euspen's 22nd International Conference & Exhibition, Geneva, CH, May/June 2022
www.euspen.eu

Three-dimensional nanostructures enabled by customised voltage waveform-induced local anodic oxidation lithography

Jian Gao[1], Xichun Luo[1], Wenlong Chang[1], Yi Qin[1], Wenkun Xie[1], Pengfei Fan[1], Rashed Md. Murad Hasan[2] , Yanquan Geng[3], Yongda Yan[3]

[1] *Centre for Precision Manufacturing, DMEM, University of Strathclyde, Glasgow, UK*
[2] *Department of Electrical and Electronic Engineering, Chittagong University of Engineering and Technology, Chittagong, Bangladesh*
[3] *Center for Precision Engineering, , Harbin Institute of Technology, Harbin, P. R. China*

jian.gao@strath.ac.uk

Abstract
Atomic force microscope-based local anodic oxidation nanolithography has been recognised as an effective approach for the fabrication of nanoscale patterns for next-generation electronic devices. Particularly, the use of oscillating tips can reduce the spatial size of the processed patterns and significantly increase the tool lifetime. However, it is still very challenging to achieve three-dimensional nanostructures as oxidation occurs only in a nanoscale water bridge formed between the tip and the sample, where multiple parameters must be precisely and strategically controlled to obtain nanopatterns with different heights. In this paper, a new local anodic oxidation lithographic technique is researched with the application of customised voltage waveforms to generate 3D nanostructures on silicon wafers. The relationship between pulse waveform parameters and oxidation growth was investigated. Through adjusting the tip-scan frequency and modulation of pulses, it was shown that waveform-modulated local anodic oxidation could fabricate 3D nanostructures in a certain area in a single scan.

Local anodic oxidation lithography, atomic force microscope, voltage waveform, 3D nanostructures

1. Introduction

Scanning probe microscope (SPM) is a promising nanofabrication tool because of the advantages in atomic-level resolution, direct surface patterning ability and low instrument cost. Advanced scanning probe lithography (SPL) have demonstrated the excellent performance in creating micro- to nanoscale patterns [1,2]. Under critical environment, SPM even shows great potentials in atomic and close-to-atomic scale manufacturing (ACSM), i.e. Manufacturing III [3–6]. However, to create patterns down to several nanometres or close-to-atomic scale, mechanical scratching method is inadequate in the accuracy and repeatability. The in-process interactions could be very complex and difficult to control because of chemical reaction and random atomic diffusion that commonly occur at the tool-work interface [7–9]. To address these challenges, a chemical reaction-based process has attracted increasing attention and promising results have been achieved [10,11]. Among these methods, atomic force microscope (AFM) -based local anodic oxidation (LAO) lithography has become a popular research topic because of its good reproducibility for nanoscale patterns, *in-situ* imaging, compatibility with other lithographic processes, low environmental requirements, ease of operation, time-saving, etc [12]. Besides, LAO could be applied to a wide range of materials, including metals, semiconductor materials, 2D materials and organic polymers. The nanostructures enabled by LAO have been successfully used as tunnel junctions for nanoelectronics [13,14], waveguides for nanooptics [15], and as masks for further dry or wet eching to obtain nanostructures with higher aspect ratios [16–18].

Previous research has demonstrated that LAO can be used to generate nanodots, nanolines, and even 3D structures [6,12]. During the lithographic process, the oxidation growth can be effectively controlled by adjusting scanning speed, humidity, tip-sample bias and separation, charge build-up, etc. However, the challenges faced by LAO are also critical. The configuration of AFM-based process dictates a lower processing efficiency compared to other lithographic techniques [19], and the height of oxide patterns is often limited to a few nanometers due to the limitation in the size of water meniscus. Therefore, the LAO for 3D patterns is challenging on the efficiency and scale. Since the invention of LAO lithography [20], many researchers have worked on the process development for 3D structures. Yang et al [21] used a coupling AFM lithography, in which probes served as both cutting tool and electrode, to create 2.5 D patterns on conductive materials with the depths of 6 – 80 nm and square widths from nanoscale to microscale. Lorenzoni and Torre [22] applied single DC pulses to create the single nanodots on SiC with high aspect ratio and demonstrated the possibility to create 3D structures with multi-height dots. Kim et al [23] studied the pulse electrochemical nanopatterning on silicon and concluded that the pulse duration control could allow a precise dimensional control over nanoscale patterns. Kim et al [24] employed a simple repeated SPL method and successfully fabricated 3D pyramidal patterns on the silicon surface. However, these processes require a complex procedure and introduce a high error rate and low processing efficiency while obtaining 3D patterns. To further develop the LAO lithography, a more precise and efficient method needs to be developed.

