

Nanometre-scale oxidation of silicon surfaces by dynamic force microscopy: reproducibility, kinetics and nanofabrication

M Calleja[†], J Anguita[†], R García^{†||}, K Birkelund[‡],
F Pérez-Murano^{‡¶} and J A Dagata[§]

[†] Instituto de Microelectrónica de Madrid, CSIC. Isaac Newton 8, 28760 Tres Cantos, Madrid, Spain

[‡] Departament d'Enginyeria Electrònica, Universitat Autònoma de Barcelona, 08193-Bellaterra, Spain

[§] National Institute of Standards and Technology, Gaithersburg, MD-20899, USA

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Abstract. Local oxidation of silicon surfaces by scanning probe microscopy is a very promising lithographic approach at nanometre scale. Here, we present two approaches to optimize the oxidation for nanofabrication purposes: (i) we analyse the reproducibility and kinetics of the oxidation of Si(100) surfaces when there is no tip and sample mechanical contact and (ii) we study the effect of modulating the voltage in the aspect ratio of the oxide structures grown. The finite tip–sample separation has remarkable practical consequences: the same tip can be used to perform thousands of modifications without any sign of wear. In addition, the structures generated do not show any degradation over long periods (months). It is also found that the kinetics is independent of the force microscopy mode used (contact or non-contact). On the other hand, the application of an AC voltage to induce the oxidation significantly modifies the aspect ratio of the structures. A detailed description of the oxidation mechanism is proposed to account for both results.

1. Introduction

Local oxidation of semiconductor and metallic surfaces induced by the intense electrical field present at a suitable biased tip–sample junction in a scanning probe microscope (SPM) is a promising nanolithography approach for the fabrication of nanometre-scale electronic devices. The first scanning tunnelling microscopy oxidation of silicon surfaces in ambient conditions [1] has led to strong scientific activity [2–12, 14–15]. Some contributions are focused on the understanding of the kinetics and mechanism of the oxidation [3–5, 8], while other papers are exploring dynamic force microscopy modes for improving the reproducibility of the process [6–8, 14]. Finally, some contributions illustrate how the as-grown oxide can be used for the fabrication of functional nanostructures such as the gate of a MOS transistor [9], point quantum devices [10] or a single electron transistor [11, 12].

Sustained progress and routine use of this technique for fabrication of nanometre-scale devices requires a comprehensive understanding and control of the oxidation mechanism. Several aspects illustrate that the complexity

of the problem remains open: such as the saturation of the oxide growth rate at long exposure times, or the details of the electrochemical process responsible for the oxidation of the sample.

In this paper, we address two issues, (i) the oxidation when the tip and the sample are a few nanometres apart and (ii) the increase of the aspect ratio of the oxide structures by voltage modulation. The non-contact atomic force microscope (AFM) oxidation increases the reliability of the oxidation process by reducing the tip wear. It also emphasizes the relevance of the water meniscus formation. The oxidation performed under voltage modulation improves the aspect ratio of the oxide and underlines the role of the space charge build-up. Both results must be considered to optimize the oxidation and to understand its mechanism.

2. Experimental

Non-contact oxidations were performed with a commercial AFM (Nanoscope III, Digital Instruments, Santa Barbara, USA). The silicon cantilevers were metallized with a layer of about 20 nm of Ti. The average force constant and resonance frequency of the cantilevers used were about 40 N m^{−1} and 350 kHz respectively. The samples were n-type Si(100) with

^{||} E-mail address: rgarcia@imm.cnm.csic.es

[¶] E-mail address: fpm@cc.uab.es

a resistivity of $14 \Omega \text{ cm}$. For environmental control, the microscope was placed into a closed box with inlets for dry and H_2O saturated nitrogen.

The voltage modulation experiments were performed on highly doped n-type silicon (100) surfaces using silicon cantilevers with a force constant of 3 N m^{-1} , and a resonance frequency of 75 kHz . The cantilevers were metallized with a titanium coating of 20 nm . Images were obtained under an intermittent contact mode [13]. In this case, to perform an oxidation, the image mode was changed to contact mode in order to control exactly the time during which the oxidation is being produced.

