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Quantized patterning using nanoimprinted blanks

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Abstract
Quantum lithography (QL) is a revolutionary approach, increasing the throughput and lowering the cost of scanning electron beam lithography (EBL). But it has not been pursued since its inception 17 years ago, due to the lack of a viable method for making the blanks needed. Here we propose and demonstrate a new general viable approach to QL blank fabrication, that is based on (a) nanoimprinting and (b) a new wafer-scale nanoimprint mold fabrication that uses not EBL but a unique combination of interference lithography, self-perfection, multiple nanoimprinting, and other novel nanopatterning. We fabricated QL blanks (a 2D Cr square tile array of 200 nm pitch, 9 nm gap, and sub-10 nm corners, corresponding to a 50 nm node 4× photomask) and demonstrated that QL can greatly relax the requirements for the EBL tool, increase the throughput and reduce the cost of EBL by orders of magnitude, and is scalable to the 22 nm node.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Scanning electron beam lithography (EBL) has been the most common method for directly converting nanostructures from a design on a computer to real patterns on a substrate. EBL uses a pencil beam to write a resist on a wafer in a point-by-point serial fashion. Hence it offers high resolution and flexibility in patterning, but has a low throughput and high cost, which are becoming worse as the minimum feature size gets smaller [1–3], making EBL mainly used in photolithography masks, nanoimprint molds, and small-volume direct-write. Yet even in these applications, EBL throughput and cost are still a serious issue (a more serious issue for 1× nanoimprint mold and direct-write than 4× photomasks).

To drastically improve EBL throughput and cost, Fulton and Dolan proposed in 1983 to separate EBL writing into two parts: the writing of the feature edge and the filling of inside edges (so-called 'brushfire lithography') [5]. Since the filling does not require an electron beam to have a diameter and a scanning step with a resolution as fine as that for the edge writing, it can be achieved with a much lower-resolution EBL tool (both beam diameter and stages)—lowering tool cost, and with a much higher beam current and scanning speed—increasing throughput.

Pease and Maluf proposed in 1991 another revolutionary concept for high-resolution, high-throughput and low-cost EBL patterning, quantum lithography (QL) [4], in which a pixeled (quantized) pattern array with the high-resolution edges are 'prefabricated' on a substrate blank by a manufacturer using a high-resolution patterning tool, while a user only 'selects' his own patterns on the blank with a low-resolution and high-throughput EBL tool. In this way, a user can obtain the patterns with a resolution significantly higher than his/her own EBL tool, and with a throughput and cost orders of magnitude better than a ultra-high-resolution EBL.

For example, a QL substrate blank for photomasks can be a square Cr nanotile array on a quartz plate, and each tile is separated from neighbors with a small gap (figure 1). To generate a user's own pattern on the blank by QL, the Cr tile array is coated with a resist layer and the user 'selects' a subset of the tiles according to his desired patterns by 'tagging' and 'etching'. The tagging uses EBL to expose a hole in the resist coated on top of each selected tile, while the etching removes (through the holes) the 'tagged' tiles (positive tone), or removes the untagged tiles (negative tone). The gap between the neighboring tiles, which plays the role of isolation

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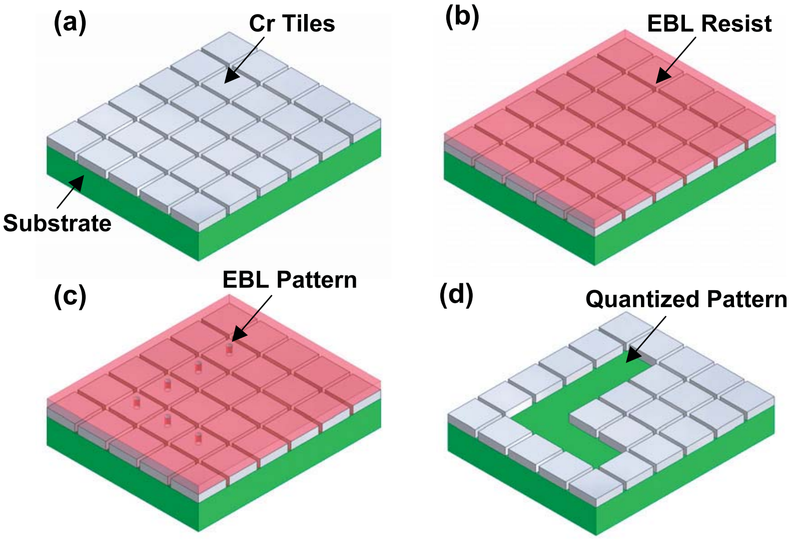

