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Nanooxidation using a scanning probe microscope: An analytical model based on field induced oxidation

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The formation of a nanometer-size oxide pattern on silicon using a scanning probe microscope (SPM) has been widely reported in the literature. No analytical model has been proposed, however, to explain the variation of the oxide height with both polarization and speed of the SPM tip. In this letter, we explain quantitatively the variation of the oxide height with the polarization and the speed of the tip with a model based on field induced oxidation. Data analysis also allows us to estimate the thermal activation energy of the oxidation process, (~ 0.15 eV). This low value is compared with activation energies measured for thermal and plasma oxidation of silicon.

Since the pioneering work of Dagata *et al.*¹ showing the possibility of creating an oxide pattern with nanometric dimensions on a hydrogen-passivated surface with a scanning tunneling microscope operating in air, other groups have worked on the oxidation of silicon surfaces using a scanning tunneling microscope (STM).²⁻⁹ More recently, similar oxidation processes have been reported using an atomic force microscope (AFM) with a conducting probe in contact¹⁰⁻¹⁶ and in noncontact modes.^{17,18} AFM offers the advantage of both realizing local oxidation and obtaining the actual topography of the associated pattern. Due to the convolution of topographic and electronic information, STM cannot give the real height (h) of an oxide pattern. From the linear variation of the oxide height (h) versus the voltage V applied between the tip and the surface, it was deduced that oxidation is associated with a field effect mechanism, but no quantitative interpretation was proposed. As to the variation of h with the speed v of the tip, a few studies give h proportional to $\log(1/v)$,^{6,18} $v^{-1/2}$,¹¹ and $v^{-1/4}$.¹⁴ In each case, no physical quantitative model was proposed to explain these laws. This letter proposes a physical model that describes both the variation of h with bias V and with tip velocity v .

The lithography was performed with a Digital Instruments Nanoscope III microscope, with metal coated AFM tips, on 17–25 Ω cm (100) p -type silicon (boron doped). In order to minimize surface roughness [typically, we measure a root mean square (rms) surface roughness less than 0.12 nm over a $2 \times 2 \mu\text{m}^2$ surface], a thermal oxide (100 nm) was first realized. This oxide was subsequently cleaned with a standard RCA process, etched in 50% hydrofluoric acid (HF) for 2 min, and rinsed in ultrapure [de-ionized (DI)] water. This treatment is known to provide a hydrogen-passivated surface.¹⁹⁻²⁴ The oxidation of the surface (anodization, i.e., the surface is positively biased with respect to the tip; the tip is grounded) was performed with V_{bias} ranging from 4 to 10 V and a tip velocity ranging from 4 to 128 $\mu\text{m/s}$. During the oxidation process, the measured current was found to be less than 1 pA, the limit of our instrumentation detection. Measurements were performed with a relative humidity of 70%.

Figure 1 gives the variation of h vs V with v as a pa-

rameter. We observe that, for a given speed, h increases quite linearly with the applied voltage V_{bias} , as is usually observed. The extrapolation of the data towards low voltage shows the existence of a threshold voltage (~ 2.8 V), in agreement with previous results.^{14,15} It is known that the oxidation process is enhanced for an electric field of the order of $\sim 1 \times 10^7$ V/cm. Moreover, for a given voltage, h decreases as the speed v increases. Figure 2 shows the linear variation of $1/h$ vs $\log(v)$ with V as a parameter. This presentation of the data corresponds to a field induced oxidation (FIO) mechanism, proposed by Cabrera and Mott,²⁵ for the formation of very thin oxide films. A quantitative analysis of the measured oxide height is proposed in the following.

