3D-Fractal Engineering Based on Oxide-only Corner Lithography

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***Abstract*—This paper reports a new highly simplified machining process for three dimensional (3D)-fractal nanofabrication based on oxide-only corner lithography. It consists of a repeated sequence of wet etching (silicon), thermal oxidation and wet etching (silicon oxide). The previously reported 3D-fractal fabrication process needed additional low pressure chemical vapor deposition (LPCVD) steps of silicon nitride, as well as local oxidation of silicon (LOCOS). Employing this new procedure, a three generation folded silicon oxide fractal sheet with approx. a 10 µm footprint has been fabricated.**

Keywords—nanofabrication, fractals, corner lithography, silicon dioxide, wet etching, single crystalline silicon

I. INTRODUCTION

3D engineered fractal structures [1] can find application in numerous fields, like optical sensing, photovoltaics, microfluidic mixing, sieving and catalytic conversion. Previously, a process based on a combination of silicon nitride “corner lithography”, anisotropic and isotropic etching, and local oxidation of silicon (LOCOS) was developed to micro-fabricate 3D fractal structures [1]. This process has now been greatly simplified, and it will be shown in this paper that 3D fractal structures can be fabricated by a repeated sequence of anisotropic etching, thermal oxidation and isotropic etching only. By means of this oxide-only process various generations of 3D fractal structures can be made, as schematically shown in Fig. 1.

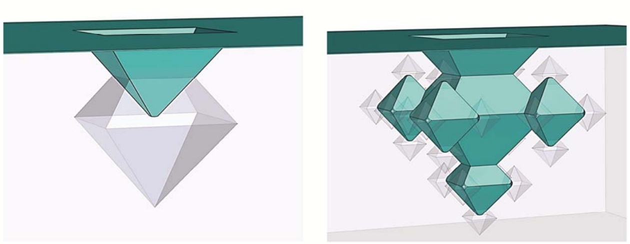


Fig. 1. Schematic representation of 1st (left) and 3rd (right) level 3D fractals

II. FUNDAMENTALS OF OXIDE-ONLY 3D-FRACTAL ENGINEERING

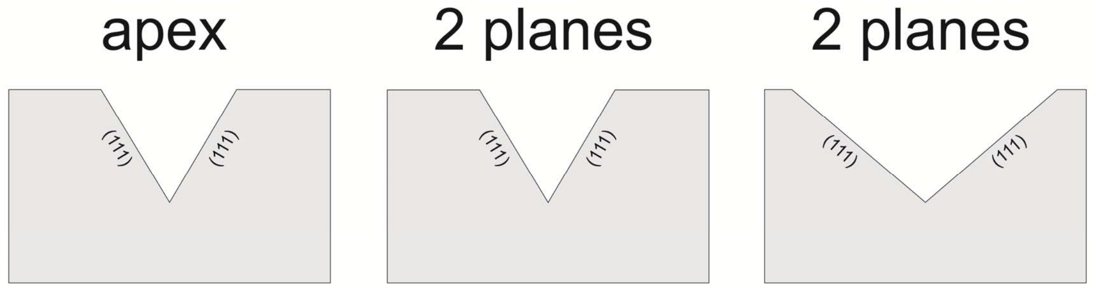
Our “conventional” way of engineering of 3D fractal structures, as reported previously, is based on a combination of anistropic etching of silicon and corner lithography [1-3]. In more detail, this conventional method is an iterative process that involves conformal deposition of layers of silicon nitride by LPCVD, and thermal oxide (SiO_2) in anisotropically etched silicon structures – i.e. inverted pyramids and octahedrons – in combination with selective time-stopped (an)isotropic wet etching. The employed wet etchants to realize 3D fractals are potassium hydroxide (KOH) and tetra methyl ammonium hydroxide (TMAH) to shape (100)-oriented single crystalline silicon, and (buffered) hydrofluoric acid ((B)HF) and phosphoric acid (H_3PO_4) to isotropically and selectively pattern conformal films of silicon nitride and SiO_2. Although this conventional method yields large arrays of 3D fractal structures, in practice it is a time-consuming and rather expensive procedure, hence the need for a much more simplified process flow. We have found such a procedure, based on the notion that silicon nitride based corner lithography in combination with LOCOS, can be replaced by a single silicon oxidation step, making use of the stress induced thinning of silicon oxide in sharp concave corners [4].

