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Nanoscale negative-tone quantized patterning by novel selective electrochemical etching of a nanoimprinted sub-200 nm bimetallic tile array

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Abstract

Quantum lithography (QL) is a revolutionary approach to significantly increase the throughput and lower the cost of electron beam lithography in writing large-area masks with nanoscale features. A major challenge in QL is that its principle can be readily applied to positive- but not negative-tone QL. In fact, negative-tone QL, which is as indispensable as positive-tone QL in practical usage, has not been achieved. Here we propose a new method to overcome the obstacle, and report the first experimental demonstration of negative-tone QL. The new method uses a new type of nanoimprinted blank with the nanoscale tiles made of an aluminum/chromium bi-layer of metals, and a novel electrochemical process that removes only non-tagged quantized tiles of the new blank while keeping tagged ones. The demonstrated negative-tone QL has a 200 nm pitch and 30 nm gap and can be further scaled down to even smaller pitch sizes.

(Some figures may appear in colour only in the online journal)

Quantum lithography (QL), proposed by Pease and Maluf [1], is a revolutionary approach to increase the throughput and lower the cost of scanning electron beam lithography (EBL). In QL, a pre-patterned two-dimensional (2D) tile array with precisely defined edges and narrow gaps is used as a blank, and a low-resolution but high-throughput EBL tool tags a set of selected tiles to form an intended digitized pattern (figure 1). The tagging, which simply exposes a small hole in the resist on top of a selected tile, allows the removal of the entire tagged tile in a subsequent etching by flowing an etchant solution through the hole without fully exposing the resist covering the whole tile, thus drastically reducing the EBL exposure time and significantly relaxing the requirements on EBL tools' beam resolution and beam placement accuracy. To make QL practical, one key obstacle was the lack of a cost-effective method to create pre-patterned quantized blanks. This obstacle has been solved by quantized patterning using nanoimprinted blanks (QUN) [2]. Another key obstacle is that currently only the positive-tone QL is achieved, but not the negative-tone. The negative-tone is also indispensable in practical usage, and it can further reduce exposure time and cost in writing of coarse patterns.

In negative-tone QL (N-QL), the tagged tiles are retained while the non-tagged ones are removed. To achieve this, Pease and Maluf [1] suggested to deposit, through the tagging hole, a copper dot on the tagged chromium tile to form a bimetal electrochemical couple, so that in a subsequent etching the Cu/Cr tile will be retained while the non-tagged tile, which has Cr only, will be removed. But it is unclear whether this suggestion, which is yet to be tested experimentally, would

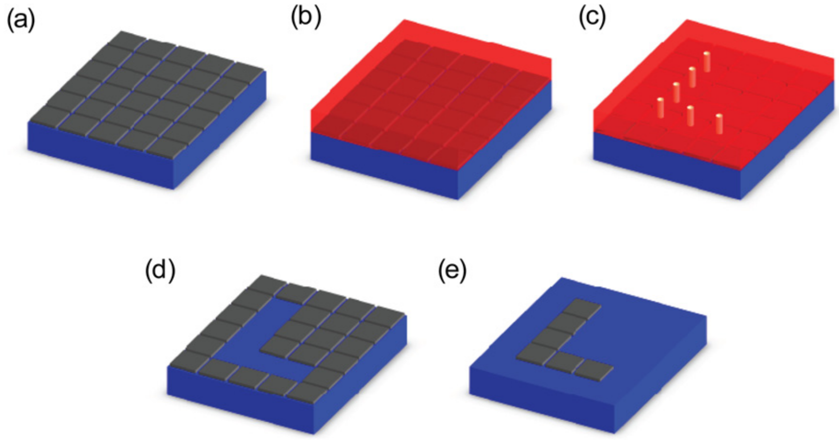

Figure 1. Schematic of positive- and negative-tone QL: (a) a QL blank with a pre-patterned square tile array; (b) EBL resist spin-coated on the QL blank; (c) a set of tiles forming the designed pattern tagged with holes exposed in e-beam resist using EBL; (d) positive-tone QL with tagged tiles removed and non-tagged tiles kept; (e) negative-tone QL with tagged tiles kept on the blank and non-tagged tiles removed.