As proposed by Gordon *et al.*,¹⁶ ionic diffusion of OH⁻ or O⁻ (the exact nature of the diffusing specie is not known) takes place through the oxide layer, from the oxide surface towards the silicon-silicon oxide interface. Due to the contact potential V_0 (Mott potential) difference between the adsorbed oxygen layer and the initial oxidized silicon, the associated electric field E_0 enhances the diffusion mechanism. In the present case, the applied voltage between the tip and the sample surface (V_{bias}) superimposes with the contact potential. The quantitative analysis of the phenomenon, derived

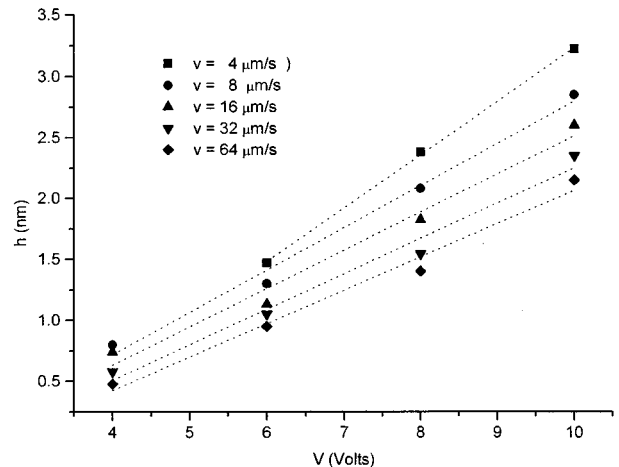


FIG. 1. Variation of the height h of the oxide vs the voltage V (the surface is positively biased with respect to the tip).

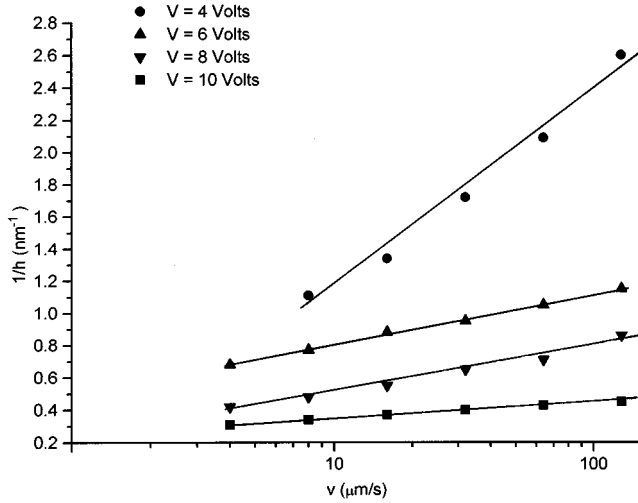


FIG. 2. Variation of the inverse of the height of the oxide vs the speed of the tip.

from the approach proposed by Cabrera and Mott for the oxidation of very thin oxide films is adapted. The electric field is so strong that the velocity of drift of the ions is no longer proportional to it. If W is the energy that an interstitial ion has to overcome to diffuse (W includes the activation energy for diffusion added to the initial potential barrier of width $2a'$ between two interstitial sites), it can be shown that the kinetics of growth is given by²⁵

$$\frac{dh}{dt} = u \exp(h_1/h), \quad (1)$$

where

$$h_1 = qa'V/kT, \quad (2)$$

with V equal to $V_0 + V_{\text{bias}}$, q the electronic charge of an electron, k the Boltzman constant, T the temperature, and u is given by

$$u = u_0 \exp(-W/kT), \quad (3)$$

with u_0 of the order of 10^4 cm/s.²⁵

Equation (1) is valid only for $h \ll h_1$ with h_1 typically of the order of a few nm. It also shows that the growth rate is very large for small h . This relation has to be compared with the case of thin films where $dh/dt = A/h$, leading to the usual quadratic form where h^2 is proportional to t .

As Eq. (1) is valid only for small h , we have to determine a higher limit h_L where oxidation is no longer assisted by the electric field. This corresponds to an electric field E_L lower than $\sim 1 \times 10^7$ V/cm,^{16,26} i.e., we get