3. Non-contact force microscopy experiments

The oxidation of Si(100) surfaces by operating the force microscope in a non-contact mode offers several advantages with respect to tunnelling or contact AFM oxidations: namely, the little wear shown by the metallized tip, which increases the reproducibility of the process.

The protocol for non-contact AFM oxidation of Si(100) is as follows [8]. The cantilever–tip ensemble is oscillated at a frequency close to its resonance frequency with an amplitude of a few nanometres. The force gradient in the region of tip–sample attractive forces shifts the cantilever resonance frequency to lower values, which implies a change of the amplitude. This effect is used to control the tip–sample separation. Then a voltage pulse is applied (sample positive), and at the same time the feedback loop is disabled. The electrostatic force deflects the cantilever towards the surface. It also produces a reduction of the amplitude. To start the local oxidation, the voltage must be above a threshold value (V_{th}) [7, 8]. V_{th} depends on the initial oscillation amplitude (A_s), tip geometry and relative humidity. Common values are in the $6\text{--}12 \text{ V}$ range.

The voltage applied between the tip and the sample polarizes the water layer adsorbed onto the sample. When the voltage is above a certain value, the water molecules are driven towards the regions where the field is more intense. The result is a liquid bridge connecting the tip and the sample [8, 14]. The field-induced liquid bridge provides the oxygen species for the oxidation to proceed. Once the bridge is formed, a different voltage (above or below V_{th}) can be applied to grow the oxide. This voltage is responsible for the formation of oxygen species (hydrolysis of the water). The voltage also drives the ions towards the silicon interface.

The behaviour of the oscillation amplitude before, during and after the application of a pulse of 12 V for 50 ms is shown in figure 1. At the bottom of the image, the position of the silicon substrate is plotted. The electrostatic force deflects the cantilever 4 nm towards the sample. The deflection is also accompanied by a reduction of the amplitude from 6.6 nm to 1.8 nm , so there is no tip–sample mechanical contact.

The potential of non-contact AFM oxidations for nanofabrication is shown in figure 2. An array of 1024 dots has been formed by a sequential application of a voltage pulse of 14 V for 1 ms . The dots are 60 nm apart and have an apparent width and height of 44 nm and 1.2 nm respectively. The image illustrates the reproducibility of the oxidation in non-contact AFM. Routinely, the same tip is able

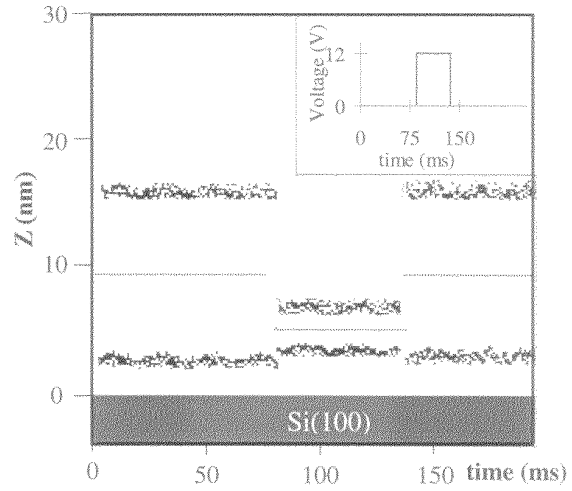


Figure 1. Cantilever oscillation amplitude versus time before, during and after the formation of a dot. The oscillation is referred with respect to the Si(100) position. The amplitude is represented by its maximum and minimum values. The dashed lines show the equilibrium position of the cantilever. The inset shows the voltage pulse. The feedback is switched off during pulse application and restored afterwards.

to write thousands of dots without showing any sign of wear. Figure 2(b) shows the same array after being exposed to the laboratory ambient for 95 days. No apparent changes are found. This image shows the stability of the marks formed and reinforces its potential for technological applications.