In this paper, we present a modulated waveform-induced local oxidation process on silicon wafers. The patterning process was

operated under the tapping-mode AFM using a conductive probe, the feature size of nanodots could be controlled to sub-20 nm through the use of ultra-short pulses. During the LAO process, the grounded probe kept scanning along a trajectory across an area while a customised waveform was applied to the sample. The relationships between height and position of desired nanodots with the modulated waveform were discussed to verify the possibility for achieving 3D patterning, with the expectation to contribute to the patterning control of LAO lithography at close-to-atomic scale. Besides, the waveforms are easily programmed so that the parametric control of feature sizes and positions of nanodots could be enabled by simply matching the arbitrary waveform to the tip trajectory.

2. Local anodic oxidation lithography

Figure 1 shows a schematic of LAO lithography using a tapping mode AFM. A cantilever is oscillating with a frequency at a distance above a silicon surface. The bias between the conductive tip and sample could induce a series of physical and chemical reactions and enable the nanopatterning on the sample surface. In a certain humidity environment, the tip and sample surfaces will adsorbed with water layer. Once the tip is close enough to the surface, the tip-sample bias could induce the formation of water meniscus filling in the volume between the tip and sample [25]. At the same time, the passing through of electrons could induce the electrochemical reaction within the water bridge and form the oxidation patterns in the reaction region.

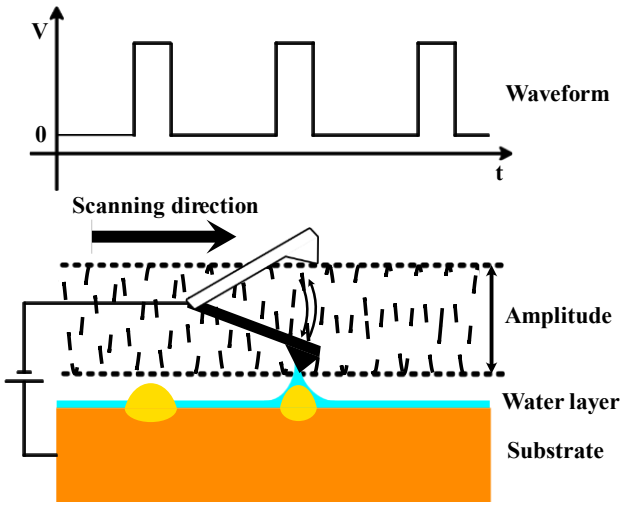

Figure 1. A schematic of modulated waveform-induced local anodic oxidation lithography.

In this work, the sample was made by a p-doped silicon (111) wafer with resistivity ρ = 1 – 20 Ω-cm. The cleaning of specimens was operated with ultrasound in an $NH_4OH/H_2O_2/H_2O$ (1:1:5) solution for 10 min to remove surface particles and blown with a dry N_2 gas jet. The probes used in the work were Bruker TESP-SS with tip radii of curvature at 2 – 5 nm to allow the creation of small patterns. The frequency is 320 kHz and spring constant is 42 N/m. The LAO experiment was performed using a Bruker Dimension 3100 AFM microscope under the tapping mode, the feedback loop was always on to keep scanning at a constant tip-sample distance. The experiment was conducted in a constant temperature (20 ℃) and humidity (25 – 30 RH) room. During the oxidation, the conductive tip was grounded and the sample was connected to a positive bias to enable the local oxidation on the silicon surface. The voltage modulation was controlled by a dual-channel arbitrary generator (TGF4042, Aim - TTi) and amplified by a power amplifier (E01.A2, CoreMorrow).

3. Results and discussions

A variety of methods can be used to control the growth of oxidation dots during the local anodic oxidation; however, the modulation of waveform allows a simple and flexible control over the oxidation growth. To create various nanodots with controllable heights during scanning, the influence of pulse amplitude and duration and the match between tip scanning and pulse frequency need to be studied. In this work, scanning area was set in a 1 μm square region and scanning frequency was set as 0.25 Hz, so the scanning speed was 0.5 μm/s. Other parameters as tip oscillating amplitude and tip-sample distance were kept constant so that only the pulse amplitude and duration affected the feature size of the oxidation dots, while the tip scan and intervals between pulses determined the position of the oxidation point, thus their combination enabled the possibility for 3D patterning.

