3D-fabrication of tunable and high-density arrays of crystalline silicon nanostructures

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Abstract

In this report, a procedure for the 3D-nanofabrication of ordered, high-density arrays of crystalline silicon nanostructures is described. Two nanolithography methods were utilized for the fabrication of the nanostructure array, viz. displacement Talbot lithography (DTL) and edge lithography (EL). DTL is employed to perform two (orthogonal) resist-patterning steps to pattern a thin Si₃N₄ layer. The resulting patterned double layer serves as an etch mask for all further etching steps for the fabrication of ordered arrays of silicon nanostructures. The arrays are made by means of anisotropic wet etching of silicon in combination with an isotropic retraction etch step of the etch mask, i.e. EL. The procedure enables fabrication of nanostructures with dimensions below 15 nm and a potential density of 10¹⁰ crystals cm⁻².

Keywords: nanocrystals, arrays, silicon, anisotropic etching, edge lithography, displacement Talbot lithography

Supplementary material for this article is available [online](#)

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

1. Introduction

Silicon quantum dots (Si-QDs) are currently attracting a lot of attention due to their enormous application possibilities in the fields of quantum electronics, spintronics, photonics, photovoltaics, biology, and nonvolatile memories [1–4]. Porous silicon shows photoluminescence in the visible range and nanostructured silicon is expected to show increased photoluminescence due to quantum confinement [5–8]. The reason for the increased photoluminescence is that the indirect bandgap of bulk silicon could be altered into a direct bandgap in quantum confined silicon structures [9, 10]. Silicon nanocrystals can be synthesized by bottom-up as well as top-down fabrication techniques. Bottom-up methods include plasma based synthesis, solution-based synthesis, sol-gel based synthesis, and

formation of a silicon-rich matrix (for example silicon oxide) followed by a high-temperature anneal [4]. Common top-down methods include mechanical ‘crushing’ followed by chemical etching, and electrochemical etching [4]. Depending on the preparation method, different strategies can be followed to obtain matrix-embedded and free-standing silicon nanocrystals. Most of the reported methods yield silicon nanostructures that are ‘randomly’ positioned, i.e. with a varying distance between adjacent crystals, which can also be considered as non-ordered or irregular arrays. Valenta *et al* [11] fabricated high-density arrays of Si-QDs by e-beam lithography (EBL) followed by Si nano-pillar etching, and a combination of thermal oxidation and hydrofluoric (HF) etching to decrease the size of the structures. In this report, we describe the top-down fabrication of high-density, single-crystalline silicon

tetrahedral nanostructures with dimensions <15 nm by wet-chemical (an)isotropic etching for potential applications in optical sensing and electronics. The advantage of our top-down approach is the fact that the nanocrystals are fabricated in a highly-ordered array, and are not fully embedded in a scaffold. Therefore, they are accessible for making electrical contacts. Previously, Berenschot *et al* [12] reported on the top-down fabrication of single-crystalline silicon nanocrystals with dimensions down to 25 nm by wet-chemical anisotropic etching based on photolithographically machining of nanotetrahedra, with a density of $\sim 10^7/\text{cm}^2$. For optical measurements a high amount of silicon nanocrystals on a given footprint is desirable, which is not achievable with standard UV-contact lithography. We report the development of ordered arrays with high-density nanostructures ($10^{10}/\text{cm}^2$), realized by combining wet-chemical (an)isotropic etching with DTL [13, 14]. Hereby, the amount of nanocrystals is increased to $10^{10}/\text{cm}^2$, while their size is reduced to sub-15 nm.

V-grooves bounded by $\{111\}$ -planes are etched in silicon using Si_3N_4 as mask (pattern generated by DTL). The initial amount of V-grooves is doubled by means of local oxidation of silicon (LOCOS), removal of the Si_3N_4 mask, and a second anisotropic wet etching step. Anisotropic etching in combination with LOCOS has been reported for the fabrication of wedge-shaped emitters [15]. We elaborate on the tuning of the duty cycle of the doubled V-shaped grooves. This doubled V-groove pattern in combination with a second nano-photolithographic line pattern—generated by DTL in an orthogonal fashion with respect to the initial V-grooves—and another two anisotropic wet etch steps yield ordered high-density arrays of crystalline silicon nanostructures. This procedure is explained in detail in section 2, while the fabrication results are shown and discussed in section 3.

