Creating nanostructures on silicon using ion blistering and electron beam lithography

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Abstract
We have investigated the patterning of silicon surfaces using ion blistering in conjunction with e-beam lithography. Variable width (150–5000 nm) trenches were first written in 500 nm thick PMMA resist spin coated on silicon, using an electron beam. Next, 10 keV H\(^+\) ions were implanted to various fluences through the masks. The resist was then removed and the samples were rapidly thermally annealed at 900 °C. The resulting surface morphologies were investigated by atomic force microscopy. In the wider trenches, round blisters with 600–900 nm diameter are observed, which are similar to those observed on unmasked surfaces. In submicron trenches, there is a transition in morphology, caused by the proximity to the border. The blisters are smaller and they are densely aligned along the trench direction (‘string of pearls’ pattern). Unusual blister geometries are observed in the narrowest trenches (150 nm) at higher H doses (≥1 × 10\(^{17}\) H cm\(^{-2}\))—such as tubular blisters aligned along the trench. It was also found that for H doses of ≥6 × 10\(^{16}\) H cm\(^{-2}\) the surface swells uniformly, which has implications for the blistering mechanism. The prospects for accomplishing ion cutting, layer transfer and bonding of finely delineated patterns of silicon onto another material are discussed in the light of the above results.

1. Introduction
Conventional photolithography has been widely used in the fabrication of microelectronic devices. The main advantage of this technique is its capability for writing arbitrary patterns on a large surface at low cost. More recently, the fabrication of nanoscaled structures has been under rapid evolution. Deep submicron lithography techniques such as e-beam and x-ray lithography are theoretically capable of achieving few nanometre minimum feature sizes because they overcome the fundamental limit of photolithography imposed by the wavelength of visible and UV light [1].

Ion implantation through masks is used in most of the localized doping operations in the fabrication of microelectronic and photonic devices. In addition, ion implantation has also been used more recently in the preparation of silicon-on-insulator (SOI) wafers containing a high quality buried SiO\(_2\) ‘box’ layer with excellent interface properties [2]. This new SOI fabrication process involves ‘ion cutting’ [3, 4], a process utilizing hydrogen ion implantation as an atomic scalpel to cut a submicron slice of silicon and bond it to a thermally oxidized substrate. Typically, H ions of tens of keV are implanted to fluences of several 10\(^{16}\) H cm\(^{-2}\) in a Si
wafer, where they produce a high density of various radiation defects, whose depth profile peaks close to (slightly below) the mean ion projected range, \( R_p \) (hundreds of nm) [5]. Most H atoms attach to the Si dangling bonds, and many vacancy–H (\( \text{V}_i, \text{H}_n \)) and interstitial–H (\( \text{I}_i, \text{H}_n \)) complexes are formed [6, 7]. These include platelets, which are sub-nm interstices between pairs of \( \{100\} \) or \( \{111\} \) planes whose dangling bonds are passivated with H [8]. Upon annealing at several hundred degrees, platelets grow by Ostwald ripening [9] and by capture of wandering H atoms released by other defects [6, 7]. \( \text{H}_2 \) evaporates into the voids, the pressure builds up, at some point the platelets agglomerate by inter-platelet fracture, and finally the surface lifts off, showing micron-sized pressurized blisters and craters of exploded blisters (\( \sim R_p \) deep) [10, 11]. Examples of blisters and craters can be seen in figure 1 for instance. But if, after the implantation of a wafer ‘A’, a thermally oxidized wafer ‘B’ is directly bonded [12] to wafer A, under a subsequent thermal anneal the surface of A will be prevented from blistering and, instead, a whole top slice of wafer A will split off by inter-platelet fracture. The slice will be left bonded on B, thus forming an SOI structure. Ion cutting has since been found to be applicable to many other materials, allowing many combinations of heterogeneous integration [13].

The question arises of whether blistering and ion cut/layer transfer can be usefully combined with nanolithography. Specifically, if a wafer A is H ion implanted through a mask, the mask removed, and that wafer bonded to wafer B and annealed, will a thin lace-like layer of A material, faithfully reproducing the mask pattern and with vertical sidewalls, be transferred to B? One can see that this process requires fracture not only in a plane parallel to the surface but also perpendicularly to that surface. To clarify the issues, let us then list what mechanical processes are involved in each case.