3.1. LAO lithography with various pulse amplitudes

The amplitude of pulse is a direct factor affecting the growth rate of oxidation. To discover amplitude's effect on oxide growth, arrays of nanodots were created under different amplitudes through the use of modulated waveforms.

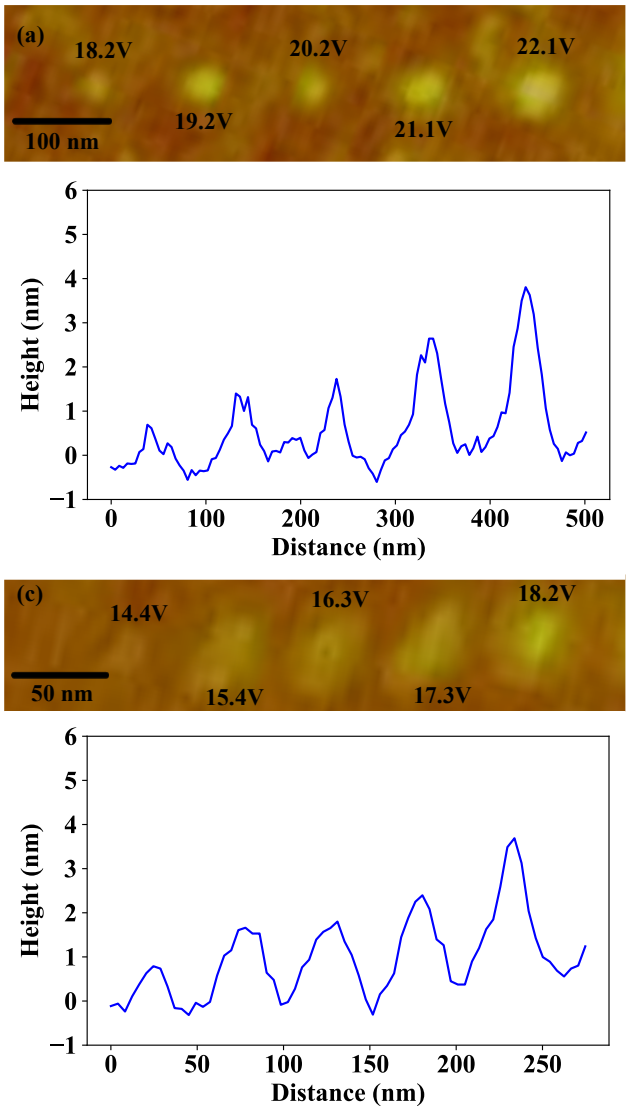

Figure 2. Size dependences on pulse amplitudes. (a) AFM image of nanodots created at pulse duration of 60 μs and with the amplitudes

between 18.2 V and 22.1 V; (b) a section view shows the height of nanodots in (a); (c) AFM image of nanodots created at pulse duration of 2 ms and with the amplitudes between 14.4 V and 18.2 V; (d) a section view shows the height of nanodots in (c).

Firstly, the pulse duration was kept at constant value of 60 µs and the size dependence of nanodots on the amplitudes is shown in **Figure 2** (a) and (c). When the bias increased from 18.2 V to 22.1 V, the height of oxide dots increased from 0.8 nm to 3.8 nm. The experiment also showed that nanodots could be created under a lower amplitude when pulse duration is at 2 ms. As shown in **Figure 2** (d), when the amplitudes changed from 14.4 V to 18.2 V, the height of nanodots shows similar increasing trends as in **Figure 2** (b).

3.2. LAO lithography with various pulse durations

Pulse duration is another influencing factor for the growth of nanodots during the LAO process. Through applying the same voltages, size dependences on the pulse duration were studied. As shown in **Figure 3** (a) and (b), at the voltage of 17.8 V, the oxide height increased from 0.7 nm to 1.4 nm under an inceasing pulse duration from 1 ms to 6 ms. At a higher voltage of 21.1 V, **Figure 3** (c) and (d) also shows that the oxidation dots can be created at much smaller pulse durations, between 10 µs to 60 µs. Based on the comparison, the aspect ratio of nanodots can be enhanced using a short and high-voltage pulse, a conclusion complied with previous research [26].