2. Experimental methods

In this work, we describe the fabrication of single-crystalline nanotetrahedra (in the following also called ‘quantum dots’ or ‘nanocrystals’). This is done by utilizing a unique combination of two nano-lithography techniques, namely DTL and edge lithography (EL) [16]. It is noted that also the combination of DTL, EBL, corner lithography (CL) [17, 18], EL and silicon anisotropic wet-etching can be used to fabricate such nanocrystals, as shown in the supporting information (stacks.iop.org/JMM/28/044003/mmedia).

We started with a silicon (100) wafer with 10 nm silicon nitride (Si_3N_4) by low-pressure chemical vapor deposition (LPCVD). The wafer was subsequently patterned by the nano-photolithography technique ‘displacement Talbot lithography’ (PhableR 100 C from Eulitha), which enables large-area, periodic sub-micrometer patterns. In short, a layer of photoresist (PFI88—diluted 1:1 in propylene glycol monomethyl ether acetate (PGMEA)) was patterned using different four exposure doses (i.e. 75, 85, 95, 105 mJ), of which experimental details can be found elsewhere [19]. Underneath the resist a bottom layer anti-reflection coating (BARC; AZ Barli-II 200) was present. Each layer, i.e. the BARC and photoresist, has

a thickness of ~ 160 nm. We patterned periodic lines of different line widths over an area of $3 \times 3 \text{ cm}^2$. The resist line width and spacing can be tuned by the exposure dose. With a standard DTL exposure the lithographic duty cycle—defined as the ratio of the line widths of the photoresist ridge and spacer—can only be below 50%. In this work, we elaborate on a method to tune this lithographic duty cycle to values of 50% (and larger) by utilizing metal lift-off and thereby inversion of the original resist pattern.

For transfer of the photoresist pattern into the BARC, the BARC layer was etched with reactive ion beam etching (RIBE) with oxygen (20 sccm, 180 s) prior to etch the underlying Si_3N_4 . The Si_3N_4 was etched by reactive ion etching (RIE) with a CHF_3/O_2 plasma according to the pattern by nano-photolithography (25 Watt, 25 sccm CHF_3 , 5 sccm O_2 , 10 mTorr, 30 s). After stripping the BARC and photoresist with an oxygen plasma, the exposed silicon areas (lines) were converted hydrophobic by 50% hydrogen fluoride (HF) etching (10 s) to remove interfacial SiON/oxide . Subsequently V-grooves were anisotropically etched using aqueous potassium hydroxide (20 wt% KOH at room temperature for 5:30 min, etch rate for Si (100): $20\text{--}25 \text{ nm min}^{-1}$) using the structured Si_3N_4 as an etch mask (figure 1(a)). The flat silicon (100) surface was converted into V-grooves bounded by two $\{111\}$ planes according to the Si_3N_4 pattern [15]. The periodicity of these V-grooves can straightforwardly be doubled. LOCOS at 900°C for 35 min (resulting in 21 nm SiO_2 on Si $\langle 111 \rangle$) was used to protect the already etched V-grooves and the sample was etched in 1% HF (20 s) to strip the thin oxide layer from Si_3N_4 , subsequently in phosphoric acid (85% H_3PO_4 , 140°C , 13 min) to remove the Si_3N_4 and again in 1% HF to dissolve the interfacial layer underneath the Si_3N_4 from the silicon substrate (i.e. to render the surface hydrophobic (figure 1(b))). A 2nd anisotropic etching step was done for 1 min in tetramethylammonium hydroxide (25% TMAH, 70°C ; etch rate for Si (100): $0.3 \mu\text{m min}^{-1}$ and for Si $\langle 111 \rangle$: $15\text{--}20 \text{ nm min}^{-1}$ [20]) to double the V-groove pattern (figure 1(c)). After doubling of the V-grooves the remaining oxide was stripped in 50% HF (figure 1(d)). 19 nm of Si_3N_4 was deposited by LPCVD (figure 1(e)). In fact, although the lithographic duty cycle is below 50%, a 50%–50% duty cycle of the doubled V-groove pattern—defined as the widths of the V-grooves etched in the 1st step (KOH) and 2nd step (TMAH)—can be accomplished by means of optimizing the etching time in TMAH (as shown in figure 1(c)); details will be discussed in section 3.2).