In order to be able to fabricate 3D fractals with oxide-only corner lithography, the grown oxide layer should be conformal on convex corners as well as equally thick on the silicon (100) and (111) crystal planes. If these requirements are not fulfilled the layer of SiO_2 cannot be properly patterned by means of time-stopped isotropic etching (i.e. due to thickness variations the SiO_2 is removed from locations where it should remain), or will not function as a proper mask during selective anisotropic etching of silicon. Therefore, this simplified process uses (dry) thermal oxidation at 1100°C. Oxidation of silicon at this temperature leads to fundamental differences in the grown oxide compared to thermal oxidation at relatively low temperatures (≤ 950 °C), in terms of layer thickness on (100) and (111)-silicon crystal planes as well as layer conformality around convex corners.

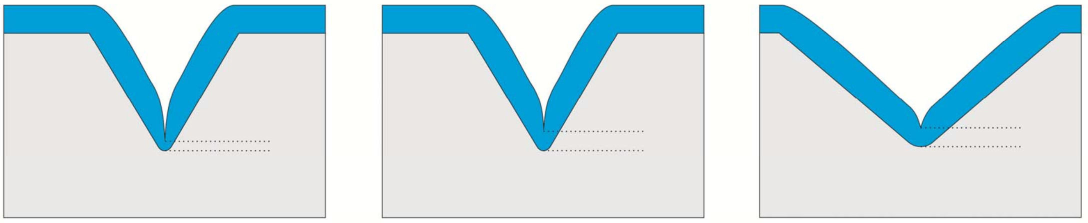
At low thermal oxidation temperatures (≤ 950 °C) the oxide thickness at convex and concave corners is thinner than a flat (100)-Si planes due to compressive stress at the corner structures [5],[6]. At temperatures of 1000 °C the formed oxide layer on convex corners is not thinned with respect to the layer thickness on planar (100)-Si, but at this temperature there is a difference in oxide growth rate on the main crystal directions of silicon [7]. Upon dry thermal oxidation of silicon at 1100 °C the mentioned aspects regarding non-conformality on convex corners and differences in oxide layer thickness on (100) and (111) Si-planes are avoided [7]. In concave corners the severe compressive stress that develops [8] does not relief, and the connected reduction in oxidation rate leads to a locally thinner layer.

The degree of sharpening of the thermal oxide layer in concave corners depends on the amount of intersecting (111)-planes: the higher the number of intersecting planes, the thinner the grown oxide layer. Thus, in ribbons – i.e. two intersecting (111)-planes – less oxide sharpening occurs compared to an intersection of three or four (111)-planes (i.e. apices) (Fig.2). These aspects yield the possibility to solely remove the SiO_2 from apices by means of timed isotropic etching in 1% HF, while oxide remains in ribbons and on planes. This is illustrated in Fig. 2.

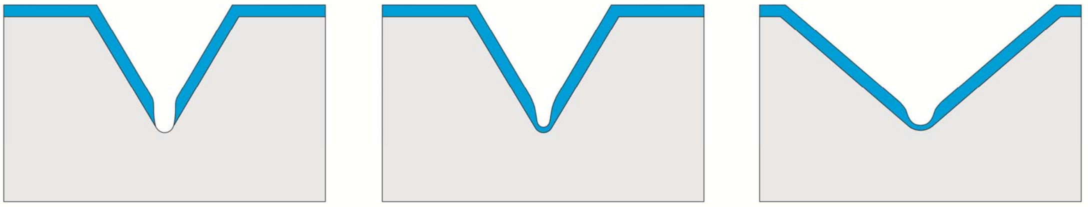
The procedure to self-form the 3D-fractal now becomes very simple: after thermal oxidation and timed-HF etching, at each apex the underlying Si can be selectively etched (anisotropic etching in TMAH), resulting in the formation of a next level octahedral structures at all apices simultaneously. Repetition of this simple sequence of anisotropic Si-etching / thermal oxidation at 1100°C / isotropic SiO_2-etching results in multi-level 3D-fractal structures.



