Sub-5 nm Structures Process Development and Fabrication Over Large Areas

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Abstract

In this report, the electron beam lithography process development of sub-5 nm lines on 25 nm thick Hydrogen Silsesquioxane (HSQ) resist is investigated using a 100 kV electron beam lithography acceleration voltage. The exposed patterns are developed using varying developer temperatures under two sample agitation modes. In addition, lift-off processes are developed and optimized to transfer the patterns on silicon substrates. The influence of several process parameters such as development temperature, exposure current, exposure dose, pattern density and pitch on the line-width is investigated. Lines with lateral width of 3 nm on a 100 nm pitch have been successfully exposed and the pattern transfer of the periodic lines, bent lines, and nanopillars on Chromium layer using lift-off have been demonstrated. This report describes the electron beam lithography process development of dense sub-5 nm lines and also, presents the limitations of the lift-off technique for lines on the nanometer scale.

Keywords

nanolithography; electron-beam lithography; lift-off; photonics; x-ray zone plates; nanoelectronic; moore’s law; nanostructures

Introduction

The patterning and transfer of ultra-small features in the nanometer regime on a wide variety of substrate materials have become an important area of research in recent years [1, 2]. The main driver of this field has been the micro- and nanoelectronics industry where the transistors keep diminishing in size as predicted by Moore’s law [3]. This trend has also benefited other scientific and technological areas involving the fabrication of ‘nano-devices’ for a wide range of applications in sectors such as bio-medical, environment, energy, communications [4] and sensing [5]. As a result, the process development of sub-10 nm patterning and transfer of features have become very critical to ensure the realization of nano-scale devices. In general, nanofabrication can be divided into two areas – firstly, lateral or horizontal placement engineering of two-dimensional (x, y) patterns on a surface and secondly, the pattern transfer in the (z) dimension. The first one is nanolithography and the second step involves process such as lift-off, deposition or etching of material. This work deals with both aspects of nanofabrication. In this study, HSQ resist (Dow Corning XR-1541 2%) with thicknesses of approximately 25 nm and 55 nm was spun on silicon substrates (1st table).

All the samples in this work were exposed using a Vistec EBPG5000+ tool, using a beam current of 200 pA current and a beam step size of 2.5 nm unless specified otherwise. A range of developer temperatures was used with the aim of determining the optimum development temperature for a 2.4% TMAH developer solution (Tetramethylammonium Hydroxide, commercially known as CD-26 developer), which is the most

<table>
<thead>
<tr>
<th>Resist dilution</th>
<th>Spinning speed (rpm)</th>
<th>Acceleration (rpm/min)</th>
<th>Spinning time (sec)</th>
<th>Post-spinning baking</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XR-1541 2%</td>
<td>2000</td>
<td>584</td>
<td>60</td>
<td>3 min at 100°C hotplate</td>
<td>52-55</td>
</tr>
<tr>
<td>XR-1541 2%/MIBK = 19/41</td>
<td>1000</td>
<td>584</td>
<td>60</td>
<td>3 min at 100°C hotplate</td>
<td>22-25</td>
</tr>
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Table 1. Resist spin-coating parameters used in the current study. MIBK (methyl isobutyl ketone) is the original solvent for 2% XR-1541 resist and was used in dilutions.

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widely used developer for XR-1541 resists. Several experimental investigations of the dependence of line-width on development temperature, pitch and electron beam exposure dose were carried out. In addition, a lift-off process to transfer the lines on silicon substrates and the limitations of the latter technique were investigated. The process development reported in this work can be useful in the fabrication of a wide range of nanostructures with applications in several scientific and technological areas such as in the fabrication of X-ray zone plates for microscopy, photonic sensors for bio-medical devices and graphene-based devices for electronic applications.

EXPERIMENTAL

It is worth discussing some key properties and behavior of the HSQ resist as they are critical in achieving the sub-20nm resolution described in the results presented in this work. HSQ resist consists of silicon oxide-based cage monomer units that polymerize upon electron beam exposure to form an amorphous glass-like dielectric material. The resolution of the HSQ resist can be improved by varying the baking temperature during the pre- and post-exposure processing. Prior to electron-beam exposure, the HSQ resist is baked at 100 °C on a hotplate in the cleanroom wet-bench which is a simpler and time-effective practice compared with oven or vacuum-oven baked approaches. The resist would cross-link and form an insoluble network at more elevated temperatures. Thermal dissociation of Si-H bonds and re-arrangement of Si-O bonds to form glass occurs above 650 °C but a stable form is reached at even lower temperatures [6]. In addition, the resist surface roughness was found to increase at higher temperatures [7] and a lower sensitivity of the resist to the electron beam exposure was observed, which lead to higher exposure dose requirements. HSQ resist is also found to be unstable in air since it is observed that a slow and gradual crosslinking can occur if HSQ coated samples are exposed to air for several days after the spinning process. Similar effects were reported which led to patterned features larger than the designed size [8, 9]. In our experiments, the air exposure of HSQ resist after spin coating was minimized and the sample was loaded in the e-beam vacuum chamber within half an hour, which includes time to load sample on the holder and align the holder stage and the sample.