Figure 1. Schematic of quantum lithography (QL) [4]. (a) A manufacturer prefabricates substrate blanks consisting of periodic tile array (e.g. Cr) on a substrate (e.g. Si or glass); (b) the blank is coated with resist; (c) a user tags a set of tiles according to a desired pattern by using an electron beam to expose a hole in the resist above each selected tile; and (d) the tagged tiles are removed by wet etching through the holes (positive-tone QL). For photomasks, the gap between the neighboring tiles is much smaller than the wavelength of the exposure light used in photolithography and hence it will not appear on the final image of a resist exposed. For making nanoimprint molds and direct-writing on wafer, the gap must be sealed after QL.

during an etching, is much smaller than the wavelength of the exposure light used in photolithography, hence it does not appear in a developed photoresist, making it virtually invisible in photolithography. For making nanoimprint molds and direct-writing on wafers, the gap must be sealed after QL, as discussed later. Compared with conventional EBL, QL can have higher pattern edge resolution (limited by QL blank manufacturing), while offering orders of magnitude higher throughput and lower cost, because of an extremely short exposure time and a low EBL tool cost.

However, the promise of QL is hinged upon a viable (both technologically and economically) method to generate the substrate blanks that have the needed prefabricated high-resolution quantized pattern array. Previously a viable method was unavailable: photolithography lacks the needed resolution and EBL lacks the necessary throughput and viable cost. Here, we propose and demonstrate a new approach to quantum lithography which is based on blanks prefabricated by nanoimprint lithography (NIL), we term it ‘quantized patterning using nanoimprinted blanks’ (QUN).

2. Quantized patterning using nanoimprinted blanks (QUN)

2.1. Principle and requirements of QUN

In our QUN blank fabrication (figure 2), a wafer-scale nanoimprint mold of a 2D tile array pattern is fabricated first without using EBL. Then nanoimprint lithography duplicates the mold patterns in a resist on a substrate. Finally the resist pattern is transferred into an array of metal tiles on the substrate. Clearly, a key to our approach is a viable method to fabricate the wafer-scale nanoimprint mold with fine features that are needed for QUN blanks. Once made, a mold can duplicate large-area nanopatterns by nanoimprint with a high fidelity and high throughput [6–8].

The requirements for the QUN mold are stringent in terms of tile period, tile gap, and total mold area, as well as tile sidewall smoothness. For a 4× mask in 193 nm photolithography, the 65 nm node (45 nm node) requires thin Cr tiles on quartz to have a pitch of 260 nm (180 nm), a tile gap less than 48 nm (we choose the gap = 0.25× wavelength, below photolithography resolution), and a mask area of 4 × 4 inch^2 (assuming one inch^2 exposure area). For a 1× nanoimprint mask and direct-write, the 65 nm node (45 nm node) requires the tiles in quartz or metals to have a pitch of 65 nm (45 nm), tile aspect ratio of one or higher, a tile gap as small as possible, and a mask area of 1 × 1 inch^2 or larger, which is certainly much harder to fabricate than 4× photomasks. The edge roughness should be less than 10% of the minimum feature size. These requirements exclude EBL as a viable method for making the wafer-scale NIL molds needed for QUN blank manufacturing.