work properly, since the deposited Cu dot covers only a small part of the Cr tile and is not sufficient to protect the whole Cr tile from being etched. The 'brush fire lithography' proposed by Fulton and Dolan [3] might in principle be used for N-QL, but, in practice, it is impossible to make electrical contacts to all selected tiles to retain them. Here we propose and experimentally demonstrate for the first time a new method to achieve negative-tone QL, which uses a new type of nanoimprinted QL blank with each tile consisting of aluminum/chromium bimetal rather than a single metal, and a novel two-step electrochemical etching.

In our approach, each tile on the negative-tone QL blank substrate has a bimetal structure consisting of a thin aluminum layer on top of the chromium layer rather than a single chromium layer in conventional QL [2]. The chromium in a bimetal tile, which is an electrochemical couple, will be etched away in diluted hydrochloric (HCl) acid; however, any tiles made of a single chromium layer (i.e. without Al layer) will not be etched in the same HCl solution, due to the formation of a thin passivation layer of chromium oxide. Hence, in our negative-tone QUN (N-QUN), we will first use an aluminum etchant to etch away the top Al layer through the tagged holes, and then, after stripping the resist, use diluted HCl solution to etch away all non-tagged tiles which are Al/Cr bimetal electrochemical couples.

In our experiments, the fabricated N-QUN blank consists of a 200 nm pitch array of square Al/Cr bimetal tiles. The substrates of the N-QUN blanks are silicon wafers with a layer of silicon dioxide on top, which electrically isolates the Al/Cr tiles from each other in subsequent electrochemical etchings. The blanks were fabricated by UV-curable nanoimprint lithography [4, 5] with a mold of a narrow-gap mesa [2] (figure 2(a)). The mold was fabricated by combining anisotropic silicon etching [6], self-perfection technology [7] and double cycles of nanoimprinting [8] and etching, and has sub-10 nm gaps between square mesas.

The imprinting was performed using a Nanonex NX-2000 nanoimprinter, a UV-curable nanoimprint resist layer (Nanonex NXR-2000) and a water-soluble sub-layer (Nanonex NXR-3000) (figure 2(b)). After a series of reactive ion etchings, including CHF_3/O_2 plasma to remove residual UV imprint resist layer and O_2 plasma to remove the NX-3000 sub-layer, 20 nm chromium and 10 nm thick aluminum were deposited by e-beam evaporation (figure 2(c)) and a subsequent lift-off process completed the fabrication of the N-QUN blank (figure 2(d)).

Figure 3 shows the schematic of the bimetal structure of the new N-QUN blank and a scanning electron micrograph (SEM) of the fabricated bi-layer blank with a 200 nm pitch array of 170 nm × 170 nm Al/Cr bi-layer tiles and a gap of about 30 nm between tiles. The roughness on the top surface of the tiles originates from aluminum granules formed during the evaporation process.

Before EBL exposure, custom-designed patterns were decomposed into a set of dots according to the grid lattice on the N-QUN blank. Information about the grid lattice, including accurate periods along two major axes and the precise angle between the axes, was measured from the SEM image of the N-QUN blank. The N-QUN blank was spin-coated with 65 nm thick PMMA (molecular weight of 996K) and baked at 160 °C for 12 h to drive out the solvent and ensure a reliable adhesion between the resist and the substrate. The dot dosage used in our EBL exposure was 6 fC, which can reliably form a 20 nm diameter hole in the PMMA resist covering the Al/Cr tiles. The exposed blank was developed in a mixture of three parts 2-ethoxyethanol and seven parts methanol for 7 s, and then rinsed in methanol for 10 s and in isopropanol for 45 s. After EBL exposure and development, holes (∼20 nm diameter) were created in the PMMA resist that covers the tagged tiles, exposing the top aluminum layer of the tagged tiles. Non-tagged Al/Cr tiles were still completely covered by a PMMA resist layer, therefore they were not exposed to the aluminum etchant in the next etching step.

