

Silicon Nanostructure Fabrication by Direct FIB Writing and TMAH Wet Chemical Etching

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ABSTRACT

The development of nanoscale devices requires rapid prototyping methods that can be applied in combination with well-known clean room processing techniques. We show that focused ion beam (FIB) Ga⁺-ion implantation can be used for creating masks for the fabrication of silicon nanostructures by IC-compatible, anisotropic tetramethylammonium hydroxide (TMAH) wet etching. The FIB writing modifies only a thin (approx. 50 nm) surface layer of the substrate, which makes the process fast compared with the direct milling of 3D structures. The masking properties of the gallium doping have been investigated, and a high selectivity of at least 2000:1 between the implanted and non-implanted areas has been obtained. The suitability of the process for nanoscale device manufacturing has been investigated by fabricating high resolution gratings, freestanding beams and bridges as well as nanochannels separated by vertical, high aspect ratio sidewalls.

Keywords: FIB implantation, silicon, TMAH, wet chemical etching, nanofabrication

1 INTRODUCTION

In the research and development phase of various micro and nanotechnological systems, fast prototyping would be very welcome for testing basic concepts and for shortening the time needed in getting the first practical measurement and test results. In addition, any novel fabrication step in early prototyping should be compatible with the most common clean room processing methods. Focused ion beam (FIB) writing enables maskless and resist-free fabrication of a wide variety of arbitrary shaped nanostructures by means of milling, deposition, etching and ion implantation [1]. The etch stop properties of gallium ion implanted silicon have been utilized in the processing of 3D nanostructures, fabricated both by plasma [2] and potassium hydroxide (KOH) wet chemical etching [3].

In this work the local FIB Ga⁺-ion implantation is used as an etching mask in the fabrication of single crystalline silicon nanostructures by TMAH wet etching. TMAH solution is in a standard way used in micromachining as an anisotropic wet etchant of silicon. The advantage of TMAH is its compatibility with semiconductor circuit processing because the etch solution does not contain any metallic ions

in contrast to KOH. Also low toxicity and smooth surfaces achieved with concentrations exceeding 22 w% of TMAH in water are beneficial consequences of the etching. Conventionally the processing requires deposition and lithographic patterning of separate masking materials such as SiO₂ and Si₃N₄, which is now avoided by utilizing the direct write FIB implantation.

The straightforward combination process of FIB and TMAH enables the determination of the final structure shapes and dimensions in advance and is especially rapid compared with the direct FIB milling of 3D structures. The reason is that only a thin surface layer needs to be modified, which improves the writing speed by several orders of magnitude.

2 PROCESS CHARACTERISTICS

The etch stop properties of FIB modified and thus gallium-doped single crystalline silicon in TMAH have been analyzed earlier [4]. The ion energy of 30 keV used in the experiments produces in silicon a vertical ion range of 28 nm with a straggle of 10 nm. The ion lateral range of 6 nm with the straggle of 8 nm limits the minimum writable linewidth together with the shape of the ion beam.

The implantation is performed with a Helios Nanolab 600 dual beam system (FEI company). A liquid metal source is used for generating the Ga⁺ ion beam. The lowest ion current, 1.5 pA, is used for high resolution, nanoscale patterns, whilst larger, low resolution patterns can be treated using a high current beam. The maximum ion current of 21 nA modifies an area of 600 × 600 μm² into an etch resistant state in less than a minute.

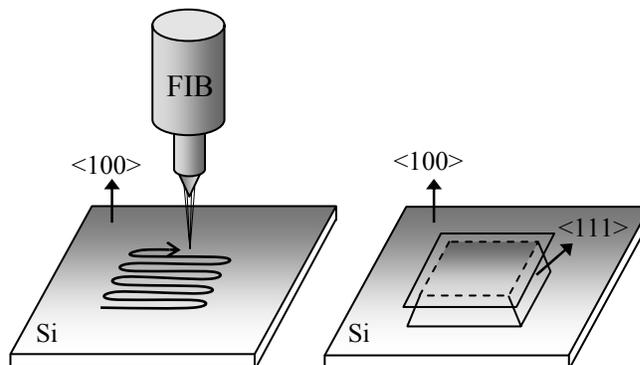


Figure 1. Principle of a combined local FIB implantation-TMAH wet etching process.