2.2. Methods and results of fabricating NIL molds for QUN without using EBL

We developed a new process for fabricating nanoimprint molds that can meet the needs of QUN blanks with 2D tile array and sub-10 nm features. The process does not use EBL, but uniquely combines interference lithography, self-perfection technologies (to remove edge roughness and reduce the gap size), and double cycles of nanoimprint lithography and etching. The key steps are (figure 3): (i) creation of 1D grating master mold on 4 inch wafer using interference lithography [9] (if necessary duplicate the 1D grating to other daughter molds

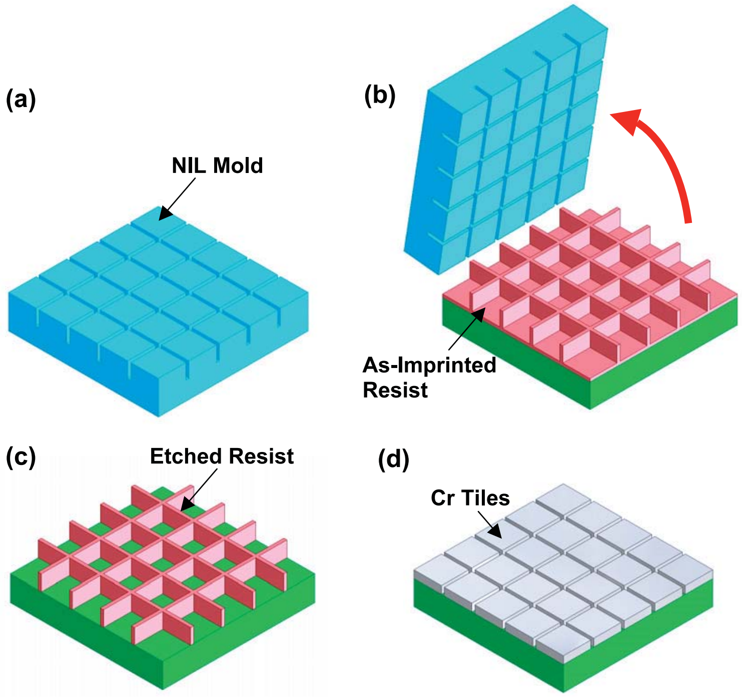

Figure 2. Schematic of fabrication of QL blanks using nanoimprint. (a) A nanoimprint mold with 2D square tile array with a narrow gap between the tiles is fabricated, (b) the mold pattern is duplicated in a resist by nanoimprint; (c) the resist residual layer is removed by RIE; and (d) evaporation and lift-off of Cr leaves Cr tiles on the substrate (note: these group of specific materials is just one of many options). After the blank fabrication, the blanks will be used in QL and other subsequent fabrications.

by nanoimprint); (ii) smooth the grating edges and convert the square profile grating mold in (100) Si to a triangle profile grating mold using a crystalline anisotropic etching [10]; and (iii) use the 1D triangle profile grating mold to create the 2D tile imprint mold by two cycles (in two orthogonal directions) of nanoimprinting, dual shadow evaporations and RIE, which reduces the gap between features from 100 to sub-10 nm.

Specifically, we used 351 nm wavelength argon laser for interference lithography to fabricate a grating mold with 200 nm period, 100 nm linewidth and 100 nm gap over an entire 4 inch wafer area [9, 10] (figure 3(a)). The period corresponds to the pitch needed for 50 nm node 4× photomask. (Note: once a grating is made, frequency doubling methods can be used to further reduce the period [11]). To be suitable for QUN, the gap between grating lines must be narrowed and the edge roughness also needs to be reduced. The edge roughness removal and the grating profile conversion to triangle were carried out together by a crystalline anisotropic etching of a (100)-oriented Si wafer (KOH-based) (figure 3(b)) [10]. The (111) planes in (100) Si ensure almost atomically smooth surfaces, and a triangular grating profile. The mask for wet etching was a 1D grating in thermal oxide created by nanoimprint using the 1D square profile grating mold generated by interference lithography. The triangle mold was used to create a triangle profile in the resist coated on the final mold substrate (i.e. quartz or Si) (figure 3(c)). Shadow evaporations of Cr from two opposite glancing angles can make the gap between the deposited Cr lines as small as sub-10 nm, depending on the shadowing angle (figure 3(d)). After etching the gap into the substrate by RIE, the Cr was removed by lift-off in a chemical solution. The imprinting in a resist by a triangle mold, double Cr shadowing, RIE and a lift-off were repeated one more time in a direction orthogonal to the first one, creating a 2D trench (i.e. 2D protruding mesas) patterned on a mold, which can have an area larger than 4 inch wafer (figures 3(e), (f)).