There are several process parameters during the electron beam lithography exposure of a resist that can be varied and optimized to achieve features of high resolution, such as the electron beam acceleration voltage, electron beam current, beam step size, and developer temperature. In this work, the electron beam parameters producing the best resolution were chosen as follows: acceleration voltage of 100 kV, beam current of 200 pA and beam step size of 2.5 nm. The temperature of the developer was varied to investigate its influence on the lateral width of the linear grating structures. Figure (1) shows the influence of temperature beyond the optimum value on the line-width and the set of SEM (scanning electron micrograph) images in Figure (2) shows the quality of the line-width at different temperatures was found to be 50 °C below which, the line quality is observed to degrade, and above which, the linewidth is observed to increase. The pitch and designed line-width were chosen to be 55 nm and 5 nm (2-exel at 2.5 nm resolution) respectively. The HSQ resist thickness was approximately 22 ± 3 nm of HSQ resist. The optimum development temperature fig 1.

While the improvements in line-width resolution and pattern quality are observed as the development temperature is raised to the optimum of 50 °C, the opposite trend is observed for temperatures above this value. The HSQ resist contrast increases with increasing developer temperature, which was also previously demonstrated elsewhere [10], while the sensitivity decreases leading to higher dose requirements. In this work, we demonstrate that this trend seems to reverse after the threshold optimum developer temperature of 50 °C is reached. As reported earlier, there are processes taking place during development which could explain the current results [11, 12]. The cross linking of the HSQ resist dominates at room temperature. As the temperature is increased, thermal vibrations allow a faster mobility of the cations to the exposed-unexposed resist interface, as a result resist removal occurs via the dissolution mechanism. Above the optimum temperature of 50 °C, the lateral width of the lines is observed to grow wider as reported in previous work [9, 10].

Figure 1: Influence of developer temperature on the width of nano-scale lines
2 (a) Impact of ultrasonic agitation of pattern quality
The impact of manual and ultrasonic agitation during sample development on the pattern resolution and quality were also investigated. Figure (3) shows the variation of line-width with electron beam dose under different modes of agitation. Ultrasonic agitation is shown to reduce resist crosslinking between the lines and most importantly, reducing the line-width by a factor of 2. One possible explanation is that ultrasonic agitation improves the reaction by increasing the flow rate of the developer cations to the exposed/unexposed resist interface. As a result, the hydrogen gas formed during this reaction is removed at a faster rate from the sample surface, thereby, further improving the developer/resist reaction. It is also worth noting, that the ultrasonic agitation does not destroy the sub-10 nm lines which demonstrates the latter’s mechanical integrity. In addition, all the samples were carefully and consistently held with the pattern facing up in the developer solution during the ultrasonic agitation.

2 (b) Dependence of line-width on electron beam dose
There is a strong dependence of line-width with the electron beam dose. Figure 4 (a) and (b) shows this trend for a 25 nm thick resist at a 35 nm pitch and a 55 nm thick HSQ resist at a 50 nm pitch, respectively. The general trend is a decrease in line-width with decreasing electron beam dose. However, there is a minimum dose beyond which the energy required to initiate resist cross-linking is insufficient, resulting in under-exposure.
2 (c) Smallest line-width

Using the same process parameters and steps described in above sections, 1-exel lines, 3 nm wide with a 100 nm pitch (Figure 5) and line edge roughness of 0.7 nm were obtained using a 25 nm thick HSQ resist.

It is worth noting that a line-width size comparable to that obtained in this work has been reported [10], however the process parameters and steps involved in the latter work are substantially different from the current work. Some of the key process parameters of the reported work are as follows: resist thickness 10 nm, acceleration voltage of 10 kV and a salt developer (1 % NaOH, 4 % NaCl). In the current work, a line-width of 4.3 nm has been achieved using a thicker resist resulting in structures with higher aspect ratio, which is an important requirement in nanofabrication for several device applications. 1-exel lines which are 6.1 nm wide at 100 nm and 50 nm pitch (Figure 6) have also been achieved using the same process parameters using a 55 nm resist thickness. Figure 6 (b) shows the cross-section of the 6.1 nm lines. According to the authors’ knowledge, these are the smallest line-widths reported using the specific, yet simple set of process parameters and steps described in this work.

