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1991 J. Phys.: Condens. Matter 3 S77

(http://iopscience.iop.org/0953-8984/3/S/012)

J. Phys.: Condens. Matter 3 (1991) S77–S83. Printed in the UK

Interface analysis during etchback of silicon oxide

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Received 25 April 1991

Abstract. Etching of thermal oxides on Si(100) wafers in acidic fluoride-containing solutions is monitored by simultaneous optical and electrical measurements, the latter including the dark current and the probe light induced photocurrent. For *in situ* optical characterization a new ellipsometric configuration is used, which allows accurate measurements at low probe light intensity. This approach is shown to reduce photocorrosion of the investigated n-doped samples to a level where ellipsometric information about the silicon electrolyte interface becomes accessible. *In situ* ellipsometric results show some residual film. This is contrasted by *ex situ* STM giving no evidence for a silicon surface covered with several monolayers of an absorbing film.

1. Introduction

Recent experimental progress has reinforced the interest in the wet chemical treatment of silicon surfaces. Specifically, aqueous solutions of NH_4F have been studied in great detail in an electrochemically controlled environment [1–3]. The anodic etchback of oxides on n-doped Si in these solutions produces a surprisingly high current in the dark [4]. The etched surfaces have turned out to be well passivated with hydrogen and fluorine as determined by *ex situ* techniques [5]. Under different levels of illumination photocurrect doubling and quadrupling [6] and chemical oscillations [7] were found, but up to now these effects have not been fully understood on a microchemical or atomic level.

The necessity in collecting more information *in situ* during oxide formation and dissolution (especially when the etching reaches the Si-SiO_2 interface) led us to develop an ellipsometer using very low probe light intensity.

2. Experimental procedure

The Polypyrole-teflon electrochemical cell is controlled by a Heka potentiostat using a SCE reference electrode and a platinum counter electrode. The working electrode is made from approximately 4 × 5 mm samples of about 10 nm of thermal SiO_2 on n-doped silicon (2.5 Ω cm). The ohmic back contact is made using Galn amalgam. The oxide was prepared on previously RCA-cleaned commercial (100) wafers (Wacker) at 900 °C in a dry oxygen atmosphere. The aqueous NH_4F solution was of 0.5 m and

0953-8984/91/SA0S77+07$03.50

buffered with H_2SO_4 to a pH of 4.5. All chemicals were of pA purity and oxygen-free triple-distilled water was used. All experiments were carried out at +0.5 V against SCE. Samples were immersed and emersed with the potential still applied. For the *ex situ* STM (Nanoscope II) measurements the samples were rinsed, dried with nitrogen, and handled in a nitrogen atmosphere. The ellipsometer consists of a HeNe laser, a polarizing module and an analysing module (figure 1). Inside the polarizing module the laser beam intensity can be lowered by a combination of a Faraday modulator positioned between two crossed polarizers. Applying alternating current to the modulator, the probe light intensity can be adjusted down to a few nW. In the electrochemical cell the beam entered and emerged after reflection at the sample through quartz windows.

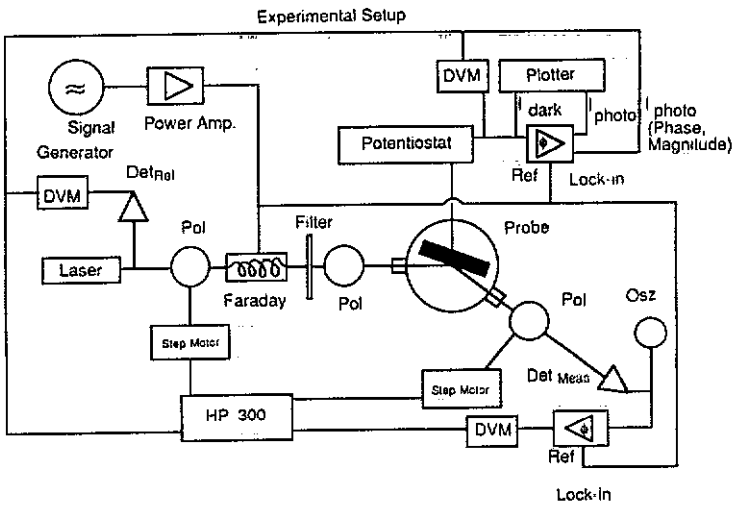

Figure 1. Schematic diagram of ellipsometric and electrochemical experimental setup.

For the experiments reported here a rotating analyser was used where the continuous rotation was replaced by positioning a step motor to a discrete set of orientations. Due to the AC intensity modulation of the probe light (2422 s^{-1}) the detector gave reliable readings even at low light levels.

As a side-effect of this intensity modulation a very small (< 1 nA) photo-generated AC component superimposed on the dark current occurs which does not affect the shape of the observed dark current. Hence it becomes possible to record simultanously the values of dark current, Delta, Psi, the reflected absolute light intensity and the phase and magnitude of the photocurrent (figure 1). An additional roughness parameter is computed from the higher coefficients of the Fourier analysis from ellipsometric intensity