In the second patterning step, the etched V-grooves were first planarized by spinning a BARC layer. Then a PFI88 resist layer was spin coated. Patterning with 90° rotation with respect to the length direction of the V-grooves was performed by DTL, followed by a modified lift-off procedure using a 10 nm e-beam deposited Cr layer (figure 2(a)). Details of this modified lift-off procedure will be given below. For the fabrication of periodic Si nanocrystals based on two orthogonal exposures by DTL, it is essential to achieve a lithographic duty cycle of 50% in this second patterning step. In the case of duty cycles other than 50%, the nanocrystals will not be equally distributed and two nanocrystals will be formed in

Figure 1. Schematic representation of the realization of doubled V-grooves [15]. (a) Patterning of the silicon (100) wafer with 10 nm Si_3N_4 by DTL, and KOH etching of V-grooves using Si_3N_4 as mask; (b) LOCOS followed by stripping of Si_3N_4 ; (c) doubling of the V-grooves using TMAH; (d) oxide stripping (e) LPCVD of Si_3N_4 .

Figure 2. Schematic of the Si nanocrystal fabrication. (a) doubled V-grooves with Si_3N_4 /Cr-strips on BARC, 90° rotated with respect to the V-grooves; (b) BARC and Si_3N_4 layer patterning by RIE; (c) stripping of Cr and BARC; (d) anisotropic etching in KOH (e) retraction of Si_3N_4 by EL; (f) LOCOS; (g) selective etching of Si_3N_4 ; (h) anisotropic etching in KOH creating silicon nanocrystals; (i) zoom-in on the Si nanocrystals embedded in SiO_2 from three sides bounding by $\{111\}$ planes.

Figure 3. Lithographic duty cycle $<50\%$ for DTL-standard ((a)–(c)) and $\geq 50\%$ DTL-Cr ((a), (d)–(g)).

close proximity to each other which can even hinder the formation of nanocrystals if the in-between distance is too small. A modified chromium lift-off method is introduced to achieve the required duty cycle. After the second DTL-patterning step and this lift-off method, RIE was used to pattern the Si_3N_4 using the same etch conditions as after the first DTL patterning step (figure 2(b)). After stripping the Cr-mask in standard Cr etchant, stripping the BARC layer in 100% HNO_3 , (figure 2(c)) and removal of the interfacial SiO_2 layer in 50% HF for 15 s, the patterned Si_3N_4 was utilized as mask for anisotropic etching of the exposed silicon areas in KOH (20 wt% at room temperature for 5:30 min, etch rate of Si (100): 20–25 nm min^{-1}) (figure 2(d)). New $\{111\}$ planes were thereby released under the Si_3N_4 mask. The etching is terminated by the $\{111\}$ planes that are pinned under the vertex which is formed by the top of the first etched and by silicon nitride protected V-grooves. The second $\{111\}$ planes are originating from the pinning of the (111) plane with the bottom line of the first etched V-grooves [12]. We then continued the fabrication with so called EL, i.e. retraction of Si_3N_4 [16]. For this isotropic etch, 50% HF was used because of the high selectivity with respect to silicon (figure 2(e)). The silicon nitride

