E-beam lithography using dry powder resist of hydrogen silsesquioxane having long shelf life

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Hydrogen silsesquioxane (HSQ) is arguably the most popular negative e-beam resist for academic research. One of the most significant advantages of HSQ is its ultrahigh resolution. However, it has a short shelf life, which increases its cost. As an alternative, a new type of dry powder HSQ resist resin (Applied Quantum Materials, referred to as AQM) was introduced here, the shelf life of which can be considered as infinitely long. A small amount of the powder can be dissolved in a solvent as needed right before exposure. Furthermore, this powder HSQ resist has a similar resolution and sensitivity parameters. By using the high-contrast development process with a salty developer, a 7.5 nm half-pitch nested "L" shape structure is achieved. *Published by the AVS.*
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I. INTRODUCTION

As the industry of nanofabrication is developing, high-resolution electron beam lithography (EBL) is of great importance in broad applications ranging from high-density magnetic storage, integrated circuits, nanosensors to photonic devices. Among all types of e-beam sensitive materials, polymethyl methacrylate (PMMA) is one of the most popular EBL resists because of its high resolution, low cost, long shelf life, and reliability. As it is a positive resist, it is not always applicable to every application because the ratio of the exposed area over the unexposed should be designed as small as possible, or the final resolution will be degraded due to backscattered electrons from the substrates. Furthermore, a large area patterning will significantly increase the exposure time; therefore, for such purposes, a negative resist is necessarily required.

Very few negative resists exist with properties similar to PMMA. The commonly used negative e-beam resists are SU-8, calixarene, polystyrene, and hydrogen silsesquioxane (HSQ). SU-8, a chemically amplified resist, has very high sensitivity but a low contrast.[1] Calixarene has high resolution but low sensitivity.[2] Besides that, it will generate acid during the exposure that will corrode nearby patterns or materials on the sample. Polystyrene, which has a good compromise between contrast and sensitivity, can achieve a resolution of several tens of nanometers.[3,4] HSQ is a popular inorganic EBL resist with sufficient etching resistivity and high-resolution capability, and 4.5 nm half-pitch structures were reported using salty development.[5–7] Furthermore, isolated 7 nm wide lines can be achieved when using 100 keV e-beam facility and on a 20 nm thick resist.[8] However, there is one notable drawback of using HSQ resist; the shelf life of this aqueous resist is too short and that limits its wide usage. (The specifications of Dow Corning® XR-1541 e-beam resist state that HSQ should be stored at 5 °C with a shelf life of only 6 months from the date of manufacture.) While PMMA is considered to have no shelf life issue at room temperature and in a standard humid environment, the short storage time and the rigid temperature requirement of HSQ make it costly in its usage. Consequently, a more advanced negative resist having an unlimited shelf life and high-resolution capability is highly demanded.

In this work, we reported a form of HSQ that has the same chemical formula as traditional HSQ, $[HSiO_{3/2}]_n$, but it is a dry powder. It will be referred to as Applied Quantum Materials-hydrogen silsesquioxane (AQM-HSQ) (AQM: Applied Quantum Materials Inc.,[9] the Canadian company making the HSQ resist), and commercially available HSQ will be referred to as Dow HSQ throughout the article. This product can be stored at room temperature and can be dissolved in methyl isobutyl ketone (MIBK) or toluene. However, this resist still does not solve another problem associated with HSQ, that is the coated HSQ film is not stable in the air moisture and must be exposed and developed quickly in order to attain the reproducible result.[10] Here, we study the contrast and resolution properties of AQM-HSQ. To date, several HSQ development techniques have been studied to increase the contrast including hot development,[11] and those using KOH developers[8] and salty developers.[7] The hot or concentrated developers are not suitable for some specific substrates/films such as silicon because they can etch silicon. A salty developer would be a meaningful choice; thus, we have decided to use it in our experiments for high-resolution patterning. In this work, we will show that the AQM-HSQ has similar properties with Dow HSQ, including sensitivity, high contrast, ultrahigh-resolution capability, and its performance in EBL.

