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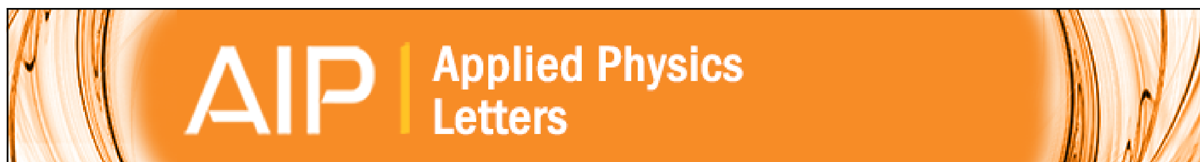

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Local oxidation of silicon surfaces by dynamic force microscopy: Nanofabrication and water bridge formation

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Local oxidation of silicon surfaces by atomic force microscopy is a very promising lithographic approach at nanometer scale. Here, we study the reproducibility, voltage dependence, and kinetics when the oxidation is performed by dynamic force microscopy modes. It is demonstrated that during the oxidation, tip and sample are separated by a gap of a few nanometers. The existence of a gap increases considerably the effective tip lifetime for performing lithography. A threshold voltage between the tip and the sample must be applied in order to begin the oxidation. The existence of a threshold voltage is attributed to the formation of a water bridge between tip and sample. It is also found that the oxidation kinetics is independent of the force microscopy mode used (contact or noncontact). © *1998 American Institute of Physics.* [S0003-6951(98)02118-4]

Several procedures have been proposed for the modification of surfaces at nanometer and atomic scales using scanning probe microscopes (SPM). Among them, the field induced oxidation of silicon[1–5] and metal[6] surfaces is arguably the most promising approach for the fabrication of nanoelectronic devices.[7] The first experiments were performed with the scanning tunneling microscope (STM).[1–3] However, the versatility of the atomic force microscope (AFM) for operating with conducting and nonconducting samples alike has prompted its application for the local oxidation of surfaces.

Recently, Minne *et al.* have applied the AFM for patterning the gate of a (MOS) transistor,[7] Snow *et al.* for the fabrication of a point contact quantum device,[8] and Matsumoto *et al.*[9] for generating a single electron transistor. However, the transition from these experiments to technological fabrication of nanodevices requires the understanding of the oxidation mechanism, the combination with other technological processes as well as the improvement of the reproducibility and throughput of the overall process.

The reproducibility of a single SPM induced oxidation experiment is strongly dependent on the tip lifetime. It has been shown that tips suffer from considerable wear when performing lithography in contact mode AFM[10] due to the combined effects of frictional and attractive electrostatic forces. This problem may be overcome if the lithography is performed in a noncontact AFM mode.[11–14]

In dynamic AFM modes, tapping mode is also included, the wear of the tip is reduced, and its lifetime increased due to the minimization of lateral forces.[15] The routine application of this mode for nanofabrication requires a complete understanding of the oxidation mechanism as well as the full description of the dynamics of the cantilever. Here, we address three relevant issues to generate nanometer size marks by noncontact AFM, (i) the dynamics of the cantilever during the oxidation, (ii) the voltage dependence, and (iii) the kinetics of the oxidation.

The experiments were performed in a controlled humidity environment with values of the relative humidity around 30%–40%. A commercial AFM was used (Nanoscope III, Digital Instruments, Santa Barbara, CA). The silicon cantilevers were metallized with a layer of 30 nm of Ti. The average force constant and resonance frequency of the cantilevers used were about 40 N/m and 350 kHz, respectively. The samples were n-type Si(100) with a resistivity of 14 Ω cm.