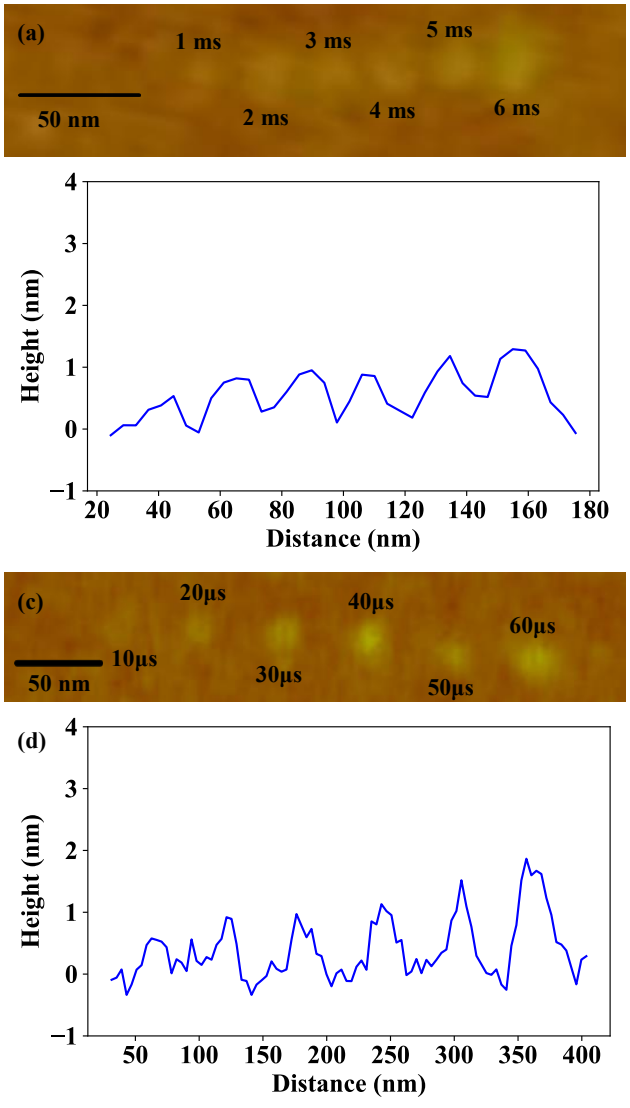

Figure 3. Size dependences on pulse durations. (a) AFM image of nanodots created at 17.8 V and pulse duration between 1 ms to 6 ms; (b) a section view shows the heights of nanodots in (a); (c) AFM image of nanodots created at 21.1 V and pulse duration between 10 µs to 60 µs; (d) a section view shows the heights of nanodots in (c).

3.3. Waveform-induced LAO lithography for 2D patterns

The previous sections demonstrated how the amplitude and pulse affected the oxidation growth at the nanoscale when other experimental parameters kept constant. The results showed that nanodots at different heights can be created as an array. If we adjust time intervals between pulses, nanodots could be created at different positions and show as a pattern on the surface.

During the AFM imaging, the tip kept raster scanning on a microscale square region, each line included both the trace and retrace. The positions of nanodots could be controlled through correspondingly adjusting the time intervals between adjacent pulses and the frequency of the tip scan. Through setting the scan frequency to 0.25 Hz, the pulse frequency to 1/4.25 Hz, the pulse amplitude to 21.6 V and duration to 200 us , a 'Z' shape pattern was created as shown in **Figure 4** (a), with the half-height diameter of nanodots between 15 - 20 nm and height between 3-5 nm. If an arbitrary waveform was used, the time intervals between adjacent pulses could be more flexibly adjusted and allow the creation of arbitrary 2D patterns. **Figure 4** (b) showed an 'S' shape pattern created by a customised waveform.