We used Nanonex NX-2000 nanoimprinter, Nanonex NXR-1000 thermal resist for thermal imprint, and Nanonex NXR-2000/3000 for UV-cure nanoimprinting, an O2-based and CF4/H2-based RIE recipe for etching resist residual layer and fused silica, respectively, and methanol for striping the final resist.

Figure 4(a) shows a SiO_2 imprint mold of 2D mesas with 200 nm period, 9 nm gap, and smooth edges, fabricated using the process described above. Using these molds, nanoimprint lithography and lift-off of Cr, QUN blanks were fabricated with 200 nm period, 170 nm × 170 nm square Cr tiles, and about 30 nm wide gap (figure 4(b)). In the QUN blanks, the edges are smooth, and the corners have a sub-20 nm resolution.

2.3. *Methods and results of quantum lithography using QUN blanks*

To tag the tiles in QUN, we used an electron beam lithography system built in house by adding a pattern generator hardware and software to a scanning electron microscope. Alignment marks were prefabricated on the QUN blanks and were located

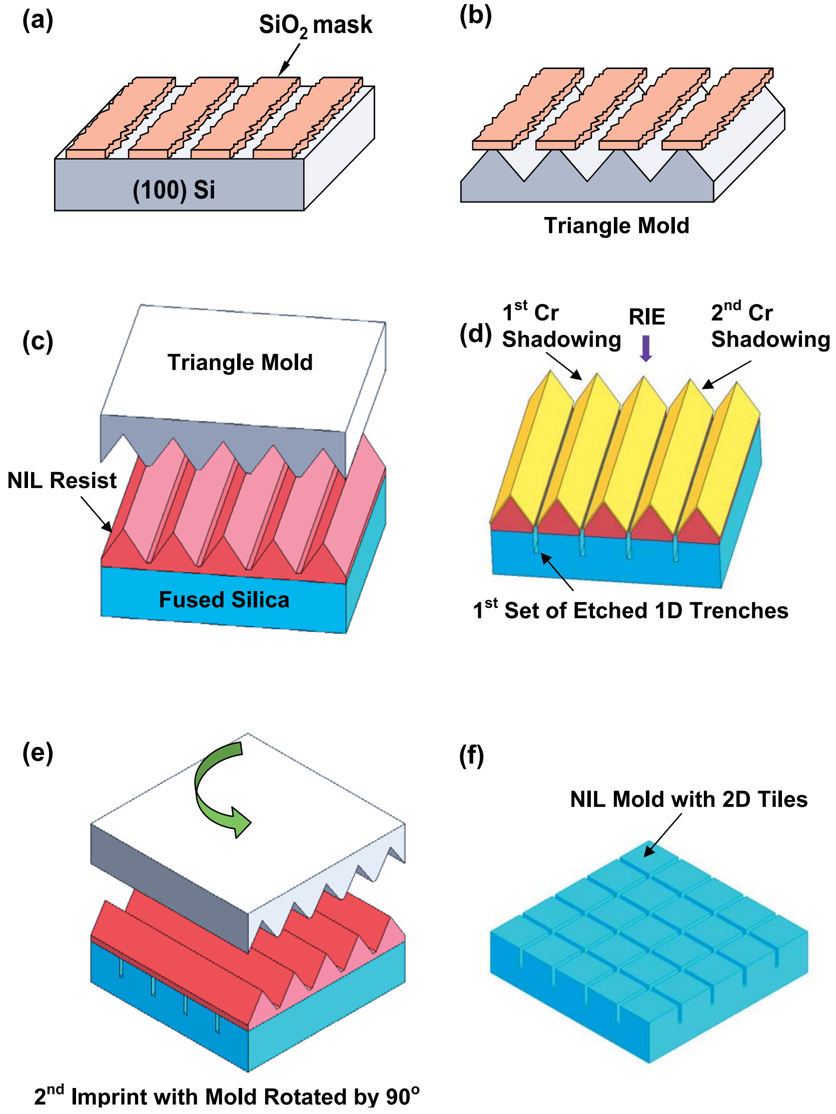

Figure 3. Fabrication of wafer-scale 2D nanotile array mold with sub-10 nm gap. (a) A 200 nm pitch SiO_2 gratings are patterned on a (100) Si substrate using a grating mold with square profile generated by interference lithography; (b) a KOH-based anisotropic wet etching of the (100) Si substrate creates an imprint mold with a triangle profile and nearly atomically smooth surface; (c) the triangle mold is used to imprint a resist; (d) Cr is shadow evaporated in two well-controlled opposite glancing angles, creating a narrow gap between Cr lines, followed by RIE of the resist residual layer and the SiO_2/Si substrate with Cr as