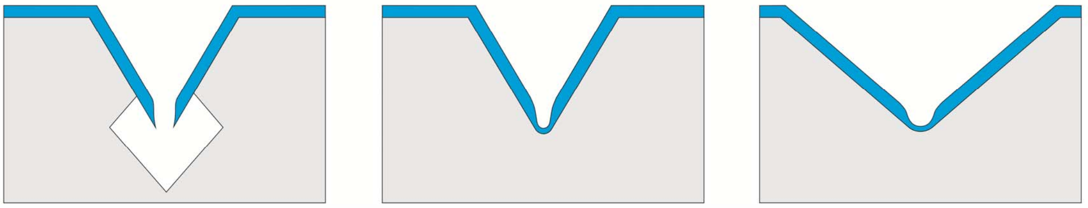
a) Anisotropic etching and mask stripping



b) Oxidation



c) Isotropic etching



d) Anisotropic etching

Fig. 2. Selective opening of the thermally grown silicon oxide at the apex of the pyramidal pit after HF etching. Note that stress induced oxidation retardation is more pronounced in concave corners where more than two planes intersect.

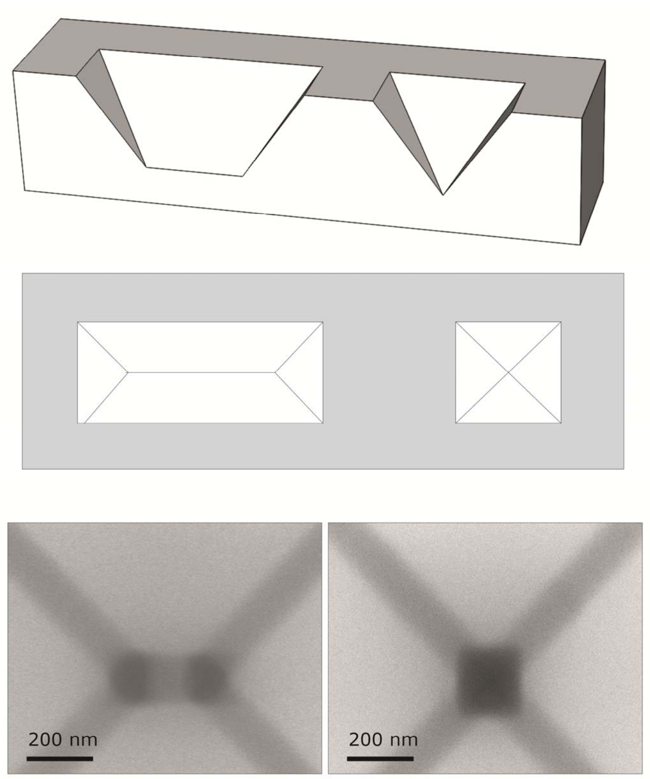


Fig. 3. Top and middle: 3D and topview schematic representations of 2, 3 and 4 intersecting (111)-Si planes. Bottom: topview SEM-images of insections of 2, 3 and 4 (111)-Si planes upon etching in HF: time-dependent opening of the apices is visible.

III. EXPERIMENTAL RESULTS AND DISCUSSION

To illustrate the selective opening of apices, we etched an inverted pyramid in (100)-Si using KOH (25 wt.%, 70 °C), with a slightly rectangular (Fig. 3, left), and square (Fig. 3, right) footprint. These structures were subsequently oxidized (dry, 1100°C for 95 min), resulting in a SiO_2 thickness of 160 nm and 155 nm on (111) and (100) oriented surfaces, respectively. Fig. 3 shows SEM images (top view) after 19 min + 30 sec etching in 1% HF (etch rate 4.4 ±0.1 nm/min) and 5 min of TMAH etching (25 wt%, 70 °C) to make a possible opening more visible in the SEM. The remaining oxide thickness on (111) surfaces is 74 nm.

