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Process considerations for layer-by-layer 3D patterning of silicon, using ion implantation, silicon deposition, and selective silicon etching

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The authors study suitable process parameters, and the resulting pattern formation, in additive layer-by-layer fabrication of arbitrarily shaped three-dimensional (3D) silicon (Si) micro- and nanostructures. The layer-by-layer fabrication process investigated is based on alternating steps of chemical vapor deposition of Si and local implantation of gallium ions by focused ion beam writing. In a final step, the defined 3D structures are formed by etching the Si in potassium hydroxide, where the ion implantation provides the etching selectivity. © 2012 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4756947>]

I. INTRODUCTION

In additive layer-by-layer manufacturing techniques, several patterned layers of a material are stacked on top of each other.^{1–16} These techniques provide an effective way of manufacturing arbitrarily shaped three-dimensional (3D) structures. Different additive layer-by-layer manufacturing approaches exist, which make use of various materials such as polymers, waxes, ceramics, semiconductors, and metals. The techniques include stereolithography,^{1,2} solid ground curing,¹ selective laser sintering,^{1,6} 3D inkjet printing,¹ laminated object modeling,^{2,7} and fused deposition modeling,^{1,8–16} including beam-assisted deposition techniques.^{10–15} The achievable dimensions of the 3D structures strongly depend on the used technology and can range from several tens of nm to tens of μm .

Recently, we proposed and demonstrated a simple process for additive layer-by-layer fabrication of 3D silicon (Si) nanostructures.¹⁷ The process consists of cycles of chemical vapor deposition of an Si layer and local ion implantation into the layer by focused ion beam (FIB) writing, and is finished off with a final etch to form the 3D Si structures defined by the implantation. This process makes use of the high etch selectivity that can be achieved in semiconductor materials by local ion implantation,^{18–28} thereby forming patterns in the material with lateral dimensions of down to 20 nm.²⁵ The proposed implementation of the layer-by-layer fabrication process is schematically illustrated in Fig. 1. First, a pattern is defined with implanted gallium ions (Ga^+) in an Si substrate using FIB writing (Fig. 1, step 1). This is

followed by chemical vapor deposition of a thin Si layer (Fig. 1, step 2), and another pattern definition by Ga^+ implantation into the new layer (Fig. 1, step 3). By repeating steps 2 and 3 over and over, the 3D structure is defined within the deposited Si layers. The local implantation of Ga^+ ions into Si results in an etch selectivity of the Si in potassium hydroxide (KOH) wet etching. Thus, the defined 3D Si structures can be formed by selective free-etching in KOH, as a final patterning step (Fig. 1, step 4).¹⁷

Well known methods such as selective epitaxy of silicon or silicon germanium rely on lithographic patterning and subsequent etching of an oxide or nitride hardmask in the areas of desired growth. While single layer structures of high quality are obtained, the continuation to an arbitrary second layer is impossible, since the hardmask areas cannot serve as starting point for silicon growth. In particular, suspended structures, which are of prime importance in micromechanical applications, cannot be achieved.

In the present work, we study in more detail the growth of Si on the four different surfaces encountered in the 3D patterning process (bulk or deposited Si, implanted or not implanted), and how the grow mode affects the achievable resolution. Furthermore, we simulate Ga^+ implantation depths at different implantation energies and derive suitable process parameters for the formation and definition of patterned 3D Si structures.

II. EXPERIMENT

To investigate the pattern formation and definition of multilayer 3D patterns in Si, we created three-layer Si structures by three implantations and two depositions. The test patterns contained all possible overlaps of the layers. We evaluated two different thicknesses of the deposited Si layer,

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Fig. 1. (Color online) Additive layer-by-layer fabrication of Si structures. Step 1: Local implantation of Ga⁺ ions into the surface of an Si substrate by FIB writing. Step 2: Chemical vapor deposition (CVD) of an Si layer. Step 3: Local implantation of Ga⁺ ions in the deposited Si layer using FIB writing. Subsequently, Steps 2 and 3 are repeated until the 3D structures are defined in the Si layers by the locally implanted Ga⁺. Step 4: Selective etching of the nonimplanted Si in KOH to obtain the final 3D Si structures. Adapted from Ref. 17.