II. EXPERIMENT

Dow HSQ and AQM-HSQ (6% dissolved in MIBK) coatings of similar thicknesses of around 210 nm were spin coated on bare silicon wafers followed by a soft baking at 90 °C for 4 min for contrast curve measurement. Next, the e-beam exposure was performed to pattern 5 μm × 5 μm squares at 20 keV

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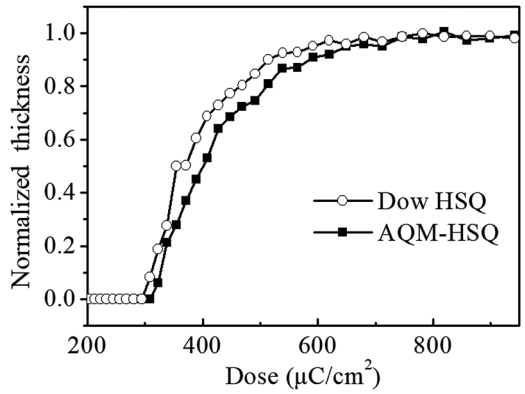

FIG. 1. Contrast curves of AQM-HSQ and Dow HSQ using a 25 wt. % TMAH developer.

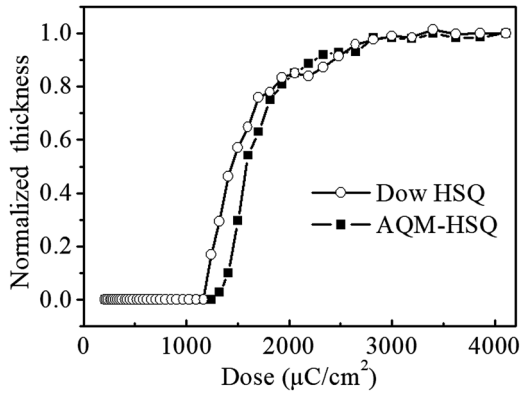

FIG. 2. Contrast curves of AQM-HSQ and Dow HSQ using a salty developer.

with exposure doses ranging from 80 to 1000 μC/cm^2 followed by development in 25 wt. % tetramethyl ammonium hydroxide (TMAH) for 70 s. In addition, to test the effect of the salty development, the same pattern was developed in the high-contrast salty developer, which is a mixture of 1 wt. % NaOH and 4 wt. % NaCl, for 2 min followed by deionized water bath for 5 min where the exposure dose was increased up to 4100 μC/cm^2 for both Dow and AQM-HSQ. The development time applied here is 2 min. In fact, a shorter time can also dissolve all the unexposed resist, which can be as low as 30 s, and the corresponding dose can be adjusted lower.

To obtain high-resolution patterns using dry powder resist of HSQ, 35 nm thick AQM-HSQ was spin coated on a bare silicon wafer. To avoid the thermally induced contrast degradation, soft bake was not carried out, and the lithography process was performed shortly after spin coating. The e-beam exposure was carried out at 25 keV followed by the high-contrast salty development for 15 s and deionized water bath for 5 min. One important point is that if the salty development is applied the rinse time should be not less than 2 min, otherwise, the residual salt will crystallize on the top of the substrate. In this work, three different pattern types that are (1) nested "L" structure, (2) dot array, and (3) bowtie structure were tested.

The nested "L" structures with varying periods from 10 to 35 nm were exposed using a single pixel line at 1.5 nC/cm. The dense dot arrays were exposed at 0.0006 pC/dot, and their periods ranging from 15 to 25 nm. The bowtie structures have a fixed feature size of 100 nm and the narrow gap between the two tips ranging from 2 to 16 nm.

III. RESULTS AND DISCUSSION

A. Result of contrast curve

As shown in Fig. 1, the threshold dose for AQM-HSQ and Dow HSQ is 310 and 325 μC/cm^2, respectively. The dose-effect gets saturated at 750 and 620 μC/cm^2 for AQM-HSQ and Dow HSQ, respectively.

The value of D_0 and D_{100} of AQM and Dow HSQ is consistent, which shows that Dow HSQ resist is slightly more sensitive to electrons than AQM-HSQ. From the contrast curves, the steep of the linear part of the two curves is almost the same if some deviation points are ignored. As presented in Table I, the quantified contrast values can be calculated by the following equation $\gamma = [\log(D_{100}/D_0)]^{-1}$, where the "γ" is contrast.

The contrast curves of both the resist with the salty developer are shown in Fig. 2, and their contrast values are presented in Table II. The threshold doses for AQM-HSQ and Dow HSQ are 1320 and 1240 μC/cm^2, and the saturation doses are 2820 and 3000 μC/cm^2, respectively.

The experimental results indicate that AQM-HSQ is slightly more sensitive than Dow HSQ in both 25 wt. % TMAH and the salty developer. We argue that it is contributed by the absorption of moisture from the ambient atmosphere where the powder HSQ is stored and from the solvent of MIBK in which the AQM-HSQ is dissolved. The result of salty development shows that this resolution boosting method is effective to not only Dow HSQ but also AQM-HSQ. The contrast is high enough so that it is no longer the limiting factor of resolution in sub-10 nm fabrication processing. It can be seen that this AQM-HSQ resist is capable of competing with existing negative HSQ and positive PMMA.