The principle of the localized FIB Ga⁺ implantation and the resulting shape after wet etching are shown in Figure 1. The etching properties of both <100> and <110> oriented silicon have been investigated by implanting a series of samples with variable ion doses (from 2×10^{13} ions/cm² to 4×10^{16} ions/cm²) and by etching them in 25 % aqueous TMAH solution until the doped layer is totally etched away (Figure 2 (a)). The higher the ion dose used for implantation, the deeper is the achievable etching depth around the doped patterns. The heights of the etched profiles were measured using a profilometer, and the results are shown in Figure 2 (b). The threshold dose producing an observable etching resistance was 4×10^{13} ions/cm². The critical dose for Si amorphization is approx. 10^{14} ions/cm². By approximating the Ga mask thickness as 50 nm, the etching selectivity between the treated and untreated Si is better than 2000:1 with the highest ion doses (over 4×10^{16} ions/cm²), which is comparable to the selectivities of SiO₂ and Si₃N₄ conventionally used as masking materials in Si etching with TMAH.

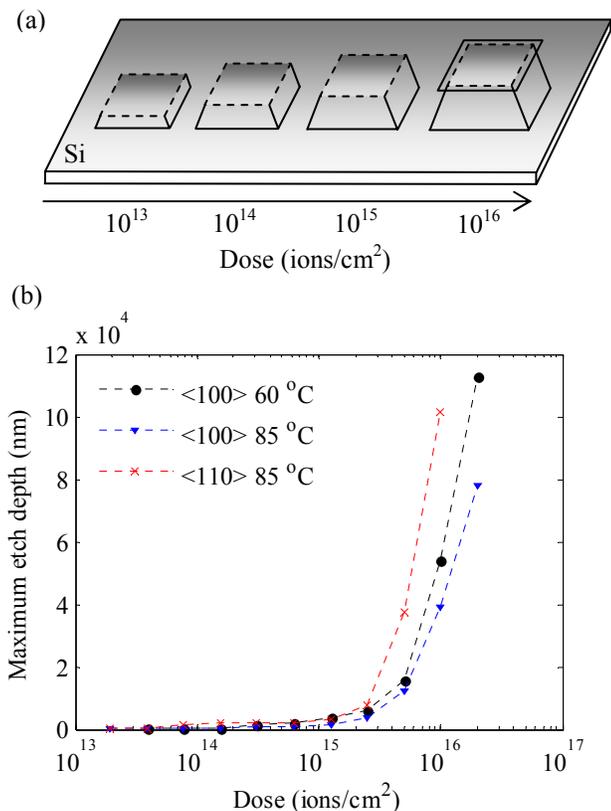


Figure 2. (a) Schematic drawing illustrating part of the etched sample series. (b) The masking capability of the implanted Ga⁺ mask in 25 % TMAH. The etch rate of the (100) Si crystal plane is 150 nm/min at 60 °C and 0.6 μ m/min at 85 °C. The (110) etch rate at 85 °C is 1.4 μ m/min. The threshold for the drastic etch rate lowering can be seen between 10^{15} ions/cm² and 10^{16} ions/cm².

The etch rate lowering phenomenon is ascribed primarily to the formation of gallium oxide at the implanted Si surface, which passivates it against the etching ambient. The gallium oxide layers have been detected to be present in both wet chemically etched and dry RIE (reactive ion etched) samples [5].

3 NANOSTRUCTURING

The suitability of the approach for nanoscale device fabrication has been characterized by patterning various types of nanostructures with FIB and etching them in 85 °C, 25 % TMAH solution. A room temperature BHF dip (15 s) was used for native oxide removal prior to the etching. The minimum ion beam current of 1.5 pA was used in all experiments in order to obtain the maximum patterning resolution, and the ion dose was optimized for each structure by varying the dwell time of the beam. The purpose of the experiments was to investigate the limits of the FIB-TMAH process in nanostructure fabrication.