40 and 120 nm, while keeping the ion acceleration voltage fixed at 30 kV in all implantations. For the experiments, we used (100) silicon wafers [p-type, 14–22 Ω cm (Wafer A) and p-type, 10–20 Ω cm (Wafer B)] and implanted an area dose of 10 pC/ μ m² of Ga⁺ ions, using a Nova 600 NanoLab focused ion beam tool from FEI (the Netherlands). To guide our choice of layer thicknesses, we simulated the implantation of Ga⁺ ions into Si using the TRIM code.²⁹

Before each Si layer deposition, we cleaned the silicon wafers by the following steps: 10 s dip in 5% hydrofluoric acid (HF), 5 min wash in deionized (DI) water, 5 min oxidation in hot H₂SO₄:H₂O₂ 3:1, 5 min DI wash, 10 s dip in 5% HF, and 5 min DI wash. We grew the Si layers from a disilane (Si₂H₆) precursor, at a pressure of 2.6 kPa and a temperature of 635 °C, using an Epsilon 2000 single wafer epitaxy tool from ASM International N.V. (the Netherlands). We patterned two different wafers. On both wafers, we did an identical layer 1 implant directly into the substrate, while the thickness of the deposited layers differed: Wafer A had a layer 2 target thickness of 120 nm (936 s deposition) and a layer 3 target thickness of 40 nm (312 s deposition). Wafer B had at target thickness of 40 nm for both deposited layers. During the wafer loading procedure, the wafers were exposed to the temperature steps of 850 °C for 13 s, followed by 725 °C for 120 s.

After the final implantation, we treated the wafers with a rapid thermal anneal in an argon atmosphere at 650 °C for 30 s. Finally, we formed the structures by an etch in KOH. First, we dipped the wafers for 3 s in 5% HF, to remove the native SiO₂, next we etched them in 30% KOH at 36 °C for 5 min 30 s, and finally washed them in DI water for 3 min and dried with N₂.

In an attempt to reduce the lattice damage of the Si surface due to the Ga⁺ ion implantation, an additional experiment was performed in which an Si wafer with Ga⁺ ion implanted patterns was *in situ* cleaned and annealed in the epi reactor at 1050 °C for 2 min prior to the Si deposition step.

III. RESULTS AND DISCUSSION

Figure 2 shows a scanning electron micrograph (SEM) of a three-layer test structure on Wafer A. The structure contains areas of overlapping implantations in layers: 1-2, 2-3, and 1-2-3, as well as areas where layers 2 and 3 overlap with the substrate. The structures in all layers are resolved, although some differences between layers can be observed.

The differences in the appearance of the layers are a consequence of the implantation method used. To maintain layer homogeneity, epitaxial growth of mono-crystalline Si would be preferred for a layer-by-layer manufacturing process. In addition, mono-crystalline Si has superior mechanical and

Fig. 2. Three-layer test structure made by three implantations and two depositions. The structure shows all possible overlaps of the three layers, as well as overlaps of layers 2 and 3 with the substrate. (a) Overview of the whole structure. (b) Enlarged view of the overlap of layer 2 with the nonimplanted Si on the left, and with the layer 1 implantation on the right.

electrical properties that are attractive for electromechanical components. However, implantation of Ga^+ ions into Si breaks down the crystalline structure and leaves the implanted surface layer amorphous.³⁰ Subsequent Si growth will thus be polycrystalline on implanted layers, while epitaxy is still possible outside implanted areas. As a result, the thickness of the layer grown on the implanted areas can be up to double the thickness of the layer grown on nonimplanted areas.¹⁷ This effect is known from so called differential epitaxy, where the growth rates over different types of exposed surfaces vary significantly under identical conditions (gas flow, partial pressure, and temperature).^{31,32} This can clearly be seen in the enlarged region shown in Fig. 2(b), where layer 2 grows on nonimplanted silicon on the left side, and on the layer 1 implantation on the right side. On the left side the layer 2 surface is smooth (apart from a few local defects), and the left sidewall has a slope characteristic of an Si (111) plane, indicating that layer 2 grows epitaxially in this region. In contrast, the right sidewall of layer 2 is jagged, as is more characteristic of a polycrystalline layer. Furthermore, the region of the layer grown on the implanted layer 1 (right side) is thicker than the region grown on the nonimplanted layer 1 (left side). In an attempt to reduce the lattice damage of the Si surface due to the Ga^+ ion implantation, and to allow subsequent epitaxial growth of a mono-crystalline Si layer, an Si wafer with Ga^+ ion implanted patterns was *in situ* cleaned and annealed in the epi reactor at 1050 °C for 2 min prior to the Si deposition step. However in this experiment, it was observed that none of the implanted structures were resolved in the KOH etch, presumably due to the out-diffusion of the Ga^+ ions during the high-temperature annealing step.