pull-back process strongly depends on the geometry of the anisotropically etched silicon. The size of the nanocrystal that will later be formed is determined by the length of the pull-back of silicon nitride and the slow etch rate of Si $\{111\}$. In this work the pull-back length was ca. 10 nm. The exposed Si $\{111\}$ planes were locally dry oxidized (LOCOS) at 1050 °C for 1 min, resulting in an oxide thickness of $13.9 \text{ nm} \pm 0.5 \text{ nm}$ (measured on a (111) Si dummy wafer). A dry-oxidation temperature of 1050 °C was chosen because conformal oxidation will occur at convex apices. Temperatures lower than 960 °C will cause sharpening of the apices where higher temperatures than 1050 °C results in rounded apices [21]. Then the Si_3N_4 was selectively removed in H_3PO_4 (85%, at 140 °C for 25 min, etch rate of Si_3N_4 : 0.7 nm min^{-1} ; native oxide was stripped in 1% HF in advance) (figures 2(f) and (g)). The last (4th) anisotropic etching step was again done in 20 wt% KOH at room temperature for 180 s and resulted in the creation of the silicon nanocrystals (figures 2(h) and (i)). It is important that the native oxide was properly removed before etching of silicon, otherwise the etch process will not start in KOH. The resulting structures are freestanding SiO_2 patterns from LOCOS, with the silicon nanotetrahedra embedded in the tips.

Figure 4. SEM images of typical line patterns defined in the photoresist (with BARC) by displacement Talbot lithography for exposure doses of (a) 75 mJ (spacer width: 130 ± 14 nm, PR line width: 117 ± 13 nm), (b) 85 mJ (spacer width: 148 ± 8 nm, PR line width: 96 ± 7 nm), (c) 95 mJ (spacer width: 161 ± 5 nm, PR line width: 86 ± 7 nm) and (d) 105 mJ (spacer width: 167 ± 7 nm, PR line width: 77 ± 11 nm). (scale bar: 200 nm).

Figure 5. SEM images of the line pattern in PFI88-Barli-II (a) prior and (b) post to treatment with RIBE for 3.5 min. The exposure dose of the photoresist was 75 mJ which corresponds to a spacer width of 130 ± 14 nm and PR line width of 117 ± 13 nm. After RIBE the measured spacer width was 167 ± 7 nm and the PR line width was 77 ± 11 nm. (scale bar is 200 nm).

The tetrahedral nanocrystals are surrounded from three sides by oxide.

Some aspects of the 2nd line patterning step have to be highlighted, in particular how a 50%–50% duty cycle can be obtained. The following section and figure 3 clarify the differences between the first (standard) DTL line patterning step in comparison with the 2nd line patterning step based on DTL and Cr lift-off, a combination that yields an inversion of the original resist pattern.

In figures 3(a)–(c) the standard DTL procedure is shown: post to exposure and development (figure 3(a)), directional

etching of the BARC layer (figure 3(b)) is performed, followed by RIE of Si_3N_4 and stripping the BARC and PFI88 (figure 3(c)). In this way only lithographic duty cycles <50% can be obtained. In order to have the preferred 50%–50% duty cycle, a combination of DTL and metal lift-off is required, as shown in figures 3(d)–(g). This so-called DTL-Cr procedure is utilized for generation of the 2nd line pattern. For the definition of the 2nd line pattern BARC (AZ Barli-II 200) and photoresist (PFI88–diluted 1:1 in PGMEA) are spin-coated using the same parameters as for the first nanolithographic patterning step (i.e. 1st V-groove definition step). The phase shift-line

Figure 6. Tuning of the duty cycle of the second generation V-grooves formed by TMAH. (a) shallow TMAH etched V-grooves after 1 min etching in TMAH; (b) duty cycle of 50% after 6 min of TMAH etching with corresponding SEM images of the V-grooves in top view, with initial line and space of 117 nm and 130 nm, respectively (c) and as a cross section ((d) and (e)).

Figure 7. Cross-sectional scheme (a) and SEM image (b) of doubled V-grooves with Si_3N_4 layer with alternating rounded and sharp grooves after two DTL steps. KOH etched V-grooves have a rounded bottom due to LOCOS while TMAH etched V-grooves are sharp. Scale bar is 200 nm.