TABLE I. Calculated contrast values and the sensitivity at D_{50} for AQM-HSQ and Dow HSQ developed by a 25 wt. % TMAH developer. Both resists have a quite similar contrast and sensitivity while Dow HSQ has slightly larger contrast and sensitivity.

	AQM-HSQ	Dow HSQ
Thickness (nm)	210	215
Contrast	4.8	5.0
Sensitivity D_{50} (μC/cm^2)	410	355

TABLE II. Calculated contrast values and the sensitivity at D_{50} for AQM-HSQ and Dow HSQ using a salty developer. The new AQM-HSQ powder has a little bit larger contrast, although the sensitivity is slightly lower.

	AQM-HSQ	Dow HSQ
Thickness (nm)	260	260
Contrast	8.7	7.0
Sensitivity D_{50} (μC/cm^2)	1600	1450

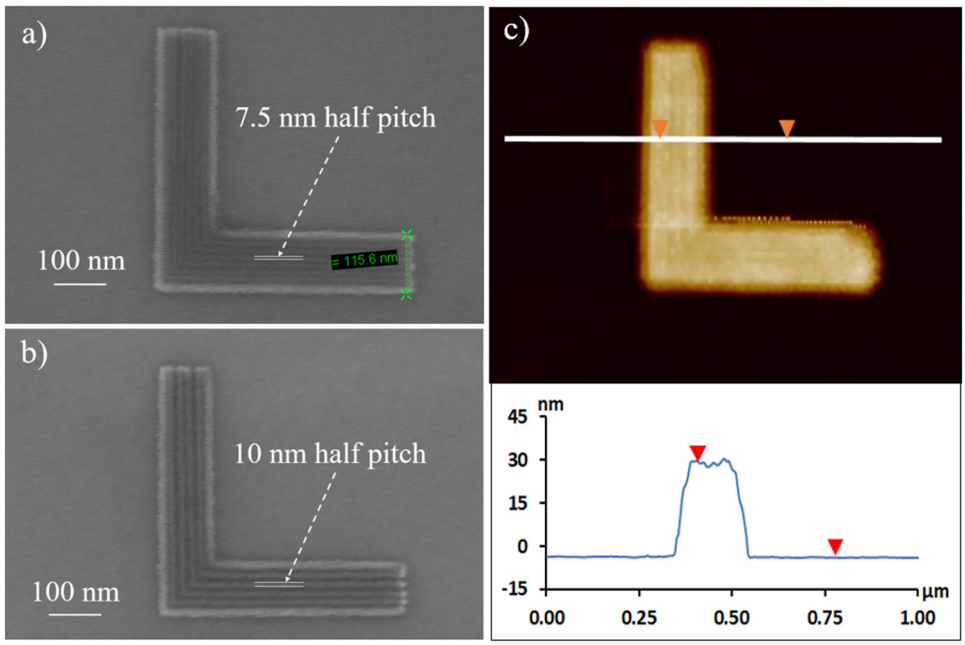

FIG. 3. SEM images of ultrahigh-resolution structures fabricated at 25 keV on a 35 nm thick AQM-HSQ film using a salty developer process. (a) 7.5 nm half-pitch nested "L" structures were achieved using AQM-HSQ and salty developer. (b) Satisfying nested "L" structures were also constructed when half-pitch is up to 10 nm. (c) The height of these structures is measured as 34 nm using AFM.

B. Result of high-resolution lithography

Scanning electron microscopy (SEM) images of the nested "L" structures with 7.5 nm half-pitch and 10 nm half-pitch are shown in Figs. 3(a) and 3(b). The patterns are well defined while the resist is quite thick compared with the pattern density. Figure 3(c) shows the atomic force microscopy (AFM) measurement of the height of the pattern as 34 nm.

Figure 4(a) shows the SEM images of dot array with 7.5 nm half-pitch. Resist thickness on this sample was measured as 40 nm, and the aspect ratio of pillars is about 5. However, some of the pillars on the right side are slightly askew, caused by capillary force in the drying process.

