during the EBL exposure. To provide good marker detection and minimize the misalignments due to contamination each alignment marker was only used once. Several tests patterns consisting

FIG 2. (Color online) Scanning electron microscopy (SEM) images of 3D nanostructuring of hydrogen silsesquioxane (HSQ). The final two-level patterns are the result of two consecutive overlay electron beam lithography (EBL) exposures. Sketches above the SEM images depict the decomposition of the pattern into the two independent EBL exposures. Smallest level step in panel (c) is 30 nm for an HSQ resist thickness of 750 nm. Tilted images have been acquired at an angle of 70° and an electron energy of 10 keV.

of lines, circles and squares were exposed with dose ranging from 10000 to 15000 $\mu\text{C}\cdot\text{cm}^{-2}$.

After the EBL exposure, the chips were developed for 4 to 6 min in a NaOH buffered solution made of 1:3 of MICROPOSITTM 351 developer (Rohm and Haas) and water. The chips were rinsed in water and IPA. They were not immediately dried by a conventional N₂ blow, but kept immersed in IPA. To prevent the collapse of the high aspect ratio structures during drying due to the capillary forces, the samples were supercritically dried^{3,15} in carbon dioxide (CO₂). The samples were immersed in IPA into the critical point dryer chamber that was then closed and sealed at an initial temperature of 10 °C. The chamber was filled with liquid CO₂ at high pressure (50 atm). Using the exhaust outlet, the chamber was cyclically purged and refilled with CO₂ until there was no IPA left. Next, the temperature and pressure were raised to 35 °C and 100 atm, respectively; well above the critical point of the CO₂ (72.8 atm at 31.1 °C). During the final step, the chamber was slowly depressurized keeping the temperature constant at 35 °C. As a result, the HSQ structures were dried in a liquid-gas interface free environment.

After the exposure and development of the first HSQ level, a second layer of HSQ resist was spin-coated at 1000 rpm for 60 s (steps 7–9 in Fig. 1). Due to the gap filling and planarization capabilities of the HSQ resist, a simple spin-coating step was sufficient to obtain a flat and uniform up to 1 μm -thick layer that completely covered and conformally embedded the already developed HSQ structures. Again, the standard alignment routines of the Vistec EBL tool were used for a very accurate positioning of the second exposure with respect to the first exposure. Analogous parameters and procedures to those described for the first HSQ layer processing were followed for the second HSQ resist exposure and development.

Eventually, a third EBL exposure, repeating steps 7 to 9 in Fig. 1, was one more time used to fabricate three-level HSQ resist nanostructures.

III. RESULTS AND DISCUSSION

The results of the 3D nanostructuring of HSQ resist by multiple-step 100 keV EBL are shown in Fig. 2. The 3D HSQ patterns in the scanning electron microscopy (SEM) images are the outcome of two consecutive but independent EBL exposures. The sketches above the SEM pictures depict the decomposition of the structure into the two independent EBL exposed patterns. Red and blue shapes were respectively exposed on the first and on the second HSQ resist layer. The SEM images in Fig. 2 demonstrate the high resolution and high aspect ratio capabilities of combining high energy EBL and critical point drying for the exposure and development of the HSQ resist. In particular, Fig. 2(c) demonstrates sub-50 nm 3D patterning of a high aspect ratio structure containing steps of about 30 nm wide in a 750 nm-thick HSQ resist layer, corresponding to an aspect ratio of about 25. Although the supercritical drying successfully prevented the collapsing of the high aspect ratio structures, very narrow HSQ pillars

are most likely experiencing residual capillary forces, as shown in Fig. 2(a).

According to these results, the use of the standard alignment routines implemented in the Vistec EBL tool provide a very high overlay accuracy, of the order of a few nanometers. Among all the inspected structures only in a few reduced number of patterns, the misalignment of the two consecutive exposures was visible. In addition, we believe that two or more consecutive EBL exposures allows for better control, considerably higher resolution (< 100 nm) and higher reproducibility than those that can be achieved in gray-scale lithography.⁷ Furthermore, compared to the gray-scale lithography,

FIG 3. Scanning electron microscopy (SEM) images of a two-level Fresnel zone plate (FZP) pattern made of hydrogen silsesquioxane (HSQ) resist, (a) and (b). The level step width is 100 nm and the effective outermost zone width of the FZP is 150 nm (300 nm period). The tilted SEM image in panel (c) shows an equivalent two-level grating with 300 nm period and total HSQ resist thickness of 750 nm (tilt angle of 70°, electron energy of 10 keV).

FIG 4. Scanning electron micrographs of 3D nanostructuring of hydrogen silsesquioxane. The final three-level patterns are the result of three consecutive overlay electron beam lithography exposures (tilt angle of 70° , electron energy of 10 keV).

the multiple-step exposure allows for better control of the height of the structures by simply setting the appropriate resist spin-coating speed. The use of a fresh HSQ resist layer for the second EBL exposure is very beneficial for achieving a higher contrast and a smaller level step in the multilevel structure.

An application of the multiple-step EBL technique for 3D nanostructuring is the fabrication of FZPs for X-ray focusing and imaging. In particular, the manufacture of multilevel FZP patterns can lead to a very significant increase of the focusing diffraction efficiency in comparison to the conventional binary diffractive lens.¹⁶ The diffraction efficiency of a FZP accounts for the fraction of the incoming radiation intensity that is diffracted into focus and is typically limited to values of about 10–30% for conventional binary FZPs. The use of a multilevel diffractive X-ray lens could easily increase the diffraction efficiency up to 40 or even 80% depending on the particular photon energy.¹⁷ In comparison to the multilevel FZPs fabricated in the past by multiple-step EBL,^{16,18,19} the use of HSQ resist can potentially manufacture FZPs with a much smaller effective outermost zone width and a higher pattern quality. Figure 3 shows SEM images of a two-level FZP made of HSQ resist with an effective outermost zone width of 150 nm (300 nm period). Figure 3(c) shows a two-level grating structure with 300 nm period equivalent to the lines and spaces at the outer region of the two-level FZP.

Finally, Fig. 4 contains several SEM images of HSQ resist structures with three-level structuring. The resulting structures demonstrate the possibility of repeating the process to obtain three-level features with sub-100 nm spatial resolution. Figures 4(a) and 4(b) show some patterns with steps of about 100 nm, while 4(c) and 4(d) have smaller

lateral dimensions of 80 nm and 40 nm, respectively. Figures 4(e) and 4(d) show three-level gratings with periods of 600 and 400 nm in a total HSQ resist thickness of $1.2\ \mu\text{m}$.

IV. CONCLUSIONS

Hydrogen silsesquioxane resist has been demonstrated as an outstanding material for the fabrication of a large variety of nanostructures by EBL due to its high resolution and high aspect ratio capabilities. The manufacture of sub-100 nm structures is of interest for many nanotechnological applications. Here, we investigated the feasibility of using multiple-step overlay 100 keV EBL for 3D nanostructuring of thick HSQ resist layers. Due to the excellent gap filling and planarization properties of HSQ resist, up to three consecutive overlay EBL exposures were used to produce two- and three-level high aspect ratio patterns with lateral dimensions below 50 nm and resist thicknesses up to $1\ \mu\text{m}$.

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