A first indication of the time window (Δt) available between opening of only the apices *vs.* opening of the ribbons and apices is given in Fig. 4, for a starting oxide thickness of 88 nm and 160 nm, respectively (on (111) surfaces). For each measurement point in the graphs, the samples were taken from the 1% HF solution, etched in TMAH and then inspected by SEM. This sequence was repeated and the opening of apices or ribbons as detected is indicated in the graphs. Note that the indicated time window has a considerable error margin due to the limited number of measurement points.

Starting point for the realization of 3D fractal structures in an inverted pyramid etched in (100)-Si with KOH, with a square footprint of 5 µm. After growing a thermal oxide layer with a known thickness (ca. 160 nm, 1h35min at 1100 °C), a time window exists for which only the apices are free of oxide. For the engineering of 3D fractal structures solely based on oxide corner-lithography, an etch-time of 20min30sec in 1% HF is applied. Post to this HF-step, through the apex, silicon can be etched anisotropically in TMAH (25 wt.%, 70 °C), yielding a new octahedron that is bound by the slow etching (111) Si-planes. For each fabrication level of a fractal structure, the oxidation and isotropic etch time are constant, however, the time-length of the TMAH etch step is halved for each new level (starting with an etch time of 145 min at level zero). Upon a 3 times repetition of this sequence – TMAH-etching, 1100°C-oxidation and SiO_2-etching – followed by a final thermal oxidation run, anodic bonding with a Mempax glass wafer at 400 °C, and removal of the bulk-Si, freestanding three-generation silicon oxide fractal sheets can be fabricated (Fig. 5). Note that depending on the final step, apices can remain closed or be opened.

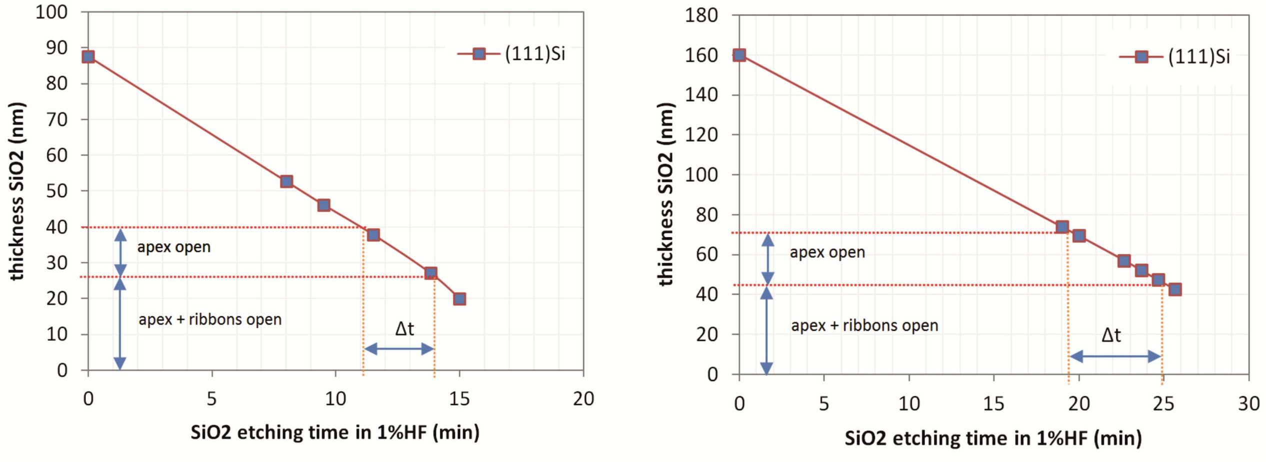


Fig. 4. Remaining oxide thickness in apices and ribbons as function of etching time in 1% HF (starting oxide thickness 160 nm (left) or 88 nm (right)): within the time window Δt only the apices are opened.