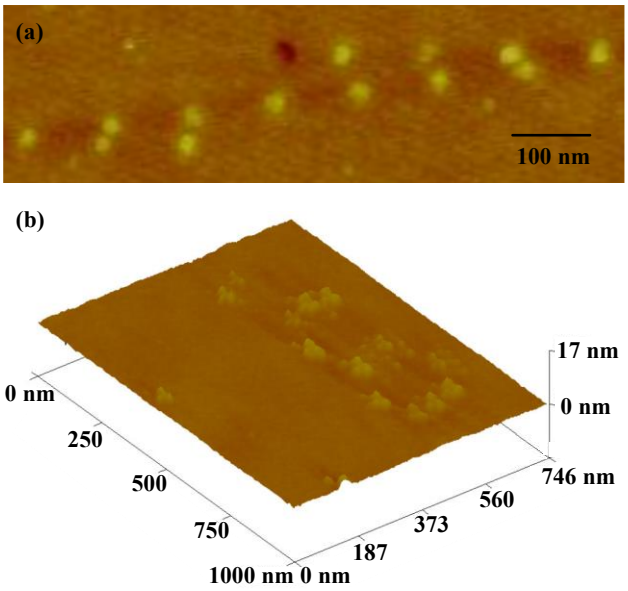

Figure 4. Schematics of 2D patterns created by waveform-induced LAO; (a) a 'Z' shape pattern; (b) an 'S' shape pattern.

3.4. Waveform-induced LAO lithography for 3D patterns

Through the design of arbitrary waveform, we can modulate the amplitude and duration for a single pulse and the inter-pulse periods at the same time thus open the possibility of 3D patterning. The digital control on the height and position of nanodots can be easily achieved through the modification of waveform. To facilitate the design of arbitrary waveform, a python program was developed to create the waveform files based on the inputs of 2D coordinates of nanodots and the heights of each nanodot, whose matching relationships to the scan parameters, pulse intervals and amplitudes were empirically plotted. In this way, the incorporation of a customised waveform into a single scan of the AFM will allow the creation of a 3D pattern, which includes various nanodots with different heights. In the customised waveform, the pulse durations were kept at 2 ms and amplitude were kept increasing

from 15.4 V and 19.2 V. Three identical pulses were scheduled in each 32-second period and the intervals between them were set as 1 s. After a single scan, the result was shown in **Figure 5** with a clear hierarchical pattern.

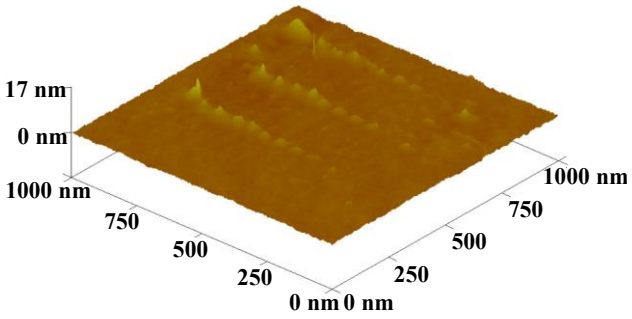

Figure 5. A schematic of 3D pattern created by waveform-induced LAO lithography.

4. Summary

The height of oxidation dot depends on the amplitude and duration of the pulse applied between the tip and sample during the LAO process. Through incorporating an arbitrary waveform between the tip and sample during the tip scanning, 2D and 3D oxidation patterns were found to be possible to achieve and the diameter of nanodots could be at close-to-atomic scale. The control over nanoscale feature size is highly flexible because waveform applied to the LAO process can be digitally programmed.

Acknowledgements

The authors would like to thank EPSRC (EP/K018345/1, EP/T024844/1, EP/V055208/1), the Royal Society-NSFC international exchange programme (IEC\NSFC\181474) and Science and Technology Based for Equipment Design and Manufacturing for Introduction Talents of Discipline to Universitis 2.0 of the 111 project (Project No. BP0719002) to provide financial support to this research.

References

[1] Tseng A A 2011 Advancements and challenges in development of atomic force microscopy for nanofabrication *Nano Today* **6** 493–509

[2] Garcia R, Knoll A W and Riedo E 2014 Advanced scanning probe lithography *Nat. Nanotechnol.* **9** 577–87

[3] Mathew P T, Rodriguez B J and Fang F 2020 Atomic and Close-to-Atomic Scale Manufacturing: A Review on Atomic Layer Removal Methods Using Atomic Force Microscopy *Nanomanufacturing Metrol.* **3** 167–86

[4] Fang F, Zhang N, Guo D, Ehmann K, Cheung B, Liu K and Yamamura K 2019 Towards atomic and close-to-atomic scale manufacturing *Int. J. Extreme Manuf.* **1** 012001

[5] Gao J, Luo X, Fang F and Sun J 2021 Fundamentals of atomic and close-to-atomic scale manufacturing:A review *Int. J. Extreme Manuf.* **4** 012001