mask with a periodicity of 500 nm is rotated 90° with respect to the first pattern and the resist is exposed at 1 mW with a dose of 105 mJ, the target cycle is 20 s with one precycle, a polarizer is used, the DTL-range is $3 \mu\text{m}$ and the gap between the wafer and the mask is $\sim 65 \mu\text{m}$. Subsequently, the resist is baked for 1 min at 110°C and developed in Olin OPD 4262 for 1 min (figure 3(a)). After development a flood exposure is performed to make the remaining resist pattern dissolvable and thus applicable for a lift-off procedure. Then a 10 nm thin Cr layer is deposited using e-beam evaporation (figure 3(d)) and a lift-off procedure is performed in OPD 4262 in an ultrasonic bath for 20 min (figure 3(e)). The remaining BARC layer is removed by dry etching with an N_2 plasma for 9:30 min [19] (figure 3(f)). With this Cr lift-off sequence a duty cycle of 50% of the line pattern can be achieved, whereas direct utilization of the BARC/photoresist pattern does not result in such lithographic duty cycle. The line pattern is inverted by utilizing the Cr lift-off procedure, which means the areas where the photoresist originally remained are etched. To summarize, a duty cycle of 50% and larger can only be achieved with this

DTL-Cr procedure, and not with the standard DTL line patterning step that directly utilized the photoresist pattern (see results and discussion part).

3. Results and discussion

3.1. Fabrication of line patterns of photoresist

In figure 4, scanning electron microscopy (SEM) images of line patterns in the photoresist with 250 nm periodicity are shown for different exposure doses. The variation of the exposure dose enables the tuning of the lines and their spacing. The photoresist lines cannot be wider than half of the period since an underexposure is not possible because the resist pattern will not become fully opened in that case. Overexposure on the other hand is possible, resulting in smaller lines and wider spacings. For all used exposure doses steep, vertical resist patterns were observed independent of the development time.

The transfer of the line pattern in the photoresist layer into the BARC was done by RIBE (5 sccm Ar, 10 sccm O_2 ,

Figure 8. Effect of the thickness of the evaporated chromium layer on the outcome of the alternative lift-off procedure prior to BARC etching: (a) 20 nm shows cracks (indicated with arrows), (b) 10 nm (no defects/cracks in metal pattern). (c) Top view image after RIE etching of the BARC layer with N_2 . The underlying V-grooves from the 1st DTL patterning step (with 90° rotation with respect to the lines from the 2nd DTL step) are clearly visible. (d) Corresponding cross-section. Scale bar in (a) and (b) is 500 nm, in (c) $2\ \mu\text{m}$ and in (d) 200 nm.

50–55 mA). RIBE results in widening of the spacer width and decreased resist ridge widths (see figure 5). The photoresist ridge width defined in the photoresist/BARC layers decreased linearly with ca. $17.5\ \text{nm min}^{-1}$ and correspondingly the spacer widths increased with this rate. For the 250 nm periodicity line patterns an etch rate (in vertical direction) of $35 \pm 4\ \text{nm min}^{-1}$ was found for the photoresist and $44\ \text{nm min}^{-1}$ for the BARC.

3.2. Fabrication of V-grooves by anisotropic wet etching

The first generation of V-grooves is aligned with respect to the crystal orientation of Si [22]. In figure 6 the tuning of the duty cycle of the doubled V-grooves is shown schematically and with corresponding SEM images. The photoresist pattern cannot be 1:1 transferred into the BARC layer as discussed above which means that the ridges will always have a smaller width compared to the spacings after RIBE. However, a 50%:50% duty cycle of the doubled V-grooves—i.e. the ratio of the widths of the V-grooves etched in the first step (KOH) and second step (TMAH)—can still be achieved by tuning of the $\{111\}$ planes. For exposure of the photoresist a dose of 75 mJ was used resulting in spacings of 130 nm and line widths of 117 nm. The depth of the second generation V-grooves and thus the duty cycle of the etched V-grooves can be controlled

by the etching time of the TMAH-step. A short TMAH etch of 1 min resulted in quite shallow second V-grooves. We tuned the duty cycle of the zig-zag structures to 50% by an additional 5 min of etching.