- **Blistering involves**: fracture parallel to surface and plastic deformation.
- **Cratering involves**: fracture parallel to surface and more or less perpendicular to it (as seen in cross section micrographs [14]).
- **Classic ion cut requires**: parallel fracture only.
- **Patterned ion cut requires**: parallel fracture and perfectly perpendicular fracture.

The fracture geometry will be determined by the local mechanical response to the stress field due to both the gas pressure and the radiation damage, taking into account the relevant boundary conditions imposed by the unimplanted regions and/or the bonded wafer B. Stress field and local mechanical properties are both influenced by the ion implantation parameters (energy, flux and fluence, temperature), and they vary during the thermal treatment [15]. What happens, then, when the mask features become smaller than a characteristic length such as the typical blister size or the ion range? Mask openings on the order of the blister size would give a transferred layer with an aspect ratio, \( \text{AR} = \text{height/width} \), of the order of 1/10, while a feature size of the order of the implant depth would allow reaching an AR \( \sim 1/1 \).

As a first step towards the elucidation of these questions, we investigate here in what way blistering and cratering are affected by implanting H ions through variable width trenches. Besides the application to ion cutting, silicon surface patterning, using blistering confined to finely delineated regions, can have an interest of its own. In order to reach as small dimensions as possible, we use very low energy H ions of 5 keV/atom, having an \( R_p \) of 75 nm [16]. The trenches studied have nominal widths varying from 5 \( \mu \)m (AR \( \sim 1/67 \)) to 150 nm (AR \( \sim 1/2 \)).

2. **Experimental procedure**

The 1 cm\(^2\) samples were cleaved from wafers of single side polished, phosphorus-doped (>3 \( \Omega \) cm), (001) oriented silicon. They were spin coated with 500 nm of PMMA resist, and trenches were traced using an electron beam lithography method at the Université de Sherbrooke nanofabrication facilities. Exposure to the electron beam was made in a Zeiss SUPRA 55VP field emission gun scanning electron microscope (SEM) equipped with the nanometre pattern generation system (NPGS) from JC Nabity Lithography Systems, using an e-beam current of 22.5 pA and an acceleration voltage of 20 kV.
On the same sample, eight kinds of trenches were prepared with nominal widths of 5000, 2000, 1000, 800, 600, 400, 200, and 150 nm. (For brevity, only four of the eight sets of data are fully reported in this paper.) The exposure dose was 125 $\mu$C cm$^{-2}$ for trench widths of 400 nm and up. For trenches of 200 and 150 nm width, the dose was 145 $\mu$C cm$^{-2}$ and 190 $\mu$C cm$^{-2}$, respectively. These doses were chosen to make sure that no resist remains at the bottom of the trenches after development and to obtain a good verticality of the sidewalls, which is important to avoid beam shadowing effects. To develop the resist, samples were immersed in a 9:1 isopropyl alcohol–water solution during 60 s, and then blown dry with nitrogen. Figure 2 shows a SEM image of the smallest trenches ($\approx 150$ nm). Earlier similar work on fabrication of PMMA structures used for ion masking was reported in [17].

The samples were implanted with 10 keV molecular hydrogen (H$_2^+$) at fluences between 2 and $2 \times 10^{10}$ H atoms cm$^{-2}$ at room temperature (RT). Again to avoid shadowing effects, the implantations were performed at normal incidence, using the tightly collimated beam (±10 nm) of the custom-built low energy ion implanter at INRS-EMT. Another worry was charging of the insulating PMMA by the ion beam. However, it has been shown that H ion bombarded thin polymer films do not charge up, contrary to thick samples. This is due in part to ion-induced graphitization, as witnessed by a loss of hydrogen and by a decrease in the water contact angles, and possibly also to dielectric breakdown through the films [18]. Indeed, in the results to be shown (sharpness of boundaries, depth of craters), there is no evidence that the ion beam was steered away from the sidewalls or slowed down to lower energy. On the other hand, it is important to take into account that PMMA is etched by energetic H ions. Therefore, the resist must be thick enough to stop 5 keV/atom H ions not only at the start of the implantation but throughout the process. To ensure stoppage, the rule-of-thumb [19] is that the resist thickness, $t_r$, should exceed the critical value $R_p + 4.3 \Delta R_p$, where $R_p$ and $\Delta R_p$ are the projected range and its standard deviation. From the calculated values [16] of $R_p$ (127 nm) and $\Delta R_p$ (37 nm) for H ions at 5 keV in PMMA resist (1.1 g cm$^{-3}$), it was estimated that a 300 nm thick resist was sufficient. However, to take resist erosion into account, the initial thickness was chosen as 500 ± 50 nm (measured). Figure 3 shows the remaining thickness after different H atom fluences. For the highest doses, the thickness is less than the critical thickness but it still seems adequate to effectively block the hydrogen ions.