The key steps to achieve negative-tone patterning are shown in figure 4, including (a) EBL exposure and development, (b) aluminum layer etching on tagged tiles, (c) PMMA removal, (d) diluted HCl etching of chromium

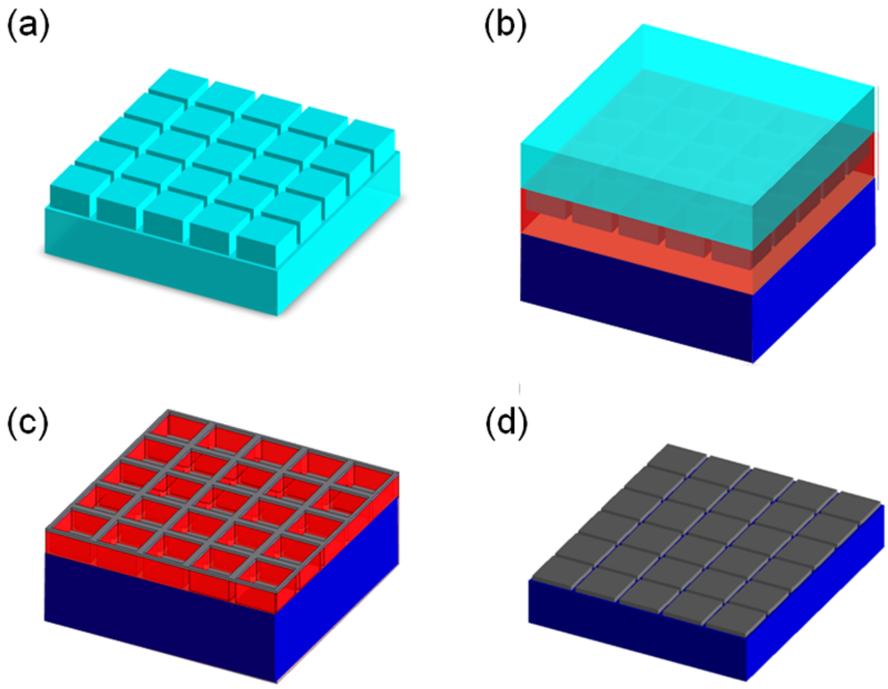

Figure 2. Flowchart of nanoimprint-based fabrication of N-QUN blanks: (a) a mesa mold with narrow gaps fabricated by a series of advanced nanofabrication techniques [2]; (b) UV-curable nanoimprint using the narrow-gap mesa mold; (c) subsequent deposition of chromium and aluminum after removal of residual resist; and (d) completed N-QUN blank after lift-off.

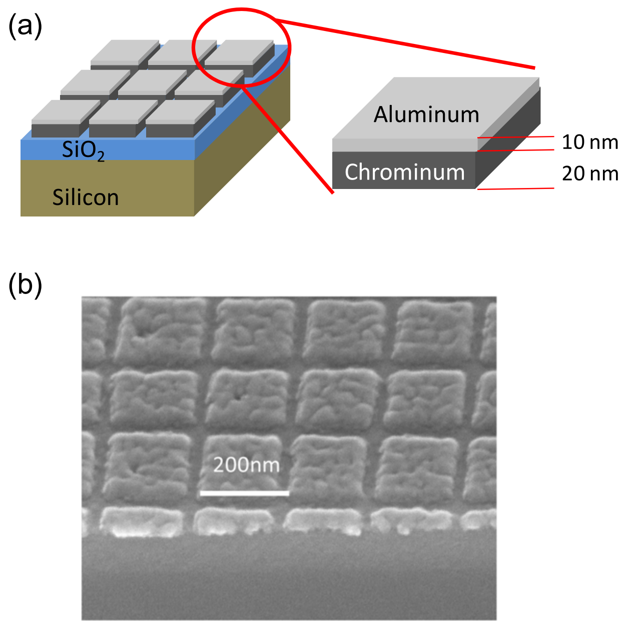

Figure 3. (a) Schematic and (b) SEM picture of bi-layer aluminum/chromium tile in the N-QUN blank.

on non-tagged tiles and (e) removal of aluminum residual for final patterns. The left and right columns in figure 4 show the processing on the tagged and non-tagged tiles, respectively, which removes the non-tagged tiles while retaining the tagged tiles.