Upon more detailed inspection of the doubled V-groove pattern, it becomes clear that the shape of the bottom of the V-grooves differs between the first anisotropic and second etching step, which is due to the LOCOS step that is only applied to the first generation V-grooves. From the high-resolution SEM image of the cross section of a sample with a conformal deposited Si_3N_4 layer (figure 7) it can be seen that every first generation groove (KOH-etched) has a rounded silicon mold, in contrast to second generation (TMAH etched) V-grooves with ‘atomically’ sharp $\langle 111 \rangle$ plane intersections next to it. We attribute this to the LOCOS step prior to the doubling of the V-grooves, which causes rounding of anisotropically etched V-grooves in silicon [23].

3.3. Fabrication of orthogonal line patterns

From the SEM images in figure 5 it can be seen that a duty cycle of 50% cannot be achieved with solely PFI88-Barli-II, because the line width of the remaining photoresist after etching of the underlying BARC layer becomes too narrow

Figure 9. (a) Expected geometry after the third KOH etching step and (b) SEM image of etched anvil structures after the retraction EL of 7.9 nm Si_3N_4 (90° rotated view compared to (a) and 45° tilted). White dotted lines indicate the amount of retraction. Scale bar is 20 nm.

Figure 10. SEM image of silicon nanocrystals embedded from three sides in the SiO_2 scaffold. Cr was deposited prior imaging to avoid charging. Scale bar is 20 nm.

(i.e. a duty cycle below 50%). However, as explained in the Experimental Methods section, it is important to have a duty cycle close to 50% for the formation of an ordered array of Si nanocrystals. Therefore, for the second DTL step an alternative lift-off procedure with Cr is utilized prior to BARC etching.

In this case the lift-off procedure has to be applied on top of the BARC layer. This implies that the ‘conventional’ procedure—i.e. a combination of lithography, deposition of a thin metal film and ultrasonic lift-off in acetone—cannot be used, since the BARC layer will dissolve in acetone upon exposure

of the photoresist to this solvent. In order to avoid BARC dissolution, an alternative lift-off procedure is exploited. In fact, in photoresist developer OPD4262 the BARC layer does not dissolve. Moreover, if the patterned PFI88 layer undergoes a flood UV-exposure prior to metal deposition this PR is dissolvable in OPD4262.

In order to have a good outcome of this alternative lift-off procedure, several aspects have to be taken into account with respect to the deposition method, as well as the type of metal to be used. The deposition should be directional, for which reason evaporation is preferred. The metal should not

Figure 11. TEM images of final nanocrystals. At some locations fully developed sub-15 nm nanocrystals have been formed (c), while at other locations some silicon is still present in the ‘stem’ of the 3D silicon oxide mask ((a) and (b)).

dissolve in OPD (thus aluminum is not suitable) and should have a high etch selectivity in the RIE-steps of the BARC as well as the Si_3N_4 (see figures 3(f) and (g)). Moreover, it should also be possible to selectively remove this metal with respect to the PFI88 and BARC. Only an evaporated chromium film fulfills these requirements, and is hence applied (deposition parameters on a flat surface: Balzers BAK 600 system, pressure 10^{-6} mTorr, current 20 mA, deposition rate 0.02 nm s^{-1}).

It is found that the thickness of the evaporated Cr film is important. If a too thick film is deposited, i.e. 20 nm, cracks appear in the Cr (figure 8(a)), resulting in masking failures and hence in an improper transfer of the line pattern into the BARC and/or Si_3N_4 . Such undesired cracks are not observed in a 10 nm Cr film (figure 8(b)), and this thickness acts as a perfect film in the alternative lift-off procedure. The SEM images of figures 8(c) and (d) are taken after lift-off of Cr and after RIE etching of the BARC layer with N_2 .

3.4. Fabrication of nanocrystals

In order to obtain nanocrystals after the second DTL nanolithography step, this second line pattern has to be transferred into the underlying Si_3N_4 . A crucial step is to fully open the bottom of the V-grooves in the directional RIE etching step of LPCVD Si_3N_4 . Due to a perfect conformal Si_3N_4 layer in the V-grooves (black arrows in figure 9(a)) the thickness of the nitride is 1.73 times the thickness (t) deposited on a $\{111\}$ -plane (figure 7(a)). Therefore an etch factor of 2 was applied in the RIE Si_3N_4 etching step followed by the third KOH etching step.