After the implantation, the PMMA resist was removed with acetone in an ultrasonic bath. Even after long acetone cleaning treatments, some traces of resist have been observed particularly at the border of the trenches. The samples were then further treated with an oxygen plasma for 10 min. Finally, the samples were annealed at 900 °C for 30 s (ramp-up time of 3–4 s) in nitrogen using an Infrared Rapid Thermal Annealing (IR RTA) furnace (HeatPulse 610). The surface topography of the samples was then observed by atomic force microscopy (AFM) in contact mode with a Nanoscope IIIa (Digital Instruments). The morphology and the blister density were quantified and statistically analysed using the WSxM program [20].

### 3. Results and discussion

#### 3.1. Blistering at 5 keV on free Si surfaces

In order to provide a reference for comparison, the main features of silicon blistering by low energy H ions must be given. At 5 keV the threshold dose is $1.5 \times 10^{10}$ H cm$^{-2}$, and the maximum blister density is attained for $2 \times 10^{10}$ H cm$^{-2}$, as illustrated in figure 1(a). The blister diameters and heights are in the ranges of 600–900 nm and 10–15 nm, respectively. At higher dose, e.g., $4 \times 10^{10}$ H cm$^{-2}$, numerous craters are observed (figure 1(b)) but the total density of blisters and craters is actually smaller than at the lower dose. The average depth of the craters (figure 1(c)), 72 ± 5 nm, is close to the theoretical $R_p$ [16], 75 nm, or the depths of peak H concentration, 80 ± 4 nm, or displacement damage concentration, 67 ± 7 nm, measured by ion beam analysis [21]. Since the ion beam was aligned with the (001) direction, channelling could have had some effects, but the blistering results were essentially identical when the target was tilted by 15°, probably because the damage accumulated during implantation dechannelled the beam. For $6 \times 10^{10}$ H cm$^{-2}$, the surface is again no rougher (∼1 nm) than at subthreshold doses (not shown). The mechanism responsible for this high
they are essentially identical to those obtained with a slow ramp on a wafer. These results obtained with a RTA are robust since having a chance of being bonded to B; but it could still allow layer transfer since wafer A would be already blistered before it is both blistered and cratered, at 6 &times; 10^{16} \text{ H} \text{ cm}^{-2} \text{ at } 5 \text{ keV ions}. At the atomic level \cite{22}, high doses are characterized by a very broad displacement damage depth profile, and by a Raman Si–H spectrum totally dominated by a peak identified with H passivated internal (001) surfaces, i.e. platelets and small flat cavities. It appears, then, that above a critical dose (\( \geq 6 \times 10^{16} \text{ H} \text{ cm}^{-2} \) at 5 keV), instead of having a micron-wide fracture plane at a specific depth (\( \sim R_g \)), one has a rather thick layer full of nm size platelets and cavities (probably pressurized with gas) which results in a macroscopically uniform swelling.