2 (d) Pattern transfer using the lift-off process

Lift-off processes were carried using 1% Hydrofluoric acid (HF) in ultrasonic bath with the exposed sub-10 nm lines at varying pitch on a 55 nm thick resist. The lateral widths of the trenches were measured before and after the lift-off process and the results are shown in Figure (7). This is attributed to the non-conformal deposition of the Chromium layer on the sub-10 nm lines. In addition, the ultrasonic agitation could lead to the removal of the chromium at the edges of the lines. It is also important to note that ultrasonic agitation is critical in the lift-off process with HF otherwise a complete removal of the resist is not possible.

Figure (8) shows the lift-off results where the HSQ lines covering a 10x10 μm area were exposed using 1-exel exposure at 45 nm pitch with an electron beam dose of 4800 μC/cm2 (1.2 nC/cm). (The number of exels is the number of beam step sizes that can fit into the designed feature in both the x and y directions). To show the versatility of the proposed lift-off process, as a proof-of-concept we also demonstrated lift-off on 90º bent line gratings and nanopillar arrays, which are shown in Figure 9 (a) and (b).
Figure 6 (a) and (b): 1-exel lines 6.1 nm wide at a 100 nm pitch, exposed on a 55 nm thick resist using a dose of 25,000 μC/cm² (6.5 nC/cm), (b) cross-section of the 6.1 nm wide lines at a 50 nm pitch, exposed on a 55 nm thick resist using a dose of 14000 μC/cm² (3.5 nC/cm).

Figure 7: Sub-10 nm lines before and after the lift-off process.
Figure 8: Nano-scale lines transferred on silicon substrates using lift-off technique, using 1-exel exposure at a 45 nm pitch, using with a dose of 4800 μC/cm² (1.2 nC/cm²).

Figure 9 (a) and (b): (a) SEM micrograph showing 90° bent trenches in 8 nm Cr fabricated via lift-off; the original HSQ pattern was written using 1-exel at 50 nm pitch with 17,000 (4.25 nC/cm) dose; lift-off using 1% HF in ultrasonic bath for 2 min; (b) SEM micrograph of a nanohole array in 8 nm Cr after lift-off; sample written at 4000 μC/cm², 100 kV beam, 5 nA beam current, 125 nm beam step size; lift-off using 1% HF in ultrasonic bath for 2 min.
Discussion

In this work, we report two novel fabrication process results. Firstly, the resolution limits of the HSQ resist were investigated using a hot development process and dense lines of 4.3 nm wide on a 100 nm pitch were achieved on a 25 nm thick resist. Comparable results were reported but on a thinner resist and using a salty developer that can add further complexity to the process [11]. The impact of ultrasonic agitation as a key process step to deliver ultrafine lines was also demonstrated, supporting the previous which also demonstrate the benefits of using ultrasonic agitation during development in some cases [9]. Secondly, lines with lateral widths of 10-15 nm were successfully transferred using the lift-off process although the exposed lines on the HSQ resist were in the sub-10 nm scale. These results demonstrate the limitations of lift-off process for pattern transfer of sub-10 nm lines on a substrate. Furthermore, lift-off on 90º bent line gratings and nanopillar arrays in HSQ resist using a chromium metal layer and hydro-fluoric acid in combination with ultrasonic agitation were shown to lead to high quality and reproducible patterns. Hence, the proposed process is versatile for a variety of nanoscale patterns. Further investigation and process development are required to optimize the existing process and develop new ones for the pattern transfer of sub-10 nm lines using lift-off techniques.

Conclusions

The ability to reproducibly fabricate devices with sub-10 nm features is becoming more and more critical for devices having a wide range of scientific and technological applications. By the same token, there have been significant research efforts in the process development of sub-10 nm features using several techniques. In this report, a process to pattern dense sub-5 nm lines on a substrate using electron beam lithography has been achieved and lines of 3 nm wide on a 100 nm pitch have been achieved using hot development. To the best of the authors’ knowledge, this is the narrowest line-width exposed using the specific process conditions reported in this work. In addition, a lift-off process for dense sub-10 nm lines is also reported where the transfer of lines with lateral widths of 10-15 nm are achieved. The latter results also demonstrate the limitations of the lift-off techniques to transfer sub-5 nm lines on substrates. The process development steps reported in this work are generic and can be applied to a wide range of substrates using HSQ resist. However, the process parameters are expected to vary depending on the substrate used. The process reported in this work would be useful in the fabrication of a wide range of nanostructures and devices such as a X-ray zone plates, optical slot-waveguides, graphene-base electronic devices and nano-fluidic channels.

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References