

Growth of silicon oxide on hydrogenated silicon during lithography with an atomic force microscope

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We present an experimental study of growth of silicon oxide strips drawn on hydrogenated silicon under the voltage biased tip of an atomic force microscope operating in ambient atmosphere. Oxide formation was found to occur at negative tip biases above a voltage threshold around $-2|V$, corresponding to the minimum electric field required for hydrogen removal from the substrate surface. We show the influence of tip-sample distance and of the chemical composition of the atmosphere on the growth. An ozone enriched atmosphere leads to a growth kinetics enhancement.

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I. INTRODUCTION

In the past few years, various lithography techniques involving proximal probe microscope, i.e., scanning tunneling microscope (STM), atomic force microscope (AFM), and scanning near field optical microscope (SNOM), have been developed. The atomic resolution reached by such microscopes has risen hopes that a substantial resolution gain can be obtained with respect to electron beam lithography, thus leading to potential application in nanoscale devices elaboration. In fact, surface patterning at a nanometric scale has already been demonstrated using proximal probe microscopes. Except results based on the mechanical interaction between a AFM tip and a soft substrate (mechanical indentation of polymer resists^{1,2} or self-assembled monolayers³), most of these lithography techniques take advantage of the spatial resolution of the electronic emission from the microscope tip to perform local physical or chemical alterations on a suitably prepared surface. Following this principle, a wide range of different techniques were investigated: chemical vapor deposition under the tip of a STM,^{4,5} local exposure of polymer resists,⁶ or local oxidation of silicon⁷ and of thin metallic films (Al, Ti)⁸⁻¹⁰ have been reported.

A considerable effort is devoted to oxide patterning by local depassivation of hydrogenated silicon surface involving STM,^{7,11-15} AFM,¹⁶⁻¹⁸ SNOM,¹⁹ because it could eventually lead to a mask generation process entirely compatible with today's microelectronics technology. Since the feasibility demonstration of silicon oxide growth induced by AFM, this technique has been used to fabricate nanoscale devices,²⁰ but few have investigated physical and chemical mechanisms^{17,18,21} involved in the oxide growth.

In this article, we study the influence of various parameters on the growth of silicon oxide strips drawn with a voltage biased AFM tip on silicon passivated surfaces. Influence of both tip voltage and scan speed on the growth rate have been investigated for heavily and lightly doped *n*- or *p*-type

silicon wafers. More specifically, we have observed the influence of tip-surface distance and of atomic oxygen concentration in the atmosphere.

On the basis of these results, a three-step growth mechanism is proposed.

II. EXPERIMENTAL SETUP AND SURFACE PREPARATION

The lithography was performed in ambient air with a Digital Instruments Nanoscope III AFM operating in contact mode. Contact mode is preferred with respect to noncontact or intermittent contact mode because a water meniscus is always present at the tip sample interface thus avoid artifacts during lithography due to the formation of that meniscus.

We used commercial tips made of *n*-type silicon ($\rho = 0.01 \Omega \text{ cm}$) with an apex radius of 10 nm, coated or not with a thin metallic layer (Ti, Co-Cr). As the metal-coated tips gave the same results as the silicon ones, the results presented in the following were obtained with silicon tips which were found to be more robust with respect to the strong frictional forces occurring in contact mode. The AFM was placed inside a glass reactor (glass bell) in order to prevent air movements and to control ambient atmosphere during lithography (gas, humidity, ...). The relative humidity in the presented experiments was kept constant at around 40%–50%.

The oxidation of the surface was performed with tip voltage ranging from -15 to $+15$ V while the substrate was grounded. The tip velocity was varied from 0.1 up to $8 \mu\text{m/s}$. Finally, the influence of distance between tip and substrate has been explored from a qualitative point of view.

Four types of commercial (100) silicon samples ($1 \Omega \text{ cm}$ *n*-type, $0.01 \Omega \text{ cm}$ *n*-type, $1 \Omega \text{ cm}$ *p*-type, and $0.01 \Omega \text{ cm}$ *p*-type) have been used. The substrates were previously hydrogenated by a conventional RCA process which consists in a series of oxidation and stripping. Oxide removal was performed in a BHF solution ($\text{NH}_4\text{F} + \text{HF}$, 7:1) at room temperature while substrate oxidation occurred in a mixture