[6] Fan P, Gao J, Mao H, Geng Y, Yan Y, Wang Y, Goel S and Luo X 2022 Scanning Probe Lithography: State-of-the-Art and Future Perspectives *Micromachines* **13**

[7] Jacobs T D B and Martini A 2017 Measuring and Understanding Contact Area at the Nanoscale: A Review *Appl. Mech. Rev.* **69** 060802

[8] Giessibl F J, Herz M and Mannhart J 2002 Friction traced to the single atom *Proc. Natl. Acad. Sci.* **99** 12006–10

[9] Gotsmann B and Lantz M A 2008 Atomistic Wear in a Single Asperity Sliding Contact *Phys. Rev. Lett.* **101** 125501

[10] Chen L, Wen J, Zhang P, Yu B, Chen C, Ma T, Lu X, Kim S H and Qian L 2018 Nanomanufacturing of silicon surface with a single atomic layer precision via mechanochemical reactions *Nat. Commun.* **9** 1542

[11] Espinosa F M, Ryu Y K, Marinov K, Dumcenco D, Kis A and Garcia R 2015 Direct fabrication of thin layer MoS2 field-effect nanoscale transistors by oxidation scanning probe lithography *Appl. Phys. Lett.* **106** 1–5

[12] Ryu Y K and Garcia R 2017 Advanced oxidation scanning probe lithography *Nanotechnology* **28** 142003

[13] Snow E S, Park D and Campbell P M 1996 Single-atom point contact devices fabricated with an atomic force microscope *Appl. Phys. Lett.* **69** 269–71

[14] Matsumoto K, Gotoh Y, Maeda T, Dagata J A and Harris J S 2000 Room-temperature single-electron memory made by pulse-mode atomic force microscopy nano oxidation process on atomically flat α-alumina substrate *Appl. Phys. Lett.* **76** 239–41

[15] Onuki T, Tokizaki T, Watanabe Y, Tsuchiya T and Tani T 2002 Nanometer-sized optical waveguides fabricated by anodic oxidation using a scanning near-field optical microscope *Appl. Phys. Lett.* **80** 4629–31

[16] Davis Z J, Abadal G, Hansen O, Borisé X, Barniol N, Pérez-Murano F and Boisen A 2003 AFM lithography of aluminum for fabrication of nanomechanical systems *Ultramicroscopy* **97** 467–72

[17] Sugimura H, Yamamoto T, Nakagiri N, Miyashita M and Onuki T 1994 Maskless patterning of silicon surface based on scanning tunneling microscope tip-induced anodization and chemical etching *Appl. Phys. Lett.* **65** 1569–71

[18] Kramer N, Jorritsma J and Birk H 1995 Nanometer lithography on silicon and hydrogenated amorphous silicon with low energy electrons *J Vac Sci Technol B* **13** 8

[19] Hasan R Md M and Luo X 2018 Promising Lithography Techniques for Next-Generation Logic Devices *Nanomanufacturing Metrol.* **1** 67–81

[20] Dagata J A, Schneir J, Harary H H, Evans C J, Postek M T and Bennett J 1990 Modification of hydrogen-passivated silicon by a scanning tunneling microscope operating in air *Appl. Phys. Lett.* **56** 2001–3

[21] Yang Y and Zhao W 2019 Fabrication of nanoscale to microscale 2.5D square patterns on metallic films by the coupling AFM lithography *J. Manuf. Process.* **46** 129–38

[22] Lorenzoni M and Torre B 2013 Scanning probe oxidation of SiC, fabrication possibilities and kinetics considerations *Appl. Phys. Lett.* **103** 163109

[23] Kim U S, Morita N, Lee D W, Jun M and Park J W 2017 The possibility of multi-layer nanofabrication via atomic force microscope-based pulse electrochemical nanopatterning *Nanotechnology* **28** 195302

[24] Kim Y, Kang S K, Choi I, Lee J and Yi J 2007 Fabrication of a 3-dimensional microstructure by sequential anodic oxidation (SAO) *Microelectron. Eng.* **84** 308–12

[25] Gómez-Moñivas S, Sáenz J J, Calleja M and García R 2003 Field-Induced Formation of Nanometer-Sized Water Bridges *Phys. Rev. Lett.* **91** 056101

[26] Calleja M and García R 2000 Nano-oxidation of silicon surfaces by noncontact atomic-force microscopy: Size dependence on voltage and pulse duration *Appl. Phys. Lett.* **76** 3427–9