Figure 4(b) shows the image of the bowtie structure, where the gap is as small as 3 nm between the two triangular that can be applied to fields like nano-antenna fabrication.[12]

There are some challenges during SEM imaging such as ultrathin HSQ resist, which mainly consists of SiO_2 (insulating) causing difficulty in focusing and resulting in images with poor contrast. While it is difficult to focus, one needs to be very fast to focus the target pattern to avoid contamination/damaging which is quite significant on ultrathin resists. Although contamination/damaging is not possible to avoid, it can be minimized by decreasing the acceleration voltage. During the imaging, the patterns become worse and worse after every scan; therefore, we first focused on a structure nearby the pattern area, then scanned the individual patterns at a single scan after zooming in by slightly forgoing the contrast.

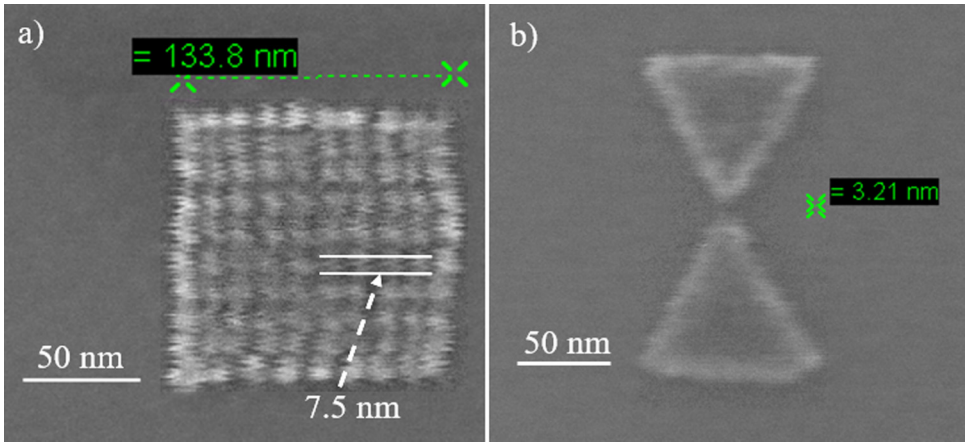

FIG. 4. SEM images of ultrahigh-resolution structures fabricated using a Raith 150 system at 25 keV. (a) 7.5 nm half- pitch dense dot arrays were patterned on a 40 nm thick film. (b) Around 3 nm gap bowtie structure has been formed on 35 nm thick resist coating.

C. Discussion

Overall, the contrast curve and resolution capabilities of Dow HSQ and AQM-HSQ are quite similar. Dow HSQ is typically developed in aqueous alkali solutions such as TMAH, which is one of the most commonly used developers for HSQ, but results in a very low contrast. In development, the dissolution rate of resist molecules depends on the bond strength.[13] On the one hand, when resist is exposed at low exposure doses, unexposed and slightly exposed areas on the resist can be easily removed even by a weak developer such as TMAH-based solutions. In other words, the weak developer allows better sensitivity but worse contrast.[14] This contrast of AQM-HSQ has been verified using the weak TMAH-based solution, as shown in Fig. 1. On the other hand, when it is exposed at high doses which significantly decrease the dissolution rate, the silicon bonds in HSQ become more stable. In this case, a weak developer may not dissolve slightly exposed areas, thus stronger developer is needed to dissolve those areas to obtain high contrast, as shown in Fig. 2. Therefore, in some cases high exposure doses are required to obtain a large contrast, but with low sensitivity. Additionally, there is a possibility that strong developers can attack fine structures such as 6 nm dots[15] where a developer dilution becomes necessary.

Structures with higher resolution would be possible by using different resolution improvement methods such as the structures could be fabricated on a membrane which can suppress the backscattering effect during e-beam exposure,[16] or ultrathin resist could be coated to eliminate the wall/pillar collapses. Moreover, higher e-beam acceleration voltages with smaller aperture would also be beneficial to improving resolution.

IV. SUMMARY AND CONCLUSIONS

We demonstrate that the dry powder AQM-HSQ can be stored in an ambient atmosphere with an unlimited shelf life and one can achieve 7.5-nm-resolution patterns by using the high-contrast salty developer. In the weak TMAH-based developer, the contrast of AQM-HSQ is 4.8, the same as that of Dow HSQ. While in the salty developer, its contrast is 8.7, higher than that of Dow HSQ. Using the salty developer or other contrast improving method in a similar equipment and at equivalent acceleration voltage, AQM-HSQ can produce the same or even better lithographic performance. The results imply that this new type of HSQ resist could be used as an alternative negative e-beam resist and is compatible with the nanofabrication process because of its long shelf life, low cost, and high resolution. As a future work, dry/wet etching resistance and etching selectivity to common materials will be studied.

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