To optimize the feature size, experiments were performed to determine the oxidation kinetics. Dots of different sizes were formed by the application of pulses of identical voltages but different duration. An estimation of the growth rate was obtained by calculating the ratio between the dot thickness and the time the pulse was applied. The experiments were performed for two voltages of 8 V and 12 V respectively. The oxide thickness increases with the logarithm of time. As a consequence, the growth rate decreases exponentially with the thickness of the oxide (h) (figure 3) and follows the equation,

$$\frac{dh}{dt} = C \exp(-h/L_c)$$

where C and L_c are parameters that depend on the applied voltage. The overall dependence is similar to the results reported in contact AFM oxidations [4, 5]. It is the presence of a water bridge connecting tip and sample which explains the similar kinetics found in contact and non-contact modes.

4. Voltage modulation studies

Additional control of the oxidation process can be obtained if the applied voltage is modulated. The dimensions of the oxide structures change if an AC voltage is applied instead of a DC voltage. This effect can be used to monitor the aspect ratio of the dots. In figure 4(a), the parameters that define the AC waveform are shown. The waveform consists of a series of pulses where T_{ox} is the oxidation time and V_{ox} the applied voltage (common values for V_{ox} lie between 5 V and 10 V); T_{res} is the reset time (V_{res} is usually negative). It has

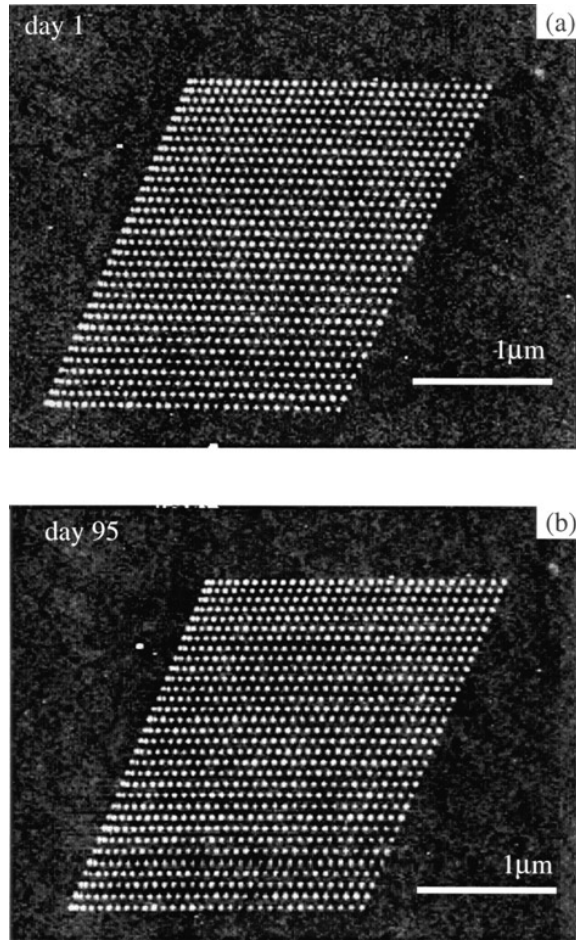


Figure 2. (a) AFM image of an array of 1024 dots. The dots are 60 nm apart and have an apparent diameter of about 44 nm and height of 1.2 nm. Each dot is formed by applying a pulse of 14 V for 1 ms; $A_s = 7.6$ nm. (b) The same array imaged 95 days after its formation.