the mask; (e) after the removal of Cr and resist in the first imprint cycle, repeat the imprinting (with a triangle mold having the grating oriented 90° from the first imprinted grating), double shadow evaporations of Cr, etching of SiO_2, and the final removal of Cr and resist, (e) completing the mold bearing 2D grid pattern.

at the boundaries of a writing field. Once having aligned with the marks of the blank, the electron beam exposed the QUN blank *without* any further alignments, and the placement accuracy of the electron beam was solely determined by our EBL. The exposure was in a 2D dot matrix format with a 200 nm step size in both *x* and *y* directions.

The Cr tile blanks (shown figure 4(b)) were coated with a 65 nm thick PMMA. The resist also filled the gaps between Cr tiles, therefore separating the Cr tiles from each other, isolating the etching of a Cr tile from its neighbors. Before EBL exposure, the PMMA was baked at 160 °C for 12 h to drive out the solvent and achieve a good adhesion to the substrate. The dot dose was varied from 2 to 28 fC, with 6 fC or more found being reliable for forming holes of an average diameter of 20 nm in the PMMA. The exposed QUN blanks were developed in a mixture of 2-ethoxyethanol and methanol (3:7) for 7 s. After development, chromium etchant, Cr-7 (Cyantek), was used to etch away the ‘tagged’ Cr tiles through the holes. In etching Cr tiles, to ensure complete Cr removal, the etching time was 5 min or longer.

Figure 5 shows scanning electron microscopy (SEM) images of a QUN blank that was tagged by e-beam with ‘NSL’ dot patterns and had the tagged Cr tiles etched away through the exposed and developed holes. Before removing