For successful layer-by-layer patterning, the thickness of the deposited layers must match the implantation depth of the Ga^+ ions. If the deposited layer is too thin, the Ga^+ ions will penetrate through the layer and implant the layer below. Figure 3 shows a TRIM simulation of the implantation of an area dose of 10 pC/ μm^2 ($6 \times 10^{15} \text{ cm}^{-2}$) of Ga^+ ions into Si, at ion energies in the range from 10 to 50 keV. The thickness of the layer that reaches a Ga^+ dopant concentration above $2.2 \times 10^{19} \text{ cm}^{-3}$, the threshold required for etch selectivity in KOH,²⁶ ranges from 29 nm at 10 keV to 85 nm at 50 keV. At 30 keV, the resulting Si layer thickness in which the critical

Fig. 3. (Color online) Simulation of the implantation of an area dose of 10 pC/ μm^2 ($6 \times 10^{15} \text{ cm}^{-2}$) of Ga^+ ions into Si, at ion energies in the range from 10 to 50 keV.

Fig. 4. (Color online) (a) Lines patterned in the 120 nm thick layer 2 of Wafer A. (b) Same pattern in the 40 nm thick layer 2 of Wafer B.

implantation dose is exceeded is about 60 nm, as depicted in Fig. 3. Furthermore, the simulation suggests that the critical implantation dose is not reached in a few nm thick layer near the Si surface.

In Fig. 4, we compare the 120 nm thick deposited Si layer 2 of Wafer A [Fig. 4(a)] with the 40 nm thick deposited Si layer 2 of Wafer B [Fig. 4(b)]. The patterned structures consist of a line pattern, with line widths down to 33 nm. The ion implanted pattern in the 120 nm thick layer is resolved, both in the areas overlapping the substrate and in the areas overlapping the implanted layer 1 [Fig. 4(a)]. In the 40 nm thick layer 2 on Wafer B, however, the lines are only visible in the regions overlapping the substrate, while in the regions overlapping layer 1 they are completely vanished. A possible explanation is that the targeted thickness of 40 nm for the deposited Si layer was not obtained on Wafer B, due to slow initial Si growth on the surface. In an effort to reduce overall process temperature, and thus reduce diffusion of the implanted Ga^+ , the customary *in situ* H_2 clean at 950 °C or above was omitted. Thus, some residues of native surface oxide may have slowed down initial nucleation in the silicon epitaxial process. A low temperature alternative, to prepare the surface for initial nucleation, would be *in situ* sputtering removal of the native oxide using, e.g., Ar ions, which is a standard approach in semiconductor processing.

A slow initial growth of the Si would not be visible in the same way in the thicker 120 nm thick Si layer on Wafer A. The thickness of the grown Si layer does not have the same impact on the resolved pattern on areas in which the underlying layer is not ion implanted, as shown in Fig. 4(b) where the implanted pattern is resolved in the area where the substrate layer has no implanted Ga^+ ions.

IV. SUMMARY AND CONCLUSIONS

We have investigated the pattern definition in additive layer-by-layer fabrication of 3D Si structures by forming Si structures in three layers. We found that the Si growth process is affected in areas where a pattern is defined by the Ga^+ ion implantation, as compared to areas without implanted Ga^+ ions. In general, the epitaxial growth of mono-crystalline Si would be preferred for the proposed

layer-by-layer manufacturing process, due to the potentially increased homogeneity of the layers, and the superior mechanical and electrical properties of mono-crystalline Si for electromechanical devices, as compared to amorphous or polycrystalline Si. However, the damage induced in the Si lattice by the implantation of the Ga^+ ions makes it difficult to grow epitaxial mono-crystalline Si layers on top of Ga^+ ion implanted areas. Therefore, either suitable process steps for the removal of the lattice damage in the Si have to be implemented, or, alternatively, it may be possible to use ion implantation of smaller H^+ or He^+ ions for the pattern definition. This could potentially cause less damage to the Si lattice structure while still providing Si etch selectivity in available etches.^{27,28} The aim of this research is to work toward a layer-by-layer manufacturing technology for 3D Si nanostructures that can be implemented as a switched process in a single automated tool. This would enable printing of 3D Si nanostructures directly from 3D computer aided design (CAD) models of the structures, without the need for full clean-room facilities, and could provide custom silicon nanostructures for low-volume high-margin application fields, such as telecommunications (e.g., 3D Si photonic crystals) and medicine (e.g., neural implants).

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