3.1 Gratings

The spatial resolution was studied by implanting a sequence of gratings with varying line widths on the <100> silicon substrate. The result after the subsequent wet etching step (35 s, 85 °C) can be seen in Figure 3. The V-groove shape is typical for anisotropic wet etching. The smallest reproducible grating period was 100 nm (Figure 3 (b)), the corresponding resolution being 20 lines/ μ m. The minimum achievable resolution is a result of several factors including the ion dose and the shape of the ion distribution in Si, the focusing of the ion beam and the imperfect anisotropy of the TMAH etching,

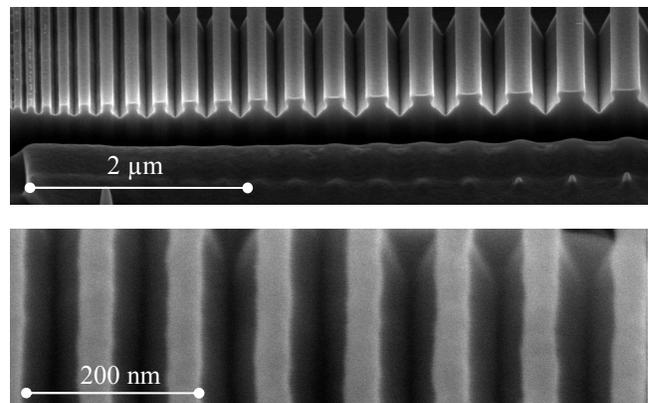


Figure 3. (a) FIB cross section of a varying period grating. The widths of the lines range from 70 nm to 260 nm. (b) Grating with a constant 100 nm period. The 50 nm width of the original line patterns is decreased to 40 nm during the process. The Ga⁺-ion dose used for patterning is 10^{15} ions/cm².

3.2 Released Structures

The insolubility of the thin Ga⁺-doped mask has also been exploited as a material for freestanding elements. The principle of the implantation pattern alignment on the <100> Si substrate leading to the release during the etching is presented in Figure 4. Figure 5 shows resulting cantilevers and bridges with the narrowest features being only 25 nm wide.

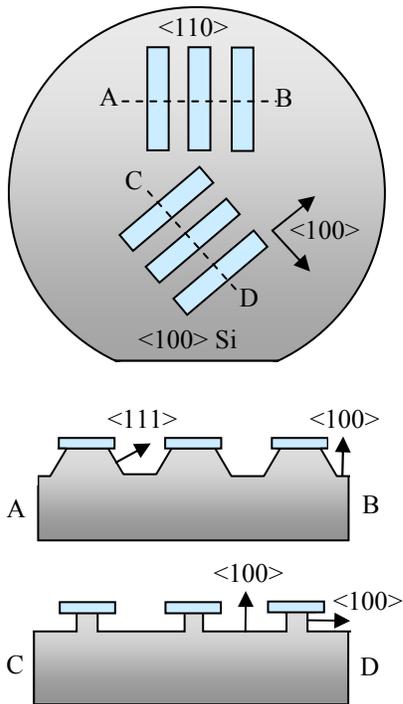


Figure 4. FIB implantation pattern alignment on <100> Si substrate: A-B gratings, C-D released structures.

3.3 Nanochannels

Single crystal <110> silicon was used as a substrate for patterning and etching nanochannels separated by very thin, nearly vertical sidewalls. The principle of the pattern alignment is illustrated in Figure 6, and the resulting channels after etching can be seen in Figure 7.

The TMAH etching anisotropy and high selectivity to the gallium implanted mask can be utilized in the fabrication of structures with high aspect ratios. A single wall with an aspect ratio of more than 1:30 is seen in Figure 7 (b). The U-shape of the groove bottoms is typical for anisotropic <110> Si etching and together with the wall spacing it limits the depth of the channels. The wall is cut by FIB milling, and the downwards widening profile of the cross section is a result of the redeposition of material during the process.

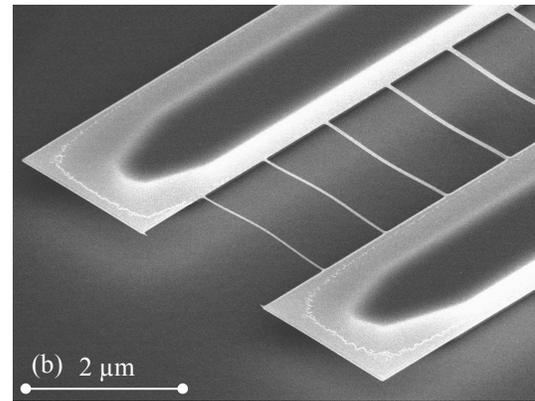
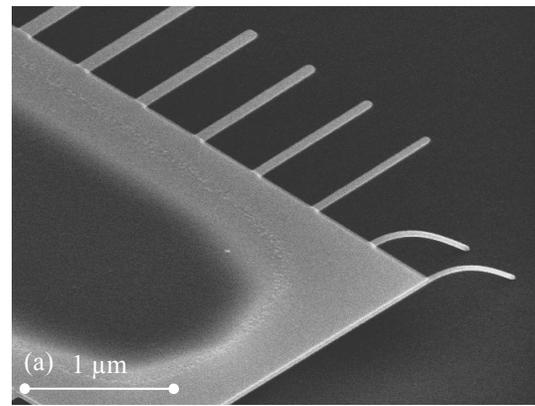


