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Scanning tunnelling microscope-induced oxidation of hydrogen passivated silicon surfaces

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Abstract

We have investigated the mechanism of scanning tunnelling microscope (STM)-induced oxidation of a hydrogen passivated silicon surface in air. The influence of the relative air humidity, the Si doping concentration and the type and applied tip–sample voltage on the oxidation process was studied. The relative air humidity is crucial, if the relative air humidity drops below 10% no oxidation is observed. The width of the oxide lines increases with increasing tip–sample voltage. The voltage required to produce oxide lines on p-type Si is −1.1 V and does not depend on the doping concentration. For n-type Si, the threshold voltage for oxidation varies from −2.4 V for heavily doped to −3.5 V for lightly doped. A simple model is developed in which the electrical field between the tip (estimated as a sphere) and the substrate was calculated. We assume that a critical field is required to induce the oxidation. With this model, a good fit can be obtained with the experimentally found line-width dependence of the voltage. In addition, the effect of the doping type and concentration can be understood if depletion, in the case of n-type silicon, is included.

Keywords: Scanning tunnelling microscopy (STM); Oxidation; Nanostructures

1. Introduction

The local oxidation of a hydrogen-passivated silicon surface with an STM in air has received a lot attention since it was first demonstrated by Dagata et al. [1] in 1990. It was only until recently, that the local oxidation of a hydrogen-passivated silicon surface was used to fabricate an electrically measurable structure [2–4]. The local oxidation was used to fabricate a MOSFET [2] and 40 nm narrow metallic wires [3]; in both cases, a thin film of amorphous silicon was locally oxidized and the oxide pattern used as etch mask. However, the exact mechanism of the oxidation process is still unclear. It has been proposed that the electrical field between the tip and the sample is high enough to produce O^- ions, by ionization of O_2 or H_2O, these radicals are highly reactive and oxidize the surface [5,6]. It has also been shown that the air humidity affects the resolution of the oxide patterns [7], whereas the tunnelling current does not affect the oxide line width [9]. In order to improve the understanding of the oxidation process, we studied the influence of several parameters on the oxidation. The influence of the relative air humidity (r.a.h.), the doping type and concentration and the applied tip–sample voltage were investigated. With a simple model, based on the electrical field between the tip and the substrate, a good fit with the experimental results can be obtained.

2. Experimental

The oxidation was studied on Si(100) p-type (B doped, resistivity 0.01 Ω cm, 1 Ω cm or 700 Ω cm) and Si(100) n-type (P doped, resistivity 0.01 Ω cm, 1 Ω cm or 1000 Ω cm). The samples were cleaned as described in [9], before they were passivated with hydrogen by a dip in 10% diluted HF for 60 s. A home-built STM with mechanically prepared PtRh tips was used. The STM was positioned in a closed box in which the relative air humidity (r.a.h.) could be reduced by purging with dry air, or could be increased by evaporating water. The r.a.h. was measured with an Omega hygrometer, accuracy 5%. The influence of different tip–sample voltages, r.a.h. values and doping types and concentration was studied by varying just one of these parameters at a time and keeping the others constant. After the oxide patterns were written with the STM, the patterns were transferred in the Si by wet etching. We etched with tetra methyl ammonium hydroxide

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(TMAH) because of its extreme selectivity; the etch rate of silicon-oxide is 10^4 times lower than the etch rate of Si(100) [8,9]. The samples were etched for 10 s with TMAH at 75 °C; this etches about 100 nm of Si. The resulting patterns were examined with a scanning electron microscope (SEM). From the SEM images the line width and the threshold voltage were determined. The threshold voltage for oxidation is defined as the magnitude of the lowest writing voltage which still produces oxide lines that, after wet etching, can be seen in the SEM.

3. Results and discussion

In this section we present the results of our investigation on the influence of the relative air humidity, the Si doping concentration and type and the applied tip–sample voltage on the oxidation process. Fig. 1 shows the effect of the r.a.h. on the oxidation process; oxide line patterns were written (-3.0 V, 40 pA and $1 \mu m\ s^{-1}$) under different r.a.h. values (10–55%). As can be seen, below 10% r.a.h. no oxidation can be observed. This implies that water is involved in the oxidation. The hydrogen-passivated silicon surface is hydrophobic [10] so not many water molecules are present on the Si surface; however, on the PtRh tip a thin film of absorbed water will be present. Therefore, the initial stages of the oxidation will most likely involve the formation of reacting species, OH^- ions by dissociation of water, on the tip. The reacting species are accelerated to the surface, where they oxidize the surface.

