Method for improving the aspect ratio of ultrahigh-resolution structures in negative electron-beam resist

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A method for improving the aspect ratio of ultrahigh-resolution structures in negative electron-beam resist is provided for enhanced pattern-transfer capabilities. The essence of the proposed method is to form a protective “cap” on top of the resist structure by means of electron-beam-induced deposition (EBID) in a self-aligned approach. This is implemented by a combination of electron-beam lithography and EBID during exposure of the resist material in the presence of a precursor gas. The results of the proposed method using hydrogen silsesquioxane resist material are presented and discussed, including various attempts to further optimize this method. © 2009 American Vacuum Society. [DOI: 10.1116/1.3263171]

I. INTRODUCTION

Performance progress in electron-beam lithography (EBL) and electron-beam-induced deposition (EBID) is improving fabrication capabilities in the sub-10-nm regime. The maskless technique of EBID has even shown feature sizes as small as about 1 nm, whereas details in resist as small as 5 nm have been realized using EBL. Nanoscale lithography via the EBID technique was recently reported by directly transferring the EBID-formed pattern to the substrate via reactive ion etching. In EBL, the pattern-transfer capabilities of the formed resist structure are crucial. The need for better resolution performance in EBL pushes resist-layer thicknesses correspondingly down to a few tens of nanometers at most. This trend places ever higher demands on the thickness uniformity and pattern-transfer capabilities of the resist layer.

This article describes how we applied EBL and EBID in a single step in order to improve the aspect ratio of high-resolution structures and thus to enhance the pattern-transfer capability. We tested our novel method on hydrogen silsesquioxane (HSQ) negative tone electron-beam resist. The basic idea is to perform e-beam exposure of the resist in a precursor gas ambient. This results in EBID formation of a protective cap on top of the exposed resist area (Fig. 1). Ideally, the cap should prevent resist material losses or mechanical damage at the top of the formed structure during development. Thus the cap should allow lateral trimming of the structure’s sidewalls via increased developer strength or prolonged development time. We expect that the developed resist structures will show an improved aspect ratio compared to structures obtained by conventional EBL. Depending on the uniformity of the cap formation and on resist development properties, we also expect an improvement of the lateral uniformity and roughness of the resulting nanostructures. Additionally, the EBID deposit could serve as a supplementary mask for the pattern-transfer process. The work presented below describes how we tested our idea.

II. EXPERIMENT

A FEI Strata DB 235 dual-beam scanning electron microscope (SEM) and a Raith eLine electron-beam lithography system were used for both EBL and EBID. The first instrument was also used for inspection of the obtained structures and for linewidth measurements. The error in linewidth measurements was about 0.7 nm. Precursor gases of methylcyclopentadienyl(trimethyl)platinum (CH₃)₃Pt(C₅H₅) and tetraethylorthosilicate (C₂H₅O)₄Si (TEOS) were used in the FEI system for deposition of platinum and silicon oxide, respectively. Tungsten was deposited in the Raith eLine system using tungsten hexacarbonyl W(CO)₆ as precursor.

Films of HSQ (FOx-12, Dow Corning) resist on silicon substrates were exposed to the e-beam. Different resist film thicknesses of between 8 and 55 nm were achieved by varying the speed of the spinner (Karl Suss RC 5/8) and by diluting the HSQ resist with methyl isobutyl ketone. All resist films were dried for 30 min in vacuum at room temperature to minimize film roughness.

Fine-line exposures in the FEI DB 235 system and the Raith eLine system were performed with the smallest probe size available, i.e., at 20 kV with beam currents of 16 and 14 pA and working distances of 5 and 10 mm, respectively. The resists were exposed in vacuum (conventional EBL) and in the presence of the precursor gas (EBL+EBID). The dose ranged from 5 to 15 mC/cm². The actual pattern con-
sisted of ten lines (2 μm long) on a pitch of 100 nm in both x and y directions. Prior to exposure, Au nanoparticles (~20 nm in diameter) were placed on the resist surface to allow in situ e-beam focusing and spot-size measurement. The measured spot size was ~3 nm full width at half maximum. After development for 1 or 5 min in MF351 developer (Rohm&Haas) and immersion in a “stopper” solution (MF351:H2O=1:9), the samples were rinsed in de-ionized water and blown dry with nitrogen.

To investigate the thickness and morphology of the deposits, several EBID exposures were also performed on a Si substrate with a native SiO2 and on a Si substrate coated with HSQ resist. These samples were not developed.