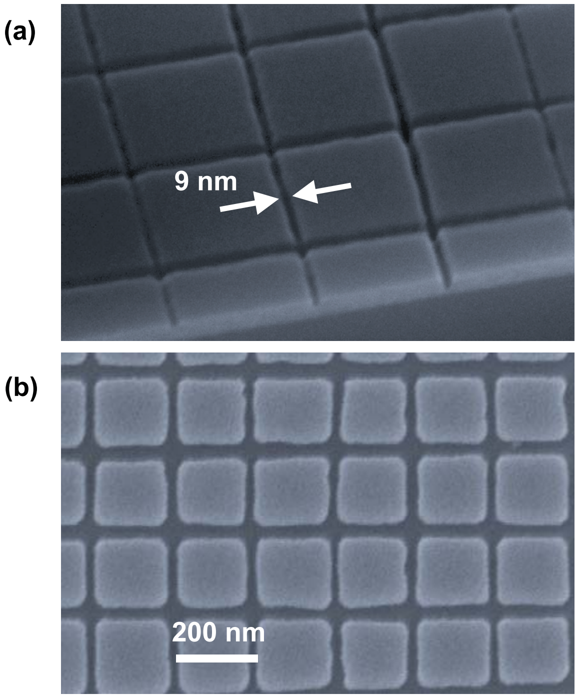

Figure 4. Scanning electron microscopy images of mold and QUN blanks. (a) A nanoimprint mold for QUN with a square tile array of 9 nm gap and 200 nm pitch in a 40 nm thick SiO_2 layer on a Si wafer fabricated by double nanoimprint and etching cycles with a grating mold on 40 nm thick SiO_2 on Si, and (b) a QUN blank with 200 nm period Cr tile array on Si fabricated using nanoimprint.

PMMA, the e-beam exposed holes are visible in SEM images (figure 5(a)), showing (a) the final holes have a wide variation in their diameter (10–30 nm) due to the noise in beam current and resist chemistry, and (b) our EBL system has a poor beam placement accuracy that makes the exposed holes deviate from the intended locations (the centers of the tagged Cr tiles). However, the exposure noise and beam placement inaccuracy have *no* effects on the final patterns made on the QUN blank, each tagged tile was etched away *perfectly* (figure 5(b)). This clearly demonstrates the key advantage of quantum lithography, namely, it relaxes the requirement on EBL beam diameter, exposure accuracy, and EBL stage accuracy (hence increasing throughput and reducing cost), while maintaining the final pattern minimum feature size and the final pattern shape and position accuracy, which are determined by manufacturers' prefabrication of the QUN blanks, not by users' writing tools.

3. High throughput of QUN

We analyzed the increase in writing throughput for QUN. Compared with conventional 'one machine writes all' EBL, the writing throughput of QUN can be increased by orders of magnitude through three factors: (a) the writing area reduction factor (ARF), (b) the writing current enhancement factor (CEF), and (c) the writing grid enhancement factor (GEF).

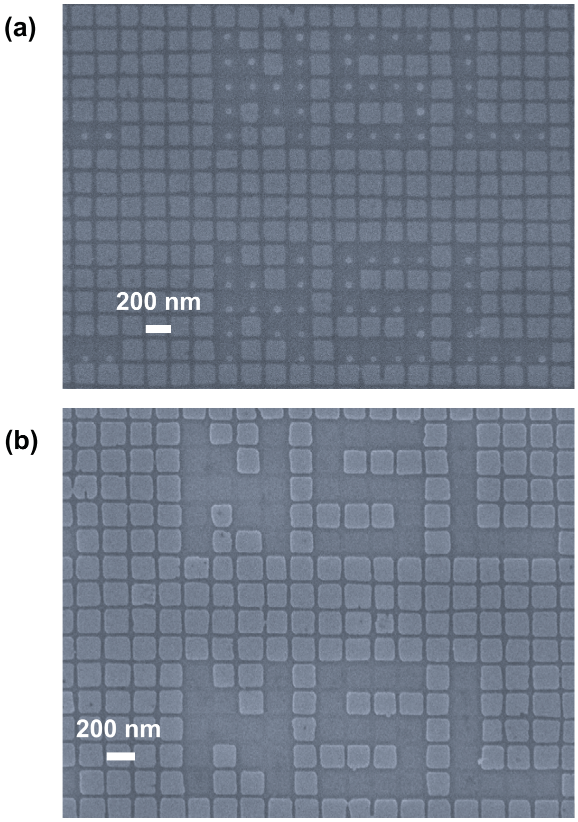

Figure 5. Scanning electron microscopy images of tagged and etched tiles. (a) A 'NSL' pattern was written on a QUN blank by quantum lithography. The image was taken after the tagging (exposing holes) of selected tiles, resist development and etching away the tagged Cr tiles, but the resist still remains, clearly showing the tagged holes; and (b) finished patterns after removing the resist. Each pixel on the QUN blank is 200 nm × 200 nm. Despite the errors in hole diameter and hole position placement, the 'NSL' was patterned perfectly and no effects resulted from the errors were observed. The slightly bright mark in area of the removed Cr tiles might be caused by a slight etching of the substrate by Cr-7 etchant.