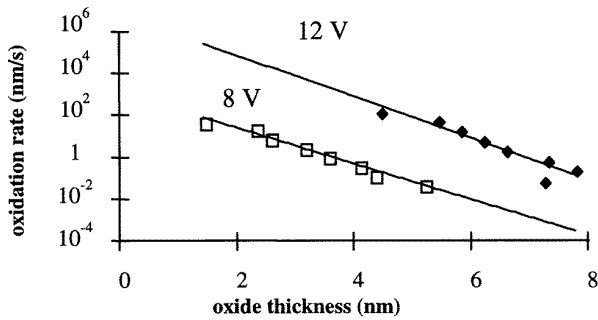


Figure 3. Growth rate versus oxide thickness for 8 V and 12 V. $A_s = 5.1$ nm, $f = 353$ kHz and RH = 40%.

been verified that the application of a DC voltage at V_{res} does not produce any appreciable oxidation on the surface. The total oxidation time (exposure time) is T_{ox} multiplied by the number of pulses. We refer to $1/(T_{ox} + T_{res})$ as the frequency of the waveform. To better control the oxidation time we have chosen to perform these experiments with the tip and the sample in mechanical contact.

In figures 4(b) and (c), two oxide dots were grown by applying DC and AC voltages, left and right respectively.

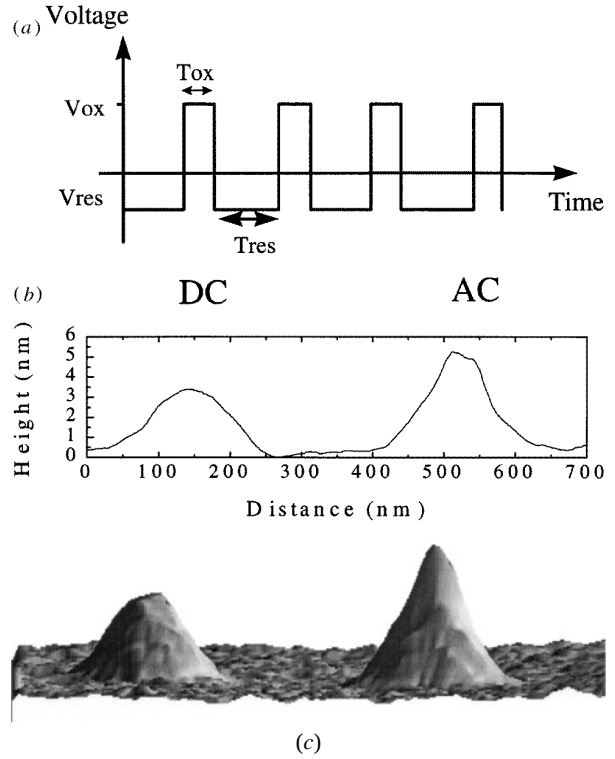


Figure 4. (a) Waveform voltage applied to the surface with respect to the tip when performing an oxidation under AC conditions: T_{ox} is the time when the oxidation is performed (the voltage applied to the sample is V_{ox} , usually between 5 V and 10 V), and T_{res} is the rest time (the voltage applied is V_{res} , usually a negative voltage). (b) Profile of two dots fabricated by applying a DC voltage (left, 8 V, 30 s) and an AC voltage (right, $T_{ox} = T_{res} = 50$ ms, $V_{ox} = 8$ V, $V_{res} = -8$ V, total time = 60 s). (c) A three-dimensional representation of the image where the profile of figure 4(b) has been extracted. It shows that the increase in height occurs at the central part of the dot.

A DC voltage of 8 V for 30 s was applied. The AC voltage consists of a train of pulses applied during 60 s at a frequency of 10 Hz ($T_{ox} = T_{res} = 50$ ms, $V_{ox} = 8$ V, $V_{res} = -8$ V). It is observed that DC and AC pulses produce a similar width at the base of the dot. However, the dot formed under AC conditions presents a height increase, at the central part of the dot, where the electrical field is supposed to be higher. Under these conditions, the height and aspect ratio increase are around 1.5. This result has also been reproduced by other authors [15].

In figure 5 we show the effect of varying the frequency of the AC voltage, from 5 Hz to 1 kHz. In addition to the height variation, a drastic change in the base width of the dot is observed. The exposure time was 50 s with $V_{ox} = 8$ V and $V_{res} = -8$ V. Compared to oxidation under DC voltage, the aspect ratio increase is due to both the height increase and width reduction.