Aluminum etchant type D (Transene Company, Inc.) was used in the aluminum layer etching at room temperature for 15 min. The etching time is expected to be long enough to let the aluminum etchant flow through the holes and allow a complete removal of the top Al layer of a tagged tile (figure 4(b)). In this step, non-tagged tiles are protected by the PMMA resist from the aluminum etchant. After rinsing the sample in deionized water, the PMMA resist was removed in acetone, exposing all tagged and non-tagged tiles on the blank (figure 4(c)). In the subsequent diluted hydrochloric acid etching (one part 37% hydrochloric acid with five parts deionized water at room temperature), the chromium in Al/Cr bimetal tiles (i.e. the non-tagged Al/Cr tiles) is etched away fast due to an electrochemical couple effect, while the isolated chromium tiles (i.e. the tagged tiles with Al layer already removed), protected by a thin layer of native chromium oxide layer, remain (figure 4(d)). Finally, after rinsing the N-QUN blank in DI water, the aluminum etchant was used again to remove all aluminum residuals (mainly coming from the Al lift-off from the non-tagged tiles) on the sample surface, leaving a finished N-QUN blank with only the chromium tiles composing designed patterns (figure 4(e)).

Figure 5 shows the experimental results at different steps of negative-tone quantized patterning using nanoimprinted Al/Cr bi-layer blanks. We used letters 'NSL' as examples to demonstrate arbitrary patterning using N-QUN. Figure 5(a) shows the PMMA-covered Al/Cr bimetallic tile blank after EBL tagging and development. The holes in PMMA resist exposed by the tagging e-beam compose an array of dots forming the letter 'L'. Figure 5(b) shows the bimetal tile blank after selective removal of aluminum on tagged tiles and removal of the PMMA resist. Due to the contrast between aluminum and chromium under SEM, an array of letters