To check the etch rate of Si_3N_4 before retraction EL, plain dummy wafers were added to the LPCVD process of Si_3N_4 . Except for the patterning step, similar processes were performed to these dummy wafers as to the device wafers. Just before the retraction etch of the device wafers, a dummy wafer was etched to determine the Si_3N_4 etch rate in 50% HF, which was found to be $7.9 \pm 0.1 \text{ nm min}^{-1}$ (5-point measurement, 10 mm edge exclusion). Figure 9(b) shows the result after the third KOH etching step and a 7.9 nm silicon nitride retraction etching step. The height of the anvil structures is determined by half the depth h of the doubled V-groove pattern (see figures 9(a) and also 2(d)). Based on the geometry we expect $h = 60 \text{ nm} / \tan(35.3^\circ) = 85 \text{ nm}$, thus a theoretical anvil height of 42.5 nm. This calculated value matches well with the measured height of the anvil as determined from the SEM image taken at sample tilt angle of 45° . Thus, the height of the realized anvil is $\cos(45^\circ) \times 57 \text{ nm} = 40 \text{ nm}$. While the result is not perfect in terms of achieved duty cycle ($L/(L+S) \times 100\% > 50\%$), the image indicates that a duty cycle of around 50% is within reach with the DTL-Cr procedure. Note also that a slightly enhanced retraction (r^1) is observed at the apices compared to the retraction (r) along the edges. A SEM image of the final devices with silicon nanocrystals embedded from three sides in the SiO_2 scaffold is shown in figure 10. Retraction of the silicon nitride was 9.9 nm. The final structures are investigated by transmission electron microscopy (figure 11). The crystalline Si surrounded by amorphous SiO_2 can be clearly seen by TEM. TEM analysis was performed at different locations along the edge of a piece of the sample. The analysis shows that at some locations fully developed sub-15 nm nanocrystals have been formed (figure 11(c)), while at other locations some silicon is still present in the 'stem' of the 3D silicon oxide mask (figures 11(a) and (b)). We attribute these remains to an incomplete removal of the Si_3N_4 in step (g), figure 2, which are also visible in figure 10. A consequence of these residues is a local masking of the convex corner of the stem. The $\{111\}$ crystal planes (d-spacing is 0.313 nm) can clearly be seen, initially not only in the apex but also in the 'stem' of the 3D silicon oxide mask.). Note also the apparent thinning of the silicon in the 'stem' region due to the final anisotropic etching step (in 20% KOH solution at room temperature), indicated by the 4.7 nm in figure 11(a). This thinning is indicative of a finite etch rate of about $0.5\text{--}1 \text{ nm min}^{-1}$ in the $\langle 111 \rangle$ -direction. Note also that the expected tetrahedral crystals appear to be etched from the apex, indicated by the triangles with side length of about 8 nm

in figure 11. It appears that the silicon oxide (dry thermally grown at 1050°C) mask, which was slightly thinned in 1% HF and 85% H_3PO_4 etching steps has been opened at the apex. This could indicate that at these growth conditions the initial oxide at the apex is slightly thinner than the expected 13.9 nm based on the thickness at the $\{111\}$ -planes. Further research into the exact oxide coverage of sharp tips at these growth conditions is needed to further clarify the TEM observations.

Conclusion

In conclusion, we have developed a procedure for the fabrication of ordered arrays of high-density crystalline silicon nanostructures by combining DTL and EL with anisotropic wet etching (employing KOH and TMAH) on wafer scale. The density of the silicon nanostructures is ca. $10^{10}/\text{cm}^2$, which is a factor >1000 higher than previously reported tetrahedral structures. TEM analysis shows that sub-15 nm size has been achieved at some locations in the array, while at other locations some silicon remained in the 'stem' of the freestanding nanostructures. The cause of this issue has been discussed and can be addressed by optimization of the selective nitride etching process in combination with the doubled V-groove duty cycle.

In future we will study the combination with CL [17, 18] and directional deposition methods to explore the possibility to individually contacting the crystalline silicon nanostructures in a wafer-scale process. High-density arrays in combination with individual contacting may find application in new optical sensing as well as electronic system concepts.