The working pressure in the chamber during exposure in the presence of the precursor gas was 2×10⁻⁶ mbar for deposition of W and 3.3×10⁻⁶ mbar for deposition of Pt and SiO2. Most exposures were done with the substrate at room temperature. Some Pt exposures were performed also at +15 and −20 °C to achieve enhanced deposition of material. The temperature during these exposures was set by a cascade of Peltier elements mounted on the stage equipped with an Al heat absorber. The temperature was measured with a chromel-alumel thermocouple.

The surface roughness and the height of the developed ultrahigh-resolution structures were measured using atomic force microscopy (AFM) on a Veeco Dimension 3100 microscope with standard silicon tips.

III. RESULTS AND DISCUSSION

The results of e-beam exposure on 8-nm-thick HSQ resist with and without simultaneous exposure to the Pt precursor are shown in Fig. 2. Structures exposed to a dose of 15 mC/cm² in EBL and in EBL+EBID have almost the same linewidth. For a development duration of 1 min, the linewidths are 16.1 and 17.0 nm, respectively, whereas for 5 min these are 11.3 and 11.5 nm, respectively. Note that the dose of 15 mC/cm² is needed for EBID and is not optimal for obtaining the highest possible resolution in EBL. Prolonging the development time from 1 to 5 min yielded a linewidth reduction of 40% for both EBL and EBL+EBID.

Corresponding AFM profile scans of the resist structures are shown in Fig. 3. The EBL+EBID resist structures are 1.2±0.5 nm higher than the EBL structures, independent of development time. As there is no effect on the linewidth, the increased thickness implies a 20% improvement of the aspect ratio. The height uniformity of the EBL and of the EBL+EBID structures is similar. To investigate possible shape changes due to interaction of the resist with the EBID mask, cross sections were made in the 8 nm EBL and EBL+EBID structures. However, no shape changes were observable in SEM. To check the effect of the inherent roughness of the HSQ surface, we compared EBID deposits on HSQ to similar deposits on the Si wafer with the native SiO2. Figure 4 shows AFM profile scans [(a) and (c)] and three-dimensional (3D) images [(b) and (d)] of Pt lines on the silicon substrate and on the HSQ surface. Clearly the height of the Pt material on Si is about 1 nm. Note that these specimens were not developed. The lines deposited on HSQ show significantly less uniformity than those on silicon. Of interest here is the inherent roughness of the HSQ layer, which was ~0.7 nm root mean square compared to only ~0.08 nm for...
the Si substrate. Assuming the EBID depositions on Si (with native oxide) and HSQ are similar, we found that the height of the deposited Pt material on HSQ (~1 nm) is about the same as the height variations due to surface roughness.

The improvement of the heights of the EBL+EBID structures, compared to conventional EBL, is shown in Fig. 5 for the case of Pt. Surprisingly, the improvement varies from 1.2 ± 0.7 nm for the thinnest (8 nm) HSQ film to 6 ± 1 nm for the thickest (55 nm) one, which corresponds to relative improvements of 20% and 11%, respectively. Development of the EBL+EBID resist for 5 min resulted in complete removal of the protective Pt cap. This disappearance of Pt was confirmed by energy dispersive x-ray (EDX) analysis. To check the cap removal quantitatively, we deposited W and Pt structures on the Si surface under the same conditions as for deposition on HSQ resist. After immersion in the developer for 1, 3, and 5 min, the structures were inspected by SEM. The W structures had already disappeared after 1 min, whereas the Pt structures were still slightly visible after 3 min. Pt disappeared after 5 min, in agreement with the EDX

Fig. 3. AFM line profiles obtained by conventional EBL [(a) and (c)] and by EBID+EBL [(b) and (d)] using Pt precursor at a dose of 15 mC/cm² for different development times. Average heights (h) are indicated.

Fig. 4. AFM profiles and 3D AFM images of line structures obtained by EBID using Pt precursor on a Si wafer with native SiO₂ [(a) and (b)] and on HSQ resist [(c) and (d)]. Dose: 15 mC/cm²; no development.
analysis. Because the same amount of EBID material was deposited on all resist films, one would expect that the cap provided the same time delay in the developer attack. However, the observed dependency of the height improvement on the initial resist thickness (Fig. 5) implies that there are different development speeds for different resist thicknesses. Several factors may play a role here. First, a previous study showed a higher effective dose for thicker films due to secondary-electron contributions.\(^3\) The increased effective dose would have caused slower resist erosion of the thicker layer. A second factor may be the average HSQ cluster size. The decrease in the surface roughness of HSQ with increasing layer thickness indicates a smaller average HSQ cluster size in the thicker layer.\(^8\) The smaller cluster size may result in a higher erosion speed in the development step. The greater height difference between EBL+EBID and EBL structures in the 55-nm-thick layer indicates that the cluster size effect is greater than the effective dose effect. For the deposition of tungsten, no difference between the height features achieved via EBL and EBL+EBID is observed at all. Apparently, the W cap material erodes so quickly that there is no significant delay in the subsequent resist erosion.