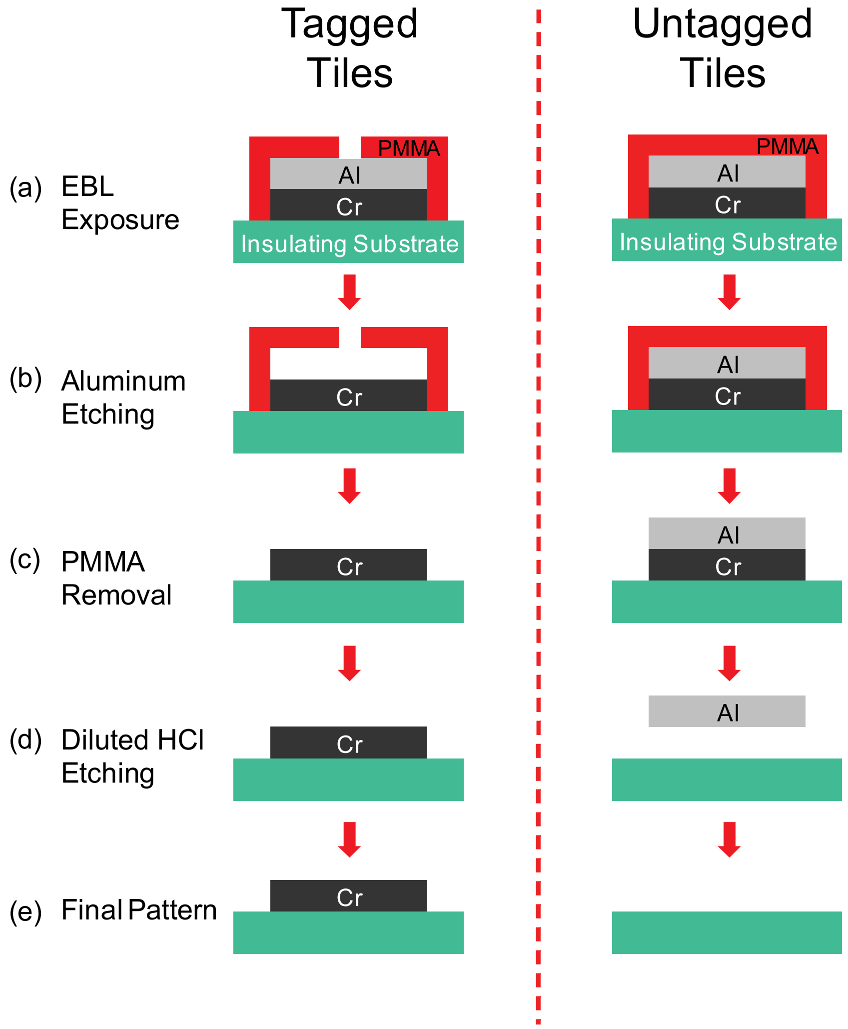

Figure 4. Procedures of post-EBL processing of N-QUN. (a) Tiles after EBL exposure and development, left column: tagged tiles, right column: non-tagged tiles. (b) Etching of aluminum layer on tagged tiles by flowing aluminum etchant through exposed holes. (c) Removal of EBL resist to expose all tiles. (d) Diluted HCl etching at room temperature to remove the chromium layer on non-tagged tiles. Chromium on tagged tiles is protected by a native passivation layer and not etched. (e) Removal of the aluminum residual to achieve final patterns of N-QUN.

'L', composed by tiles with the aluminum layer removed, can be seen on the blank, where the dark tiles are isolated chromium and the bright tiles are original Al/Cr bimetal stacks. Figure 5(c) shows the final pattern, 'L' and 'NSL' letters in Cr tiles, after immersing the exposed blank in diluted HCl, where non-tagged Al/Cr tiles were removed, clearly demonstrating negative-tone QL.

Reducing defects in QUN is of great importance to photomask and nanoimprint mold fabrication. There are two types of possible defects in a N-QUN mask: 'vacancy defect', where a tile is missing in the final pattern; and 'surplus defect', where an unwanted tile is not removed in the blank area. We find that the dominant defect type in the N-QUN masks is the vacancy defect, which is shown by the white arrow in figure 5(c).

The vacancy defect, i.e. a missing chromium tile, is mainly due to the removal of the chromium tile that should be retained in the HCl etching. The undesired removal may be caused by three reasons: (i) short-circuit electrical connection to the adjacent tiles which should be etched (i.e. they are covered by aluminum), (ii) aluminum residuals left on top of the chromium after an incomplete aluminum etching, and (iii) misalignment in e-beam tagging.

To mitigate the first cause above, the fabrication processes should be improved for better blank patterning quality, including improving the quality of the initial mold, reducing the edge roughness of tiles by self-repair methods [7], etc. To remove the second cause, the aluminum thickness, the deposition conditions and/or the aluminum etching time should be optimized, since the aluminum surface roughness, which can adversely affect the flow of the aluminum etchant, is the main reason. The key to reduce the third cause is to accurately match the e-beam scanning coordinates with the tile array lattice and carefully align the electron beam with the center of the tiles. In our experiment, we decomposed our designed pattern into a set of discretized dots according to the measured lattice on the blank tile grid and used alignment marks to help reduce these