Dot formation has been studied as a function of V_{res} , T_{ox} , T_{res} and relative humidity (RH). The influence of V_{ox} and exposure time are not analysed here, because their effect has been described in previous works [3–5, 8].

In figure 6, we show six oxide dots formed by applying different waveforms, but with the same exposure time (30 s) and oxidation voltage (8 V). The differences in shape are

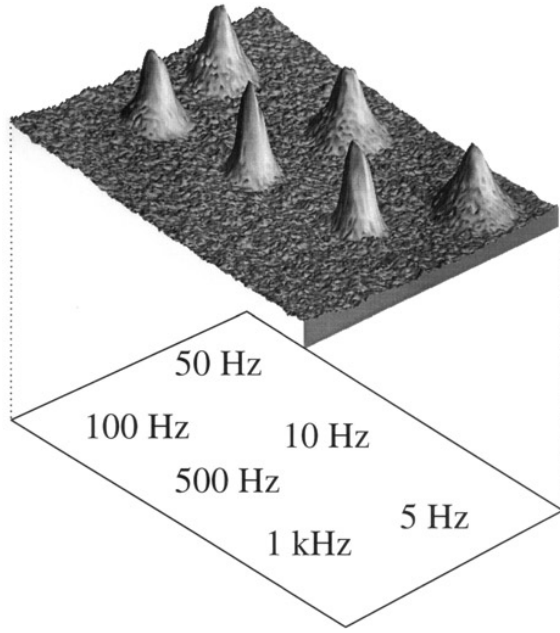


Figure 5. AFM image of six oxide dots fabricated on an n-type Si(100) surface at six different frequencies of the AC voltage, as depicted below each dot. It shows the decrease of the base width of the dot when the frequency increases.

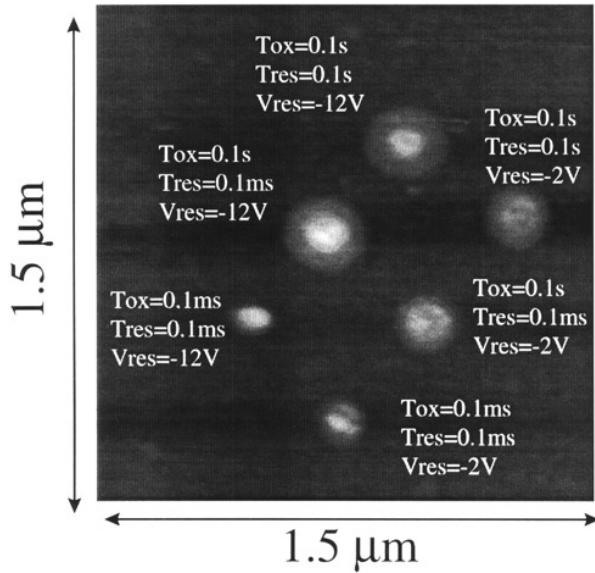
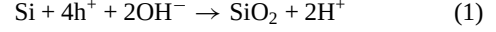


Figure 6. AFM image of six oxide dots formed by applying different waveforms, but with the same exposure time 30 s and $V_{ox} = 8$ V. The rest of the parameters that define each waveform voltage are depicted for each dot.

remarkable. From experiments like this, we have obtained that, (a) making V_{res} more negative increases the dot height; (b) decreasing T_{ox} reduces the base width; (c) T_{ox} and T_{res} have opposite effects on the height. The height increases when T_{res} increases and/or T_{ox} decreases; (d) experiments performed under low humidity conditions (20% RH) reveal a decrease of the effect of modulating the voltage.

5. Implications for the oxidation mechanism

The accepted explanation of the SPM oxidation of silicon surfaces requires the formation of a water meniscus between tip and sample. Oxygen ions (OH^- , O^-) are produced by the hydrolysis of the water within the meniscus. The ions are driven through the oxide by the electrical field. At the Si/SiO₂ interface they react with holes h^+ . The oxidation reaction can be written as,



However, the above model does not explain why the observed kinetics deviates from the Cabrera–Mott model [5] and the low density of the SPM-grown oxide. It also does not account for the voltage modulation effects presented in section 4. In fact, a complete understanding of the oxidation mechanism requires addressing the formation of the meniscus at the tip/sample interface and the hole concentration at the surface/oxide interface. It also requires considering the ionic transportation through the meniscus and through the growing oxide.