An array of 1024 oxide dots are shown in Fig. 1. The image illustrates the reproducibility of the oxidation in noncontact AFM. Routinely, the same tip is able to write thousands of dots without showing any sign of wear. To write a

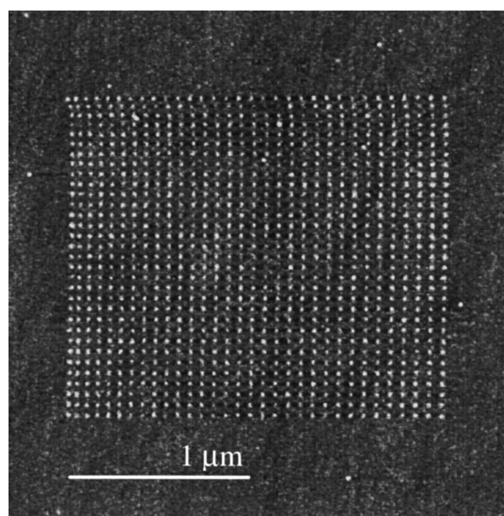

FIG. 1. AFM image of an array of 1024 dots obtained in noncontact AFM induced oxidation of a Si(100) surface. The dots are 60 nm apart and show an apparent diameter of about 30 nm and a height of 2 nm. Each dot is formed by applying a pulse of 14 V (sample positive) for 50 ms. Oscillation amplitude (set point value), $A_s = 6$ nm, working frequency, $f = 327$ kHz, relative humidity, RH = 40%.

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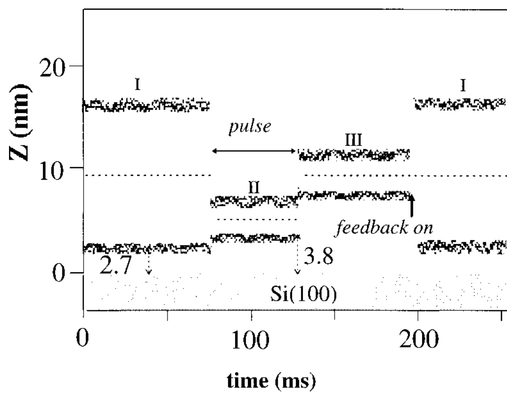

FIG. 2. Cantilever oscillation amplitude vs time before, during, and after the formation of a dot. The oscillation amplitude is represented by its maximum and minimum values. The position of the Si(100) with respect to the cantilever is also plotted. Dashed lines show the equilibrium position of the cantilever. The signal from the photodiode (oscillation amplitude) has been acquired with an oscilloscope. A pulse of 12 V and 50 ms was applied.

dot, a positive voltage of 14 V and 50 ms of duration is applied to the sample. At the same time, the feedback loop is disabled. During the oxidation (see below), there is a finite tip-sample separation, as a consequence the lateral forces are small and the sharpness and conductivity of the tip is retained.

In Fig. 2 we show the cantilever response before, during, and after the application of a pulse of 12 V for 50 ms. Three major effects are observed, (i) the deflection of the cantilever towards the surface, (ii) the reduction of the oscillation amplitude during the pulse, and (iii) the damping of the amplitude until the feedback is restored.

The cantilever is deflected 4 nm due to the attractive electrostatic force. The electrostatic force also shifts the resonance frequency to lower values, which causes a reduction of the amplitude from 6.6 to 1.8 nm (II). After the pulse the cantilever recovers its equilibrium position. However, the damping of the amplitude remains until the feedback is restored (III). The origin of this damping will be discussed in combination with Fig. 3.

The tip sample separation has been determined from phase and amplitude versus distance curves.[16] The minimum

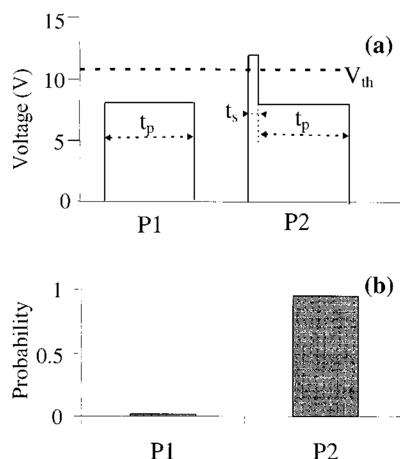

FIG. 3. Probability of dot formation for two different pulses. (a) P1 and P2 voltage sequences and (b) probability for P1 and P2; t_s and t_p are the duration of the short initial pulse above V_{th}, and the long pulse below V_{th}, respectively. Here, $t_s = 5$ ms and $t_p = 5$ s; RH=44%.