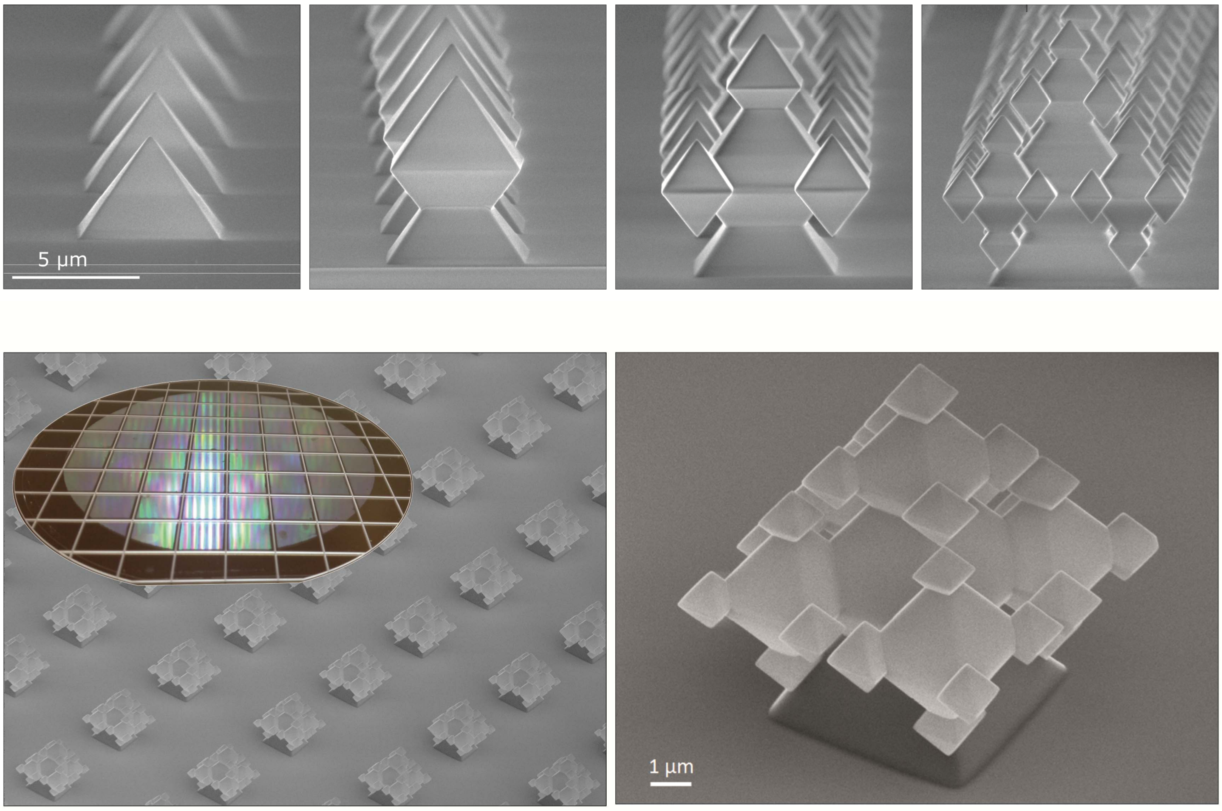


Fig. 3. Top row (left-to-right): SEM images of 0th, 1st, 2nd and 3rd generation silicon oxide fractal sheets. Bottom row: overview of fractals on glass substrate (inset: glass wafer with 1 x 1 cm^2 specimen with fractals) and zoom-in on one freestandig 3rd level 3D silicon oxide fractal sheet.

IV. CONCLUSIONS AND OUTLOOK

We have found a regime in thermal oxidation of silicon, in which the oxide formed is significantly thinner in concave apices, with respect to concave ribbons as well as all convex corners. Based on this regime, it is possible to fabricate 3D-fractals by a combination of anisotropic etching of silicon, thermal oxidation and isotropic HF etching only. This procedure was successfully applied to produce a three generation octahedral fractal structure, with a total size of about 10 µm and a smallest sub-structure size of about 1 µm.

We are currently exploring microfluidic and optical applications of the nanofabricated 3D-fractals.

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