3.3. Surface morphology in 1 \( \mu \text{m} \) trenches

These trenches have widths comparable to the blister diameters on free surfaces at 5 keV. Figure 5(a) shows the surface of the 1 \( \mu \text{m} \) trench implanted with 3 &times; 10^{16} \text{ H} \text{ cm}^{-2} \text{ after annealing. The blisters are, surprisingly, half the size of those observed on the free surface and they are densely aligned in two rows along the trench direction in a ‘string of pearls’ pattern. However, for the higher fluence of 4.5 &times; 10^{16} \text{ H} \text{ cm}^{-2} \text{ (figure 5(b)), there is a single string of larger blisters, together with craters. It is also interesting to note that the blisters and craters are always rounded in shape (if not exactly circular). Their periphery never follows a straight line along the trench boundary. This is in contrast with another case we studied, He implantation in GaAs, see figure 6. He implantation of GaAs indeed frequently results in irregularly shaped blisters even on free surfaces \cite{14}. These facts suggest that H blistering/cratering of Si is nucleated at some point, presumably one with a high H or defect density for instance, and that the crack propagates more or less in a circle from that point. On the other hand, the He-induced crack propagation in GaAs depends less on the location of the initial fluctuation and more on the local values of the stress it encounters during its propagation, hence the effect of boundaries. Figure 6 also constitutes an indication of the uniformity of the ion flux and energy all the way to the trench boundary. The trenches implanted with fluences of 10 and 20 &times; 10^{16} \text{ H} \text{ cm}^{-2} \text{ (figures 5(d), (e)) again show the 15 \text{ nm} swelling, plus some amazingly tall blisters with heights of 50–60 nm on top of the swollen surface. Figure 5(f) shows line scans from the trenches implanted with 4.5, 10, and 20 &times; 10^{16} \text{ H} \text{ cm}^{-2}. The crater depth measured on the 4.5 &times; 10^{16} \text{ H} \text{ cm}^{-2} \text{ sample is } 70 \pm 5 \text{ nm in agreement with the corresponding depth measured on free surfaces. For trench widths greater than 800 nm, the dependence on fluence of the blister and crater densities (including disappearance) is

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4}
\caption{AFM micrographs (20 \( \mu \text{m} \times 20 \mu \text{m} \)) of trenches with nominal widths of 5 \( \mu \text{m} \) after implantation of (a) 3.0, (b) 4.5, (c) 6.0, (d) 10, and (e) 20 &times; 10^{16} \text{ H} \text{ cm}^{-2} \text{ and annealing (no anneal for (d)); (f) shows line scans from (a) and (d).}
\end{figure}

3.2. Surface morphology in 5 \( \mu \text{m} \) trenches

These trenches are much wider than typical blisters. The figures 4(a)–(e) show AFM micrographs of the surfaces in these larger trenches after implantation of different H fluences and annealing, except for figure 4(d), acquired before the anneal—only a few scattered blisters appear after annealing. As expected, the resulting morphologies are unaffected by implanting in wide trenches instead of free surfaces: at 3 &times; 10^{16} \text{ H} \text{ cm}^{-2}, the surface is blistered, at 4.5 &times; 10^{16} \text{ H} \text{ cm}^{-2} it is both blistered and cratered, at 6 &times; 10^{16} \text{ H} \text{ cm}^{-2} and 10 &times; 10^{16} \text{ H} \text{ cm}^{-2}, it is essentially featureless, and at 20 &times; 10^{16} \text{ H} \text{ cm}^{-2} it is blistered again, even before annealing. However, the experiment has led to one important new observation. In figures 4(c)–(e), one can see that the entire implanted areas are raised uniformly above the unimplanted areas, in other words the Si surface swells for doses of 6 &times; 10^{16} \text{ H} \text{ cm}^{-2} and higher; this swelling takes place at RT. This is displayed more quantitatively on the line scans of figure 4(f). For 3 &times; 10^{16} \text{ H} \text{ cm}^{-2}, one can see the narrow peaks due to blisters but there is no step at the border. For 10 &times; 10^{16} \text{ H} \text{ cm}^{-2}, a sharp step of 15–20 nm height is clearly evident. The fact that swelling during RT implantation appears for the same dose for which thermally activated blistering disappears suggests that the two phenomena are related. It is indeed very likely that the swelling relaxes the constraints that favour blistering. Höchbauer et al \cite{15} measured the in-plane compressive and out-of-plane (vertical) tensile stresses in H implanted Si and found, in agreement with our hypothesis, that the stresses started to decrease above a certain fluence (\( \geq 7 \times 10^{16} \text{ H} \text{ cm}^{-2} \) in their case, for 40 keV ions). At the atomic level \cite{22}, high doses are characterized by a very broad displacement damage depth profile, and by a Raman Si–H spectrum totally dominated by a peak identified with H passivated internal (001) surfaces, i.e. platelets and small flat cavities. It appears, then, that above a critical dose (\( \geq 6 \times 10^{16} \text{ H} \text{ cm}^{-2} \) at 5 keV), instead of having a micron-wide fracture plane at a specific depth (\( \sim R_g \)), one has a rather thick layer full of nm size platelets and cavities (probably pressurized with gas) which results in a macroscopically uniform swelling.
basically the same as on free surfaces, although the sizes and morphologies may differ. Finally, one can see in figure 5(d) some traces of resist at the border of the trench: this sample shown for illustration purposes was deliberately not treated by oxygen plasma, which is absolutely needed to remove all resist traces.