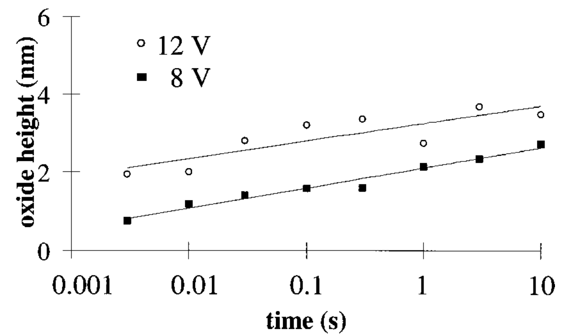

FIG. 4. Height of the oxide dot vs voltage pulse duration for 12 and 8 V, respectively. $A_s = 5.1$ nm, $f = 353$ kHz, and RH=40%.

tip-sample separation is 2.7 nm, i.e., the oxidation takes place without tip-sample mechanical contact. This is significantly different from contact AFM oxidation experiments where the tip is always in contact. There, tip and sample are wetted by a water film which supplies the OH^- ions for the anodic oxidation.

It is also observed that in dynamic AFM a minimum voltage must be applied for starting the oxidation[13] (threshold voltage, V_{th}). The existence of V_{th} in noncontact AFM oxidation is a departure from what happens in contact AFM oxidation. Although the value of V_{th} depends (increases) strongly on the amplitude, the dimensions of the dots formed at a voltage above V_{th} have a negligible dependence on the amplitude. This observation together with the defocusing effects of the water film[17] were led to hypothesize that V_{th} could be understood as the voltage needed to polarize the water layer adsorbed onto the sample and to form a water bridge between tip and sample. Based on this, an experiment to clarify the origin of V_{th} was performed.

We have calculated the probability of dot formation for two voltage sequences (Fig. 3). One sequence is formed by a pulse below V_{th}, (P1). The other is formed by a short pulse at a voltage above V_{th} followed by a long pulse below V_{th} (P2). This experiment was carried out for $V_{th} = 11$ V.

Figure 3(b) shows that the probability of dot formation for P1 is negligible. However, when the voltage consists of a short pulse above V_{th} followed by a long pulse below V_{th} the probability is close to 1 (P2). The duration of the short pulse (5 ms) was at least one order of magnitude smaller than the time required to form an observable dot. This suggests that the role of the short pulse above V_{th} is to establish an intermediate state from which the oxidation can begin.

The oscillation amplitude is also sensitive to the application of a voltage pulse above or below V_{th}. The amplitude presented in Fig. 2 shows three stages. This curve was obtained for $V > V_{th}$. When the experiment is performed for $V < V_{th}$, the amplitude shows stages I and II but stage III is always missing. The oscillation amplitude recovers its initial value I once the pulse is finished. On the other hand, the presence of the intermediate stage III would be consistent with the formation of a water bridge and it underlines the role of the voltage pulse above V_{th} in its formation.

The kinetics of the oxidation in dynamic force microscopy can be deduced from the data presented in Fig. 4, where the height of the oxide dot is plotted versus time for two different voltages (see Ref. 17). From this figure, the growth

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rate as a function of the oxide height can be obtained. It follows the equation $dh/dt \propto \exp(-h/L_c)$ with $L_c(8\ \mathrm{V}) = 0.5$ nm and $L_c(12\ \mathrm{V}) = 0.6$ nm, respectively. Here h is the oxide thickness. The growth rate decreases with oxide thickness due to the reduction of the electrical field through the oxide. The overall dependence is similar to the results reported in contact AFM experiments.[17–19] This shows that the oxidation kinetics in noncontact and contact AFM is the same.

In this letter we have investigated the reproducibility, voltage dependence, and kinetics of noncontact AFM oxidation of silicon surfaces. The threshold voltage observed in noncontact AFM is associated with the formation of a water bridge between tip and sample. It is also shown that contact and noncontact AFM oxidations have similar kinetics. The technological potential noncontact AFM for performing lithography lies on the very small wear shown by the tip after thousands of oxidations.

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