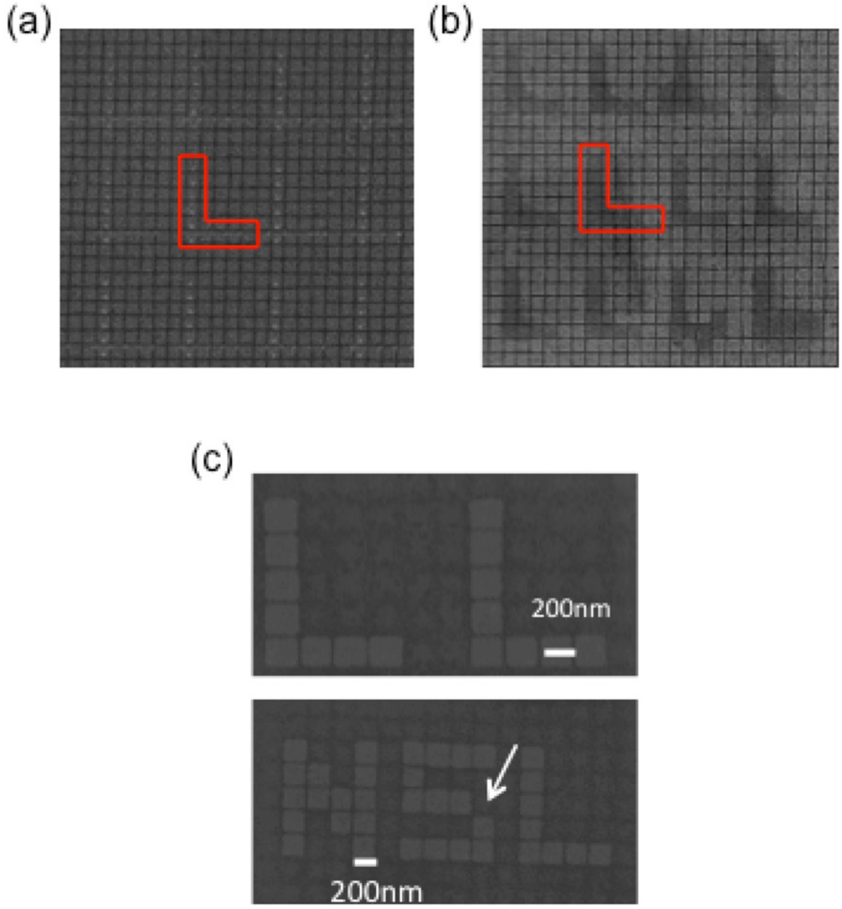

Figure 5. Demonstration of negative-tone quantum lithography using the bi-layer blank: (a) holes in PMMA resist after EBL and development composing an array of 'L' patterns; (b) aluminum on tagged tiles (dark tiles) etched away by aluminum etchant flowing through the holes exposed in PMMA resist, while non-tagged tiles (bright tiles) are unchanged; (c) final 'L' and 'NSL' patterns obtained by negative-tone quantum lithography after a series of wet etchings.

misalignment-induced defects. However, in large-area mask writing applications, *in situ* alignment during the exposure process may be required to avoid alignment error accumulated over a large area.

The surplus-type defects are mainly due to the misplacement of the tagging electron beam, i.e. the misaligned electron beam erroneously tagging a tile that is to be removed. The surplus defects resulting from misaligned e-beam exposure are usually accompanied by vacancy defects, and can be mitigated by the above methods in real applications.

The novel procedure of a series of electrochemical etching processes on the nanostructured heterogeneous stack is crucial to our demonstration of the negative-tone QUN. In-depth study on this nanoscale electrochemical approach may lead to further improvement on quantized patterning and also more potential applications. The key in the electrochemical etching of the Al/Cr bi-layer tiles in diluted HCl solution is to break down the thin passivation layer on the surface of chromium for removing the non-tagged chromium tiles. This passivation layer is formed immediately after chromium is exposed to air, and can protect chromium from being etched in diluted HCl at room temperature. By connecting the chromium with aluminum, an effective electrochemical couple is formed due to their different redox potentials. This chromium/aluminum couple generates a current flowing between the chromium and the HCl solution, which is capable of breaking down the chromium oxide passivation layer and triggering the etching of the chromium tile. Etching of chromium will continue once the passivation layer is broken down even if the aluminum is later electrically disconnected from the chromium. This property ensures a complete removal of chromium in non-tagged tiles and reduces defect density on masks fabricated through N-QUN.

In summary, we proposed a novel bi-layer Al/Cr tile array as the blank for negative-tone quantized patterning using nanoimprinted blanks. The bi-layer Al/Cr blanks were fabricated using UV-curable nanoimprint lithography for making nanoimprint molds at 200 nm node size and, to the best of our knowledge, negative-tone quantized lithography was demonstrated for the first time using this bi-layer blank. Vacancy-type defects are found to be the major defect type in this negative-tone QUN demonstration and several methods are suggested to reduce the defect density.

Acknowledgment

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