ARF is defined as ratio of the doses for writing the entire tile to the hole (assuming the writing current is the same). ARF comes from the fact that in QUN a user only tags a selected tile rather than actually writes the entire tile.

CEF is due to the fact the electron beam used in the tagging can have much larger diameter than that one would otherwise be needed in a conventional EBL to write the sharp edges, making the tagging beam have much higher current than that for a finer beam diameter. Hence CEF is defined as the ratio of the beam current for the tagging to the writing needed for the entire tile.

And GEF is due to the fact that the EBL scan grid for tagging a tile does not need as fine as that one would have used for producing the tile. Therefore GEF is defined as the ratio of the grid sizes for the tagging to the writing that would be needed for the entire tile (assuming the dwell time for each grid point is the same).

Since the total EBL writing time is a sum of the writing time and the dwell time between grids, hence the total

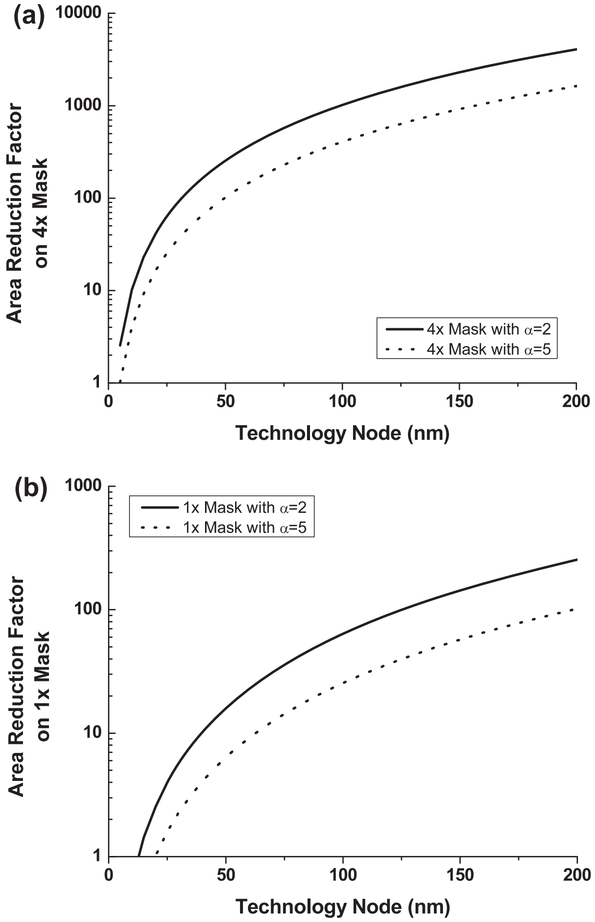

Figure 6. Throughput enhancement of quantized lithography over conventional EBL due to writing area reduction factor (ARF). (a) For 4× photomask, and (b) for 1× imprint mold writing. The calculation assumes the tagged holes are 10 nm in diameter, and the area dose for writing the holes is either 2× or 5× times higher than that for writing large area.

throughput increase in QUN is equal to ARF times CEF for the writing time dominated case, and GEF for the dwell time dominated case.

We calculated the ARF as a function of lithography node for both 4× photomasks and 1× nanoimprint masks/direct-writing wafers, assuming that the tile writing dose is equal to the tile area by the area dose for writing large area, and the dot dose for tagging a 10 nm diameter hole is equal to the hole area times either 2× or 5× of the area dose for large area to ensure reliable exposure (figure 6). For 5× dot dose, just ARF alone, the QUN throughput can be a factor of 20, 40, 80 and 170 times higher than 'one machine writes all' for 22 nm, 32 nm, 45 nm and 65 nm 4× photomasks, respectively, and 1.25, 2.6, 5.2 and 10.8 times higher for 22 nm, 32 nm, 45 nm, 65 nm 1× NIL molds and direct-write wafers, respectively. The throughput can be increased by another factor of 2.5 when the dot dose is 2× instead of 5×, and can be increased further by reducing the tagging hole diameter.