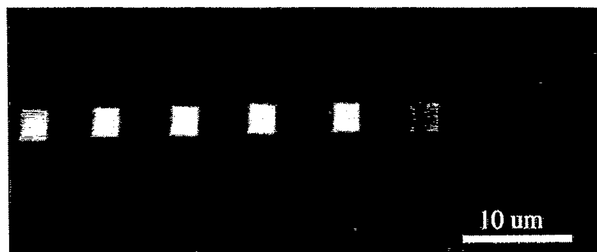

Fig. 1. SEM image of oxide lines written with different relative air humidities; from left to right: 50%, 43%, 37%, 32%, 25%, 20%, 16% and 11%; the 16% and 11% cannot be seen.

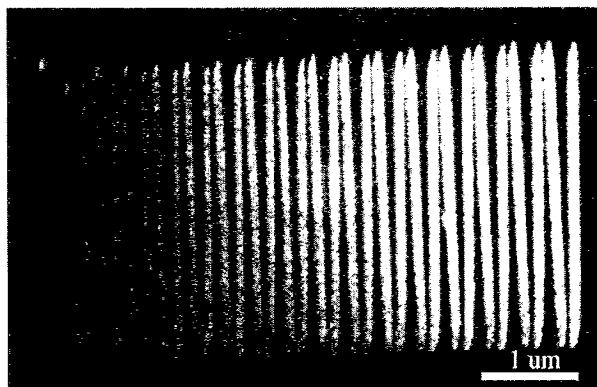

Fig. 2. SEM image of oxide lines on p-type Si written with different voltages. For each voltage 2 lines were written; the writing voltage of the first 2 lines on the left was -1.0 V, the magnitude of the writing voltage increases by 0.25 V for the next pairs of lines, the 2 lines on the right were written with a voltage of -5.0 V.

Fig. 2 shows the influence of the tip–sample voltage on the oxidation; the lines were written (r.a.h. 35%, 40 pA and $1 \mu m\ s^{-1}$), with decreasing voltage from left to right (from -1.0 to -5.0 V). With voltages between -1.0 V and $+6.0$ V no oxidation could be observed (under these conditions). This is in agreement with the assumption that negatively charged reacting species are formed, which cannot reach the surface when there are positive tip voltages. In Fig. 2 it can also be seen that the line width increases with the magnitude of the writing voltage. In case of p-type silicon, a negative tip–sample voltage results in a forward-biased Schottky diode, so the voltage drop will be mainly across the gap. In order to calculate the electrical field between the tip and the sample, we model the tip as a sphere with radius R and the substrate as a conducting plane [11]. SEM images of mechanically prepared tips show that the tip apex has a spherical shape with a radius which is typically in the range 50–200 nm. We now assume that the electrical field must be above a critical value in order to oxidize the surface. By increasing the magnitude of the writing voltage the area where the field exceeds the critical field increases, hence the line width is expected to increase. There are 3 modelling parameters: the tip radius (somewhere in the range 50–200 nm), the tunnelling gap (in the range 0.5–2 nm), and the critical field. A good fit of the line width as a function of the writing voltage with the experimental data (taken from Fig. 2) is obtained for a radius of 150 nm, a tunnelling gap of 2 nm and a critical field of 5.0×10^8 V m^{-1}; this fit is shown in Fig. 3. It is quite remarkable that with this relatively simple model such a good fit with the experimental data can be obtained.

We now turn to the case were the Si substrate is n-type. Applying a negative voltage to the tip will result in the deple-

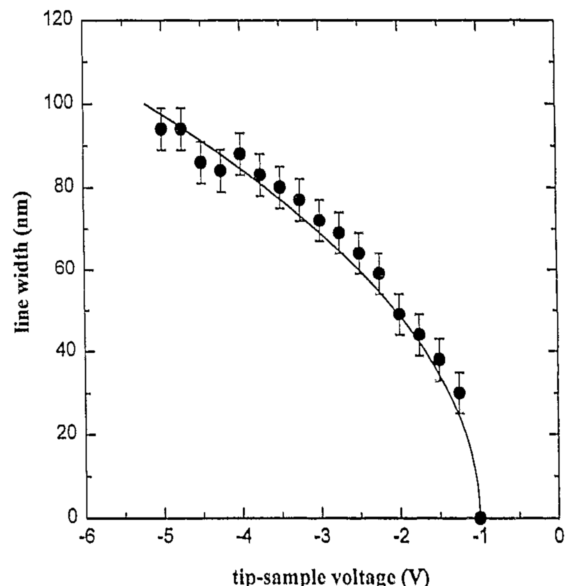

Fig. 3. The width of the oxide lines on p-type Si as a function of the applied tip–sample voltage; the ● symbols are the measured data points, — shows the theoretical fit (see text for model).