Figure 5. Released beams (a) and bridges (b). The narrowest bridge is 25 nm in width. The material of the structures is amorphous, Ga⁺-doped Si. The implantation ion doses are 4×10^{15} ions/cm² (beams) and 2×10^{15} ions/cm² (bridges), etching time in 85 °C TMAH 1 min.

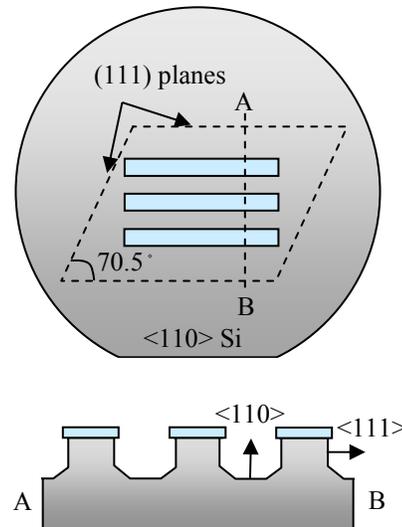


Figure 6. FIB implantation pattern alignment on <110> Si for the etching of vertical sidewalls.

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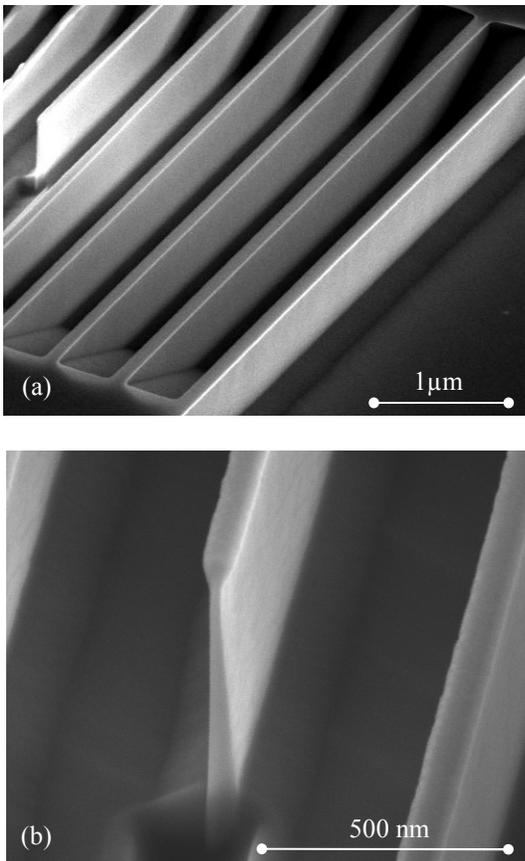


Figure 7. (a) Nanochannels with vertical walls on $\langle 110 \rangle$ Si. (b) The cross section of the single wall is obtained by FIB milling. The height of the wall is 570 nm and the width 15 nm. The implantation ion dose is 10^{15} ions/cm², etching time in 85 °C TMAH 1 min.

4 CONCLUSION

In the presented work, the direct write FIB implantation was used for patterning the thin surface layer of silicon to act as a mask in TMAH wet chemical etching. The fabrication process introduced is a rapid and straightforward method for making prototypes of nanostructures for various purposes, even on samples that need to be compatible with integrated circuit processing procedures. The dimensions of the final structures are accurately defined, and neither resists nor lithography masks are needed. The approach has been utilized in generating 3D nanostructures including high resolution gratings, freestanding elements and nanochannels with high aspect ratio sidewalls.

The prospective applications of the method include nanomechanical devices such as cantilever sensors, nanofluidics and integrated optical components with subwavelength features. In the future, mass production can be envisioned supposing the etched structures to be used for stamp fabrication in nanoimprint lithography.