The height enhancement under modulation voltage conditions (figure 4) can be related to the space charge build-up within the oxide. The oxidation reaction is a source of hydrogenous species. The proton concentration increases after long pulse times, with the $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$ neutralization reaction becoming significant. When less OH^- arrive at the Si/SiO₂ interface, this in turn, implies a decrease of the oxidation rate. However, this effect can be reduced by the application of AC voltage pulses. The negative part of the voltage pulse decreases the concentration of H^+ in the oxide. As a consequence, the oxidation rate is higher for AC voltage pulses.

The above mechanism also applies to explain the frequency dependence of the lateral dimension of the oxide (see figure 5). At high frequencies (>100 Hz) the negative part of the AC voltage reduces the lateral diffusion of OH^- at the water/SiO₂ interface, and this causes a reduction of the oxide base.

Under DC voltage pulses, the release of H_2O during the neutralization reaction could give rise to the formation of water related defects inside the oxide. This could explain the lower density of the SPM oxide. Furthermore, the H^+ accumulation within the oxide could be one of the main reasons of the deviation from Cabrera–Mott kinetics.

6. Conclusions

The SPM-induced local oxidation of silicon surfaces has been studied under two different conditions: non-contact and modulation voltage. The reliability of the local oxidation of silicon is greatly improved by keeping the tip and the sample separated several nanometres. The application of an oscillating voltage improves the aspect ratio of the oxide structures. The above experiments have shown the importance of the formation of the water meniscus and the space charge build-up within the oxide. In consequence, this implies that a complete understanding of the SPM-induced oxidation mechanism and kinetics also requires us to take into account both phenomena and the interplay between them.

Future work will allow a more complete understanding of the optimum factors needed to fabricate functional nano-devices.

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References

- [1] Dagata J A, Schneir J, Harary H H, Evans C J, Postek M T and Bennet J 1990 *Appl. Phys. Lett.* **56** 2001
- [2] Day H C and Alle D R 1993 *Appl. Phys. Lett.* **62** 2691
- [3] Teuschler T, Mahr K, Miyazaki S, Hundhausen M and Ley L 1995 *Appl. Phys. Lett.* **67** 3144
- [4] Stievenard D, Fontaine P A and Dubois E 1997 *Appl. Phys. Lett.* **70** 3272
- [5] Avouris P, Hertel T and Martel R 1997 *Appl. Phys. Lett.* **71** 287
- [6] Wang D, Tsau L and Wang K L 1994 *Appl. Phys. Lett.* **65** 1415
- [7] Pérez-Murano F, Abadal G, Barniol N, Aymerich X, Servat J, Gorostiza P and Sanz F 1995 *J. Appl. Phys.* **78** 6797
- [8] García R, Calleja M and Pérez-Murano F 1998 *Appl. Phys. Lett.* **72** 2295
- [9] Minne S C, Soh H T, Flueckiger Ph and Quate C F 1995 *Appl. Phys. Lett.* **66** 703
- [10] Snow E S, Park D and Campbell P M 1996 *Appl. Phys. Lett.* **69** 269
- [11] Matsumoto K, Ishii M and Segawa K 1996 *J. Vac. Sci. Technol. B* **14** 1331
- [12] Shirakasi J, Matsumoto K, Miura N and Koganai M 1997 *Japan. J. Appl. Phys.* **36** L1257
- [13] de Pablo P, Colchero J, Gómez-Herreo J and Baró A M *Appl. Phys. Lett.* submitted
- [14] García R, Calleja M and Rohrer H unpublished
- [15] Dagata J A, Inoue T, Itoh J and Yokoyama H 1998 *Appl. Phys. Lett.* **73** 271