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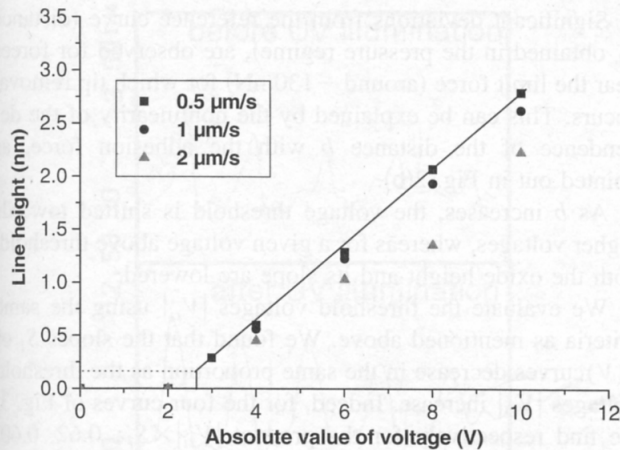


Fig. 1. Dependence of oxide line height h on the absolute voltage V applied to the tip at increasing scan speeds for an (100) n -type (0.01 Ω cm) silicon substrate.

HCl/H₂O₂/H₂O (1/4:1/4:1/2) at a temperature of 70 °C. The last stripping step is followed by substrate immersion in a 40% NH₄F solution. This treatment is known to provide a clean silicon surface passivated regarding ambient atmosphere since all surface dangling bonds become saturated by mono-atomic hydrogen.²²

III. RESULTS AND DISCUSSION

The influence of tip voltage on silicon oxide growth kinetics has been studied. For a positive bias, no oxide growth was observed in the range $[0, +15$ V]. A tip-substrate current flow was measured for both n - or p -type substrates during the lithography runs. For negative tip biases, anodic oxide growth was observed on the substrate but no current was detected by our setup during the lithography process, for any type of doping. This last result can be explained by the local insulation of the surface below the tip due to oxide formation and by the tiny number of electrons required for the oxidation of silicon.²³ Thus, oxide growth under an AFM tip should be interpreted as an electric field effect rather than a current effect as confirmed by authors who perform such anodic lithography in intermittent contact or noncontact AFM modes.²⁴ So the kinetics of oxide formation should be dependent essentially on the tip-surface distance and the voltage applied on the tip.

The dependence of oxide line height h on the absolute value of negative voltage V applied to the tip at different scan speeds for an n -doped (0.01 Ω cm) (100) silicon wafer is presented in Fig. 1. Similar results have been obtained on substrates with different doping type and concentration. Above a threshold voltage V_t lying between $[-2]$ and $[-3]$ V, oxide line thickness increases linearly with the applied voltage. Assuming that the voltage threshold corresponds to the minimum voltage required to reach an oxide thickness of 0.2 nm (minimum oxide thickness observed), the voltage threshold V_t obtained in Fig. 1 equals $|-2.7|$ V.

The linear variation of the oxide thickness h with the tip was already reported in other papers.¹⁷ It is generally attrib-

uted to the electric field induced enhancement of oxygen ion diffusion through the SiO_x layer to the SiO_x-Si interface.²⁵ Quantitative study presented in Ref. 17 seems to support this idea.

We observed a slight increase of the line height as the scan speed decreases. A logarithmic dependence has been measured¹⁷ for a much higher speed range (4–128 μ m/s).

Figure 1 exhibits the existence of a well-defined and constant voltage threshold V_t required for oxide formation. Such a reproducibility can be attributed to the fact that we carefully control the surface preparation. Substrate passivation by surface hydrogenation impedes oxidation during substrate exposure to ambient air. In order to form an oxide layer, this passivation layer has first to be removed. In our case, the hydrogen can be locally removed by the electric field which exits between the tip and the surface when tip is biased. The electric field within the tip area can be calculated, assuming that the AFM tip is considered as a charged sphere above an infinite conducting plane as is done for a STM tip.¹² The value of the electric field on the substrate surface located at a distance R from the projection on the sample of the tip apex, can be expressed as follows:

$$E(R) = \frac{a(b+a)(2b+a)}{2b[(b+a)^2 + R^2]^{3/2}} V, \quad (1)$$

where a is the sphere radius (about 10 nm), b the tip-surface distance ($b \approx 1$ nm). For $V = |-2.7|$ V and $R = 0$ (below the tip apex), we find an electric field $E(0) \approx 10^9$ V/m. Assuming that Si-H bond length X is of the order of 0.1 nm, the minimum energy ϵ required for hydrogen removal from the surface can be roughly estimated as follows:

$$\epsilon \approx eE(0)X, \quad (2)$$

where e is the electron charge.