The effects of CEF and GEF depend on the specific lithography node, e-beam tool, and grid being used. On average, CEF may give another 10× enhancement. Therefore, for the writing time limited case, if the area dose for a small dot is 5× (2×) of that for a large area, the throughput in QUN can have a total enhancement of 200, 400, 800 and 1700 times for 4× photomasks, and 13, 26, 52 and 108 for 1× masks, at 22 nm, 32 nm, 45 nm, 65 nm node respectively (table 1). For the dwell time dominated case, if the grid is 10 nm, then the total enhancement factor is 80, 160, 320, and 670 for 4×, and 5, 10, 20, and 42 for 1×, at 22 nm, 32 nm, 45 nm, and 65 nm node respectively (table 2).

Table 1. Total QUN throughput enhancement (compared with conventional EBL) for exposure time limited cases: (a) 4× photomasks, and (b) 1× nanoimprint mold or direct-write.

Node	65 nm	45 nm	32 nm	22 nm
4× masks				
ARF	70×	80×	40×	20×
CEF	10×	10×	10×	10×
Total	1700×	800×	400×	200×
1× NIL mask/direct-write				
ARF	11×	5×	3×	1.3×
CEF	10×	10×	10×	10×
Total	110×	50×	30×	13×

Table 2. Total QUN throughput enhancement (compared with conventional EBL) for dwell time limited cases: (a) 4× photomasks, and (b) 1× nanoimprint mold or direct-write.

Node	65 nm	45 nm	32 nm	22 nm
4× masks				
GEF	676×	320×	160×	80×
1× NIL mask /direct-write				
GEF	42×	20×	10×	5×

Our throughput enhancement analysis has been confirmed by our experiments. For the 200 nm period QUN blanks (50 nm node for 4×), the EBL area dose for writing the 996 K molecular-weight PMMA is ∼400 μC cm^{-2} and 160 fC for each tile (200 nm × 200 nm), while the tagging dose was only 2–6 fC, giving a ARF alone of 80–27, consistent with our general analysis above.

4. Roadmaps for writing and proximity reduction offered by QUN

Finally, we should point out quantum lithography offers two more advantages to EBL: (i) the prepatterned tile array in QL offers a roadmap to track the wafer location, which, unavailable in conventional EBL, further relaxes the requirement of intrinsic beam placement and stage precision [12], and (ii) QL significantly reduces proximity effects (e.g. the corners of the Cr tiles would not be as sharp as that of the demonstrated QUN blanks, if they have had been written by EBL). The concept and advantages of QL can also be applied to multiple beam EBL or ion beam lithography and scanning probe lithography, which suffer from similar problems as a single beam scanning EBL.

5. Discussions of other issues

Presently, we have demonstrated only positive-tone 200 nm pitch QUN. For a negative tone, early work showed that it was possible for 10 μm pitch by Maluf and Pease [4], but we have not succeeded for 200 nm pitch, because the tagged holes are too small for depositing sufficient protection materials. For making 1× nanoimprint mold and direct-writing on wafers, the gap between tiles must be sealed after QL. We have tested several methods and will report them elsewhere.

Another important point is that in real 4× mask making today, it uses much fine grid size than the lithography node size and it does non-square grid to accommodating different shapes. In the situations, the advantages of QUN get reduced by certain degrees, depending upon the sub-grid size and shapes.

6. Summary

Because of three orders of magnitude increase in throughput, significant cost reduction due to the increased throughput and reduced requirement on users' EBL tools, plus additional advantages of beam placement 'roadmap' and less proximity effects, quantized patterning (quantum lithography) based on nanoimprinted blanks opens up a viable way to high-throughput and low-cost EBL.

Acknowledgments

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