3.4. Surface morphology in 600 nm trenches

Figure 7 shows the resulting surfaces in trenches with 600 nm nominal width, which is smaller than the average blister diameter on unmasked surfaces. The trenches implanted with \(3 \times 10^{16} \text{H cm}^{-2}\) and \(4.5 \times 10^{16} \text{H cm}^{-2}\) show blisters aligned along the trenches. No double row of small blisters is present, as was the case with 1 \(\mu\)m trenches at low dose. The ‘double string of pearls’ pattern therefore requires very narrowly defined conditions of trench width and ion fluence. The blister diameter now is limited by the trench dimensions. Moreover, no craters are observed in the 600 nm trenches implanted with \(4.5 \times 10^{16} \text{H cm}^{-2}\), contrary to the case of the wider trenches. Craters are also absent in the 600 nm trenches, their creation needs trenches larger than about 900 nm. Therefore, the conditions leading to crater exfoliation are not only a critical gas pressure, attained at high enough H dose, but also a critical diameter, or more probably a critical ratio of diameter versus depth. This is understandable in terms of plate deformation and rupture mechanics. For the highest fluences, the swelling is present as usual. The blisters in figure 7(d) created by the \(20 \times 10^{16} \text{H cm}^{-2}\) implantation are circular in shape with a maximum diameter of 600 nm but sometimes less, whereas for low doses practically all the blisters have the maximum
generate blisters and craters as on free Si surfaces. However, the blister and crater morphology is affected when the width of the trench becomes comparable to or smaller than the normal blister size (∼900 nm). It was also discovered that uniform swelling of the implanted area results at high ion doses (≥6 × 10^{16} \text{ H/cm}^2 \text{ for 5 keV H}).

For relatively low doses around 3 × 10^{16} \text{ H cm}^{-2}, a dense array of blisters covering the greater part of the implanted area is observed in trenches as narrow as 600 nm; in 150 nm trenches, the small blisters (diameter ∼trench width) are more scattered than in trenches of 600 nm and more. In 600 nm trenches the blisters are densely aligned along the trench like a string of pearls. In 1000 nm trenches, a surprising pattern consisting of a double string of smaller (∼500 nm) blisters is observed. In all of the cases down to 600 nm trenches, and possibly down to 150 nm, it is anticipated that bonding to another wafer (‘B’) before annealing will cause uniform cracking at the approximate depth of implantation (∼75 nm) all along the trench (or, in general, in the whole implanted area if a more complex mask pattern is used). It remains to be seen whether vertical cracking will also take place, thus allowing patterned ion cutting and layer transfer.

Pattern transfer may be more facile for a somewhat higher dose around 4.5 × 10^{16} \text{ H cm}^{-2} because, in that case, craters are abundant, due to the higher gas pressure and perhaps also the higher stress. Cratering implies that more or less vertical cracks have propagated, which is necessary for patterned ion cutting.

For 6 × 10^{16} \text{ H cm}^{-2}, only swelling is observed, down to the narrowest trenches. This phenomenon takes place at room temperature and it could be used to trace raised patterns on silicon, but it would seem to preclude ion cutting and layer transfer. However, Desrosiers in our group surprisingly found (see [24]) that layer transfer could be accomplished, on unmasked Si surfaces, for doses at least as high as 7 × 10^{16} \text{ H cm}^{-2} (and 10 × 10^{16} \text{ D cm}^{-2}). Therefore, it seems that the swollen layer can detach from the substrate and transfer to ‘wafer B’ under the thermal treatment.

For 10 × 10^{16} \text{ H cm}^{-2}, not only RT swelling but also thermally induced blistering occurs, provided the trench is narrow enough, i.e. < 1000 nm wide; this dependence on trench width is somewhat puzzling. Because of the high dose, the blisters are ∼60 nm high, compared to ∼15 nm high at low dose. Therefore, the prospects for ion cutting and layer transfer appear promising at this dose.

Finally for 20 × 10^{16} \text{ H cm}^{-2}, both swelling and blistering take place at RT. This may give interesting raised patterns but will not permit ion cutting.

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References