The estimation gives $\epsilon \approx 100$ meV. It is known that under ultrahigh vacuum (UHV) conditions, hydrogen desorption from silicon surface occurs at temperature higher than 600 °C, which corresponds to a threshold thermal energy of $\epsilon \approx 75$ meV, in agreement with the estimated energy.

According to Eq. (1), the electric field is strongly dependent on the tip-sample distance b . We were able to vary this distance by performing lithography with a tip in the adhesive regime as presented in the following.

In fact by changing the setpoint of the cantilever deflection feedback loop, it is possible to tune the tip-to-sample force, and within some conditions (for a strong capillary force of the water meniscus at tip-sample contact), to explore lithography for a tip interacting with a “negative force,” i.e., in the adhesive regime [see Fig. 2(a)].

A more complete description of the involved mechanism is provided by examining the hysteresis force curve (which represents cantilever deflection versus Z piezovoltage).

In this curve, presented in Fig. 2(b), the linear dependence indicates a contact between tip and sample. Contact occurs for both positive (pressure regime) and negative tip deflection (adhesion regime). Just before tip removal, a small deviation from the linear dependence could be observed in our

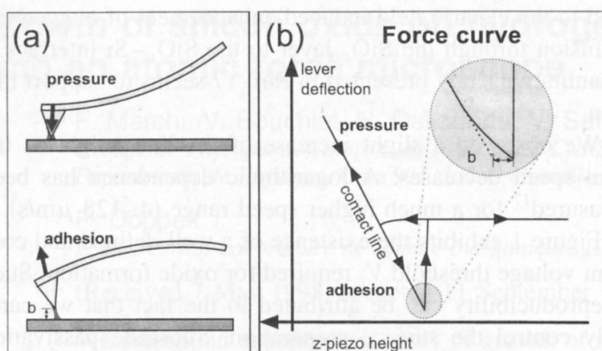


FIG. 2. (a) Sketch of the AFM tip position for two different kinds of tip-sample interaction. In the upper drawing, the tip is pushed towards the surface and exerts a pressure, whereas the lower drawing the cantilever is retracted but the tip adheres to the surface with a finite tip-sample distance b . (b) Typical deflection curve of a cantilever vs z position of the sample. This so-called "force curve" is a signature of the tip-sample interaction in "contact mode." In the grayed inset, we have zoomed the limit case of tip adhesion with a finite tip-sample distance b , which corresponds to the drift with respect to the linear regime.

experiment [see inset in Fig. 2(b)], thus proving that the tip to sample distance b was nonzero. By succeeding to regulate the cantilever deflection around that value, the tip can be scanned over the surface with a constant distance b . A precise quantitative estimate of b could not be obtained, but one could evaluate that b remains of the order of several nanometers.

We then study the voltage dependence of oxide height for different tip-sample forces. We have first checked that no noticeable change in oxide height voltage dependence is detected when the tip pressure increased. In fact in this case, the tip-sample distance does not vary. We have then measured the dependence of $h(V)$ for four increasing negative tip-sample forces in the nN range, corresponding to increasing tip-surface distances b_1 to b_4 (see Fig. 3).

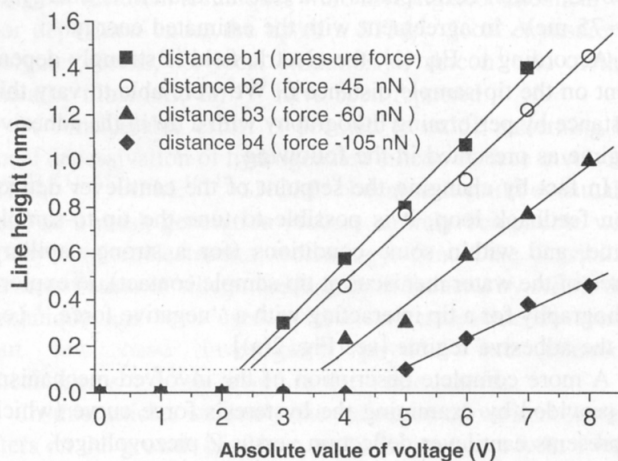


FIG. 3. Influence of tip voltage on the oxide line height for different tip-sample interacting forces. In the pressure regime the oxide height at a given voltage does not depend on the force intensity. On the opposite, in the adhesion regime, the corresponding tip-surface distance b_i increases with the negative force in intensity leading to a reduced voltage sensitivity.