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References

- [1] Janz S, Löper P and Schnabel M 2013 Silicon nanocrystals produced by solid phase crystallisation of superlattices for photovoltaic applications *Mater. Sci. Eng. B* **178** 542–50
- [2] Wang G, Ji J and Xu X 2014 Dual-emission of silicon quantum dots modified by 9-ethylanthracene *J. Mater. Chem. C* **2** 1977–81

- [3] Shcherbyna L and Torchynska T 2013 Si quantum dot structures and their applications *Physica E* **51** 65–70
- [4] Dohnalová K, Gregorkiewicz T and Kusová K 2014 Silicon quantum dots: surface matters *J. Phys.: Condens. Matter* **26** 173201
- [5] Canham L T 1990 Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers *Appl. Phys. Lett.* **57** 1046–8
- [6] Trwoga P F, Kenyon A J and Pitt C W 1998 Modeling the contribution of quantum confinement to luminescence from silicon nanoclusters *J. Appl. Phys.* **83** 3789–94
- [7] Hafsi N et al 2015 Photoluminescence from silicon nanocrystals embedded in silicon nitride fabricated by low-pressure chemical vapor deposition followed by high-temperature annealing *J. Appl. Phys.* **117** 063105
- [8] Walters R J, Bourianoff G I and Atwater H A 2005 Field-effect electroluminescence in silicon nanocrystals *Nat. Mater.* **4** 143–6
- [9] Dohnalova K et al 2013 Surface brightens up Si quantum dots: direct bandgap-like size-tunable emission *Light Sci. Appl.* **2** e47
- [10] Wilson H F, McKenzie-Sell L and Barnard A S 2014 Shape dependence of the band gaps in luminescent silicon quantum dots *J. Mater. Chem. C* **2** 9451–6
- [11] Valenta J, Juhasz R and Linnros J 2002 Photoluminescence spectroscopy of single silicon quantum dots *Appl. Phys. Lett.* **80** 1070–2
- [12] Berenschot J W et al 2009 Chemically anisotropic single-crystalline silicon nanotetrahedra *Nanotechnology* **20** 475302
- [13] www.eulitha.com/fileadmin/images/PhableR_100/eulitha_phabler100.pdf
- [14] Solak H H, Dais C and Clube F 2011 Displacement Talbot lithography: a new method for high-resolution patterning of large areas *Opt. Express* **19** 10686–91
- [15] Hashiguchi G et al 1993 Wedge-shaped silicon emitter fabricated by new method *Japan. J. Appl. Phys.* **32** 6291
- [16] Zhao Y et al 2009 Sub-10 nm silicon ridge nanofabrication by advanced edge lithography for NIL applications *Microelectron. Eng.* **86** 832–5
- [17] Sarajlic E et al 2005 Fabrication of 3D nanowire frames by conventional micromachining technology *The 13th Int. Conf. on Solid-State Sensors, Actuators and Microsystems, 2005. Digest of Technical Papers. TRANSDUCERS '05*
- [18] Berenschot E J W et al 2012 3D nanofabrication of fluidic components by corner lithography *Small* **8** 3823–31
- [19] Le-The H et al 2016 Shrinkage control of photoresist for large-area fabrication of sub-30 nm periodic nanocolumns *Adv. Mater. Technol.* **2** 1600238
- [20] Berenschot J W, Jansen H V and Tas N R 2013 Fabrication of 3D fractal structures using nanoscale anisotropic etching of single crystalline silicon *J. Micromech. Microeng.* **23** 055024
- [21] Kozhummal R et al 2012 Fabrication of micron-sized tetrahedra by Si(111) micromachining and retraction etching lithography *J. Micromech. Microeng.* **22** 085032
- [22] Vangbo M et al 1996 Precise mask alignment to the crystallographic orientation of silicon wafers using wet anisotropic etching *J. Micromech. Microeng.* **6** 279–82
- [23] Kim G et al 2002 Replication molds having nanometer-scale shape control fabricated by means of oxidation and etching *J. Nanosci. Nanotechnol.* **3** 55–9