$$h_L = \frac{V}{E_L}. \quad (4)$$

Then, the solution of Eq. (1) is

$$\frac{1}{h} = \frac{1}{h_1} \log \frac{h_L^2}{h_1 u t}. \quad (5)$$

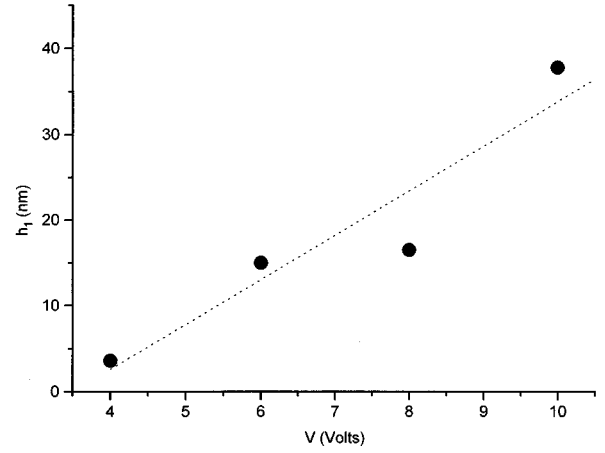


FIG. 3. Variation of h_1 vs the voltage V .

To get h versus the speed, we take the time t equal (or proportional) to the width of an oxide line W_{ox} divided by the speed v .²⁷ A close relation between h and v is therefore given by

$$\frac{1}{h} = \frac{1}{h_1} \log v + \frac{1}{h_1} \log \frac{h_L^2}{h_1 u W_{\text{ox}}}, \quad (6)$$

which corresponds to the data of the Fig. 2.

For a constant speed v , we have

$$h = \frac{qa'/kT}{\log(h_L^2 v kT / u W_{\text{ox}} qa') - \log V} V. \quad (7)$$

This relation shows that h varies linearly with V if $\log(h_L^2 v kT / u W_{\text{ox}} qa') \gg \log V$, i.e., $20-25 \gg 2$, which is a good approximation.

In summary, the proposed model explains the variation of the oxide height with the applied bias (linear) and the tip velocity [$1/\log(v)$]. The h values were deduced from 70 cross sections taken along the oxide lines (for a given bias and a given tip velocity, we get one oxide line with 100 nm length). From this analysis, we deduced a statistical value for h relative to the surrounding nonoxidized Si surface (taken as an average plane) with an average error of less than 0.2 nm. As h varies from 0.5 to 3.3 nm, the fit of our model with the experimental data is significant.

Moreover, from Eq. (6), for each series of data h vs v , the parameter h_1 was determined for a given V . Figure 3 shows h_1 vs V with the experimental data taken from the Fig. 2 (we have taken $V_0 = 1.5$ V).²⁶ Within experimental error, a linear law is found. The slope, 5.2 nm/V, is equal to qa'/kT , which leads to a' of the order of 1.3 Å, a value consistent with half the distance between two interstitial sites. With this value, we verified that the condition $h \ll h_1$ is always satisfied for our data. Finally, from the slope of h vs V [see Eq. (7)], W can be calculated, all other parameters being known. A low value is found for W , of the order of 0.15 eV. For high temperature thermal oxidation, the activation energy is of the order of 2 eV, whereas for plasma oxidation it is of the order of 0.15–0.4 eV.^{28–30} So this analysis shows that the process involved in the oxidation is

more a plasma process than a thermal one. The presence of an adsorbed water layer on the surface can explain the presence of the OH⁻ ions.

In order to test our model on other data, we have replotted the data h vs v of Yasutake *et al.*,¹¹ Hattori *et al.*,¹² and Sugimura *et al.*⁶ using relation (6). In each case, we found a linear behavior between $1/h$ vs $\log v$ and an activation energy W ranging from 0.1 to 0.4 eV, respectively, consistent with our modeling approach.

In conclusion, for the first time to the best of our knowledge, we propose an analytical model that explains the behavior of the oxide height induced by a SPM tip on a semiconductor surface with the applied voltage and tip velocity. Although this model allows one to explain the kinetics of oxide growth, an exact and quantitative understanding of the threshold voltage (depending on the substrate doping or on the relative humidity) is still an unanswered question. For the width, the kinetics depend strongly on the shape of the tip and it is difficult to model it simply. This analysis shows that the activation energy of the process is of the order of 0.15 eV, a value that tends to confirm that the chemical process involved in nanooxidation is characteristic of a low temperature oxidation mechanism.

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