Significant deviations from the reference curve (distance b_1 obtained in the pressure regime), are observed for forces near the limit force (around -130 nN) for which tip removal occurs. This can be explained by the nonlinearity of the dependence of the distance b with the adhesion force, as pointed out in Fig. 2(b).

As b increases, the voltage threshold is shifted towards higher voltages, whereas for a given voltage above threshold, both the oxide height and its slope are lowered.

We evaluate the threshold voltages $|V_{ti}|$ using the same criteria as mentioned above. We found that the slopes S_i of $h(V)$ curves decrease in the same proportion as the threshold voltages $|V_{ti}|$ increase. Indeed, for the four curves of Fig. 3, we find respectively for the product $|V_{ti}| \times S_i$: 0.62, 0.60, 0.70, 0.63.

These results confirm completely the framework of a field assisted mechanism for the involved process.

At that point, one can suggest for oxide growth the following three-step mechanism:

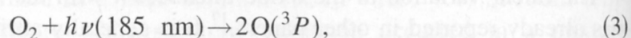
- (1) Surface depassivation by desorption of hydrogen atoms assisted by the electric field above a threshold of 10^9 V/m.
- (2) Formation of oxyanions in the water meniscus between tip and surface, a complex step which may involve both electrolytic and dissolution processes.
- (3) Diffusion of oxyanions assisted by the electric field toward to the SiO_x -Si interface.

Note that the first and the third steps require the positive polarization of the sample, which explains why local oxidation is only observed for the negative tip bias. As soon as the minimum electric field required for hydrogen removal from the surface is reached, we argue that in our experimental conditions, the limiting process is the supply of oxyanions available for the oxide growth. Let us remark that the volume of the meniscus is roughly the same as the volume of oxide formed under the tip thus native oxyanions in the water meniscus are by many orders of magnitude insufficient to provide the necessary species for the oxide growth. Consequently some out-of-equilibrium processes (water dissociation and exchange with the atmosphere) must be involved.

In order to experimentally confirm this last assumption, we have tried to modify the nature and concentration of reactive species in the gaseous environment.

The crucial influence of the atmosphere was already pointed out in early experiments.²⁶ Indeed it was shown that AFM lithography of strip lines made of silicon nitride instead of silicon oxide can be induced under a partial pressure of ammonia.

In our experiment, we decided to perform lithography in a modified atmosphere containing a given quantity of ozone produced by a low pressure Hg lamp placed inside the glass reactor. In these conditions, concentration of reactive oxygen based species is greatly enhanced. Ozone is produced in the gas phase by the following two-step process²⁷ involving an atomic oxygen triplet state 3P :



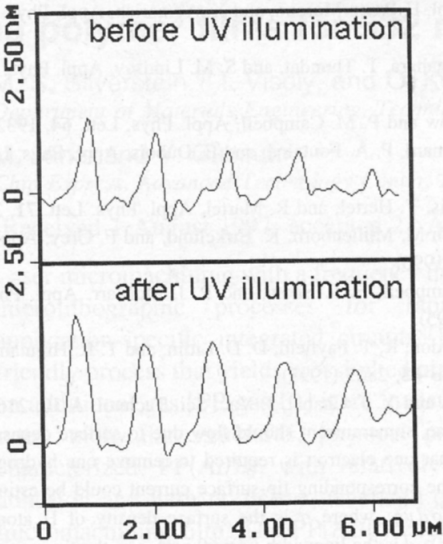


FIG. 4. Cross sections of AFM micrographs for two series of lines drawn at voltages of -10 , -9 , -8 , -7 , -6 V from left to right. The top series has been performed in ambient atmosphere, while the bottom series has been drawn under ozone partial pressure.

$$\text{O}(^3P) + ^3\text{O}_2 \rightarrow \text{O}_3. \tag{4}$$

Ozone is then decomposed by absorption of UV light at 254 nm which produces oxygen atoms in the excited state 1D and oxygen molecules in the singlet ($^1\text{O}_2$) or triplet ($^3\text{O}_2$) states.²⁸

$$\text{O}_3 + h\nu(254\text{ nm}) \rightarrow \text{O}(^1D) + \text{O}_2. \tag{5}$$

Because the UV light source employed emits both spectra lines (185 and 254 nm), the two reactions occur simultaneously and generate very reactive species (atomic oxygen ^1O and singlet molecules $^1\text{O}_2$). With pure oxygen, silicon oxidation process requires oxygen molecule dissociation on the substrate surface due to molecule chemisorption.²⁹ In an ozone rich atmosphere, atomic oxygen is already available in the gas phase. Consequently the oxyanions concentration, which exact nature is not known, increases in the water meniscus. The oxide growth rate which directly depends on that concentration should then be enhanced.

The experiment was performed in the following way: stop of the sample scan, UV irradiation of the environmental atmosphere for a given time, switch off the UV lamp, lithography, and finally sample imaging of the formed oxide lines. The substrate and the tip were not directly exposed to UV light in order to avoid artifacts due to photochemical reactions on the surface or in the water meniscus.

Figure 4 shows the effect of ozone on the height oxide lines for a 1 Ω cm n -type sample. The series of lines on the top of the image of Fig. 4 were obtained without ozone while the series of line at the bottom were obtained in ozone rich atmosphere. These cross sections clearly show that growth rate is enhanced in ozone atmosphere.

Figure 5 presents the oxide line height dependence on tip voltage $h(V)$ at different illumination duration for 1 Ω cm n -type Si sample. A linear relation between the line height

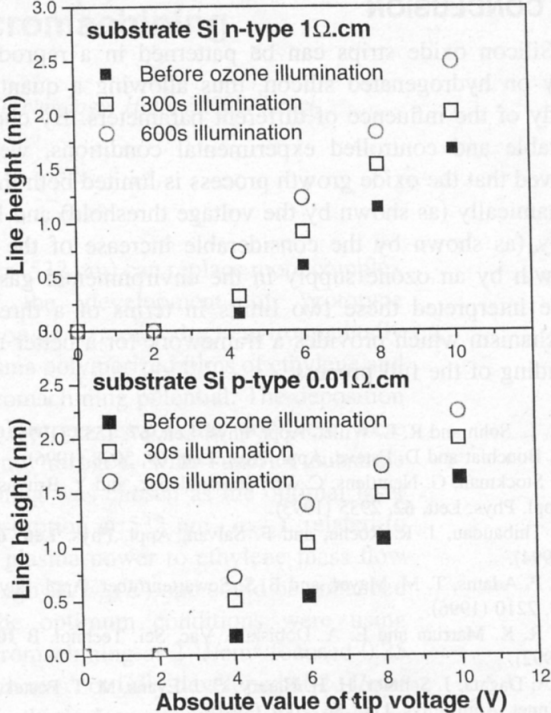


FIG. 5. Dependence of oxide line thickness on tip voltage at different time exposure to UV light (i.e., different ozone partial pressure). Top: n -type Si (100) substrate, resistivity 1 Ω cm, bottom: p -type Si (100) substrate, resistivity 0.01 Ω cm.

and the absolute voltage as well as the existence of a threshold around -2 V in presence of ozone were still observed. However, the line height increases with the lighting time of the UV lamp, i.e., with the atomic oxygen concentration in atmosphere and hence at the substrate surface. On the other hand the slopes S of the $h(V)$ curves were not affected which means that the oxide growth rate is still controlled by the electric field.

Similar results (Fig. 5 lower panel) were observed for p -type samples, but for much shorter illumination times (30–60 s). Since the atomic oxygen formation does not depend on the type of dopant but only on illumination time, step 2 is clearly not the rate limiting step of the process. In this latter case, the same enhancement would be observed independently of the type of dopant. In all cases, the voltage threshold was not affected by oxyanion concentration in the gaseous environment. Our interpretation is that the voltage threshold corresponds to the minimum electric field required for hydrogen desorption and therefore does not depend on the oxyanions nature or concentration. This ozone experiment confirms the predominant role of the atmosphere composition for the oxide kinetics. However, the precise mechanism which limit the oxide growth cannot be determined in these experiments. Internal stresses within the oxide layer¹⁸ have been suggested to be a source for growth limiting. Recent experiments³⁰ using a suitably modified AFM showed that space charge effects are also involved.

IV. CONCLUSION

Silicon oxide strips can be patterned in a reproducible way on hydrogenated silicon, thus allowing a quantitative study of the influence of different parameters. By choosing suitable and controlled experimental conditions, we have proved that the oxide growth process is limited both thermodynamically (as shown by the voltage threshold) and kinetically (as shown by the considerable increase of the oxide growth by an ozone supply in the environmental gas). We have interpreted these two limits in terms of a three-step mechanism which provides a framework for a better understanding of the full process.

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