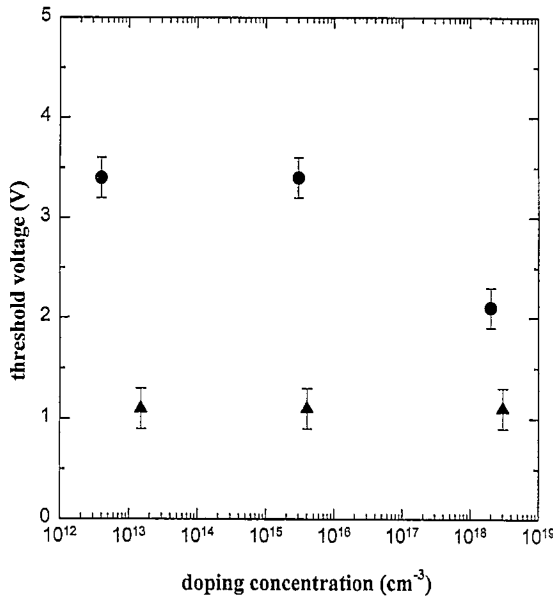

Fig. 4. The threshold voltage for oxidation (r.a.h. 45%, 40 pA and 2 μm s^{-1}) on n-type Si (the ● symbols) and on p-type Si (the ▲ symbols).

tion of the n-type Si; a reverse-biased Schottky diode is formed. This means that there can be a significant voltage drop over the depleted silicon, and, as a consequence, the electrical field between the tip sample and the surface will be lower. The threshold voltage for oxidation is, therefore, expected to be higher for n-type Si than for p-type Si. Fig. 4 shows the threshold voltage as a function of the doping type and concentration; the circles are for n-type Si and the triangles for p-type. The threshold voltage for p-type Si is independent of the doping level. This can be understood because under forward-bias conditions, the voltage drop is over the gap only; this is independent of the doping concentration. For n-type Si, higher threshold voltages are required compared to p-type Si, as expected. In addition, the threshold voltage increases with decreasing concentration. For doping concentrations below 10^{16} cm^{-3}, the threshold voltage is constant. It is rather complicated to calculate the depletion in the Si substrate due to a charged sphere above the substrate. As an approximation we consider the 3-D depletion of a metallic sphere with radius R embedded in Si. With this approximation, the results can be understood qualitatively. The potential, $\phi(r)$, at a position r from the center of the sphere at potential V can be calculated by solving the Poisson equation: $\nabla^2\phi(r) = -\rho(r)/\epsilon$, where $\rho(r)$ is the charge density and ϵ is the dielectric constant. For a depletion length l, $\rho(r) = qN$ for $R<r<R+l$, and $\rho(r) = 0$ for $r>R$, where q is the electron charge and N is the doping concentration. From this equation the electrical field at the sphere $E(r=R)$ can be determined for a given applied voltage V with respect to the semiconductor. Two regimes can be distinguished. In the first case, $l<R$, the field at the tip can be approximated by $E(R) = -2(NqV/2\epsilon)^{1/2}$ (which is the same as for the 1-D case [12]). From this equation it follows that the threshold voltage will increase if the doping level is decreased. In the case of $l>>R$, $E(R)$ can be approximated by $-V/R$. In other words, the electrical field at the tip is now independent of the doping concentration. This simple approximation explains qualitatively the experimentally observed dependence of the threshold voltage on the doping concentration for n-type Si. For high doping levels, $l<R$, the threshold is doping-concentration dependent and for low doping levels, $l>>R$, the threshold is independent of the doping concentration. This 3-D model is a very crude approximation of a negatively biased tip near an n-type Si surface; however, it shows that the threshold voltage does not depend on the doping concentration for low doping concentrations, the reason being that the field at the tip is determined by the geometry of the tip if the silicon is depleted over a large distance. This picture is not complete, an additional effect can be that due to the band bending an inversion layer is built up, limiting the voltage drop over the silicon.

4. Conclusions

In conclusion, the STM-induced oxidation of a H-passivated Si surface in air only occurs if sufficient water molecules are present. The observed increase of the width of the oxide lines with voltage and the threshold voltage dependence on the doping type and level can be understood by considering the field between the tip and the substrate. With a simple model the field between the tip and the sample was calculated, and with this model a good fit with the experimental results was obtained.

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