We performed EBL+EBID experiments with TEOS precursor to create a cap material resembling the SiO\(_2\)-like HSQ resist and to improve its resistance against erosion by the developer. Figure 6 shows the corresponding SEM images and AFM profiles of the line structures. The dose and development time were 5 mC/cm\(^2\) and 5 min, respectively. Interestingly, a height improvement of 1.0 \(\pm\) 0.3 nm (14\%) was already achieved at a dose of only 5 mC/cm\(^2\). In comparison, 15 mC/cm\(^2\) was needed to achieve the same height increase for the Pt precursor. As a beneficial consequence, the lower dose in the case of the TEOS precursor resulted in a linewidth of \(\sim\) 6 nm, comparable to state-of-the-art EBL in HSQ.\(^1\)

![Figure 5](image1.png)

**FIG. 5.** Absolute and relative height improvement for structures obtained by EBL+EBID using Pt precursor compared to EBL only vs initial thickness of resist layer.

![Figure 6](image2.png)

**FIG. 6.** SEM images and AFM profiles of line structures obtained by EBL [(a) and (c)] and by EBL+EBID [(b) and (d)] using TEOS precursor at a dose of 5 mC/cm\(^2\) and a development time of 5 min. Average values for the linewidth (\(w\)) from SEM and the height (\(h\)) from AFM are indicated.
Several Pt experiments were performed at lower substrate temperatures (−20 and +15 °C) to improve the EBL +EBID method further. The effect of temperature is twofold. On the one hand, it yields a higher deposition efficiency because of reduced desorption of precursor molecules. On the other hand, HSQ resist has a lower sensitivity at lower temperatures, requiring a higher exposure dose. As a result of the higher dose, more EBID material is deposited. Altogether lower temperatures may further improve the aspect ratio in EBL+EBID. However, at −20 °C substrate temperature, the deposition of Pt was found to be very fast and to have a strong lateral outgrowth. This resulted in significant nonuniform EBID lines and largely distorted final structures. On the other hand, deposition at +15 °C yielded a height improvement similar to that achieved at room temperature. Further process optimization is needed to find the maximum improvement of deposit height without pattern distortions.

A possible further optimization of the method is development at elevated temperature. This will accelerate the removal of the unexposed resist, thereby shortening the reaction time between the cap and the developer. However, the heated developer will be also more aggressive toward the cap, thus offering less protection of the resist top. High-temperature postexposure bake could be another improvement because it would enhance the adhesion of the protective cap to the resist via diffusion of EBID material into the resist. Furthermore, baking can enhance the cap resistance against the developer by purifying and densifying the EBID deposit via outgassing of carbon inclusions. A third option for improvement is to enhance the EBID deposition by using a higher flux of precursor molecules. However, high-resolution EBID performance in UHV conditions poses serious limitations to the gas flux increase.

In summary, a good balance between resist exposure and cap material deposition is crucial for the proposed method to function in an optimal manner. The best parameter for dose optimization is probably the substrate temperature, which influences the sensitivity of the resist and the efficiency of EBID in opposite directions. Erosion of the deposited metal cap by the developer is a serious drawback of the EBL +EBID method. The SiO₂-like cap is the most promising candidate and should be tested further with regard to both the optimal temperature and the etch resistance. In this context, the chemical composition and strength of the developer are important parameters to optimize etch selectivity between cap and resist.

IV. CONCLUSIONS

A combination of EBL and EBID techniques was applied for the first time to improve the aspect ratio of high-resolution structures with an aim to enhance their pattern-transfer capabilities. Aspect ratios up to 20% and 14% higher were obtained for Pt and TEOS precursors, respectively. The absolute feature-height improvement achieved by means of EBL+EBID compared to conventional EBL is most prominent for thicker resist layers. This effect is related to an enhanced development speed. Tungsten precursor showed no aspect ratio improvement. Erosion of the deposited cap material during development is a serious drawback. The combined EBL+EBID method requires further optimization, whereby the type and flux of precursor gas, the process temperature, and the developer conditions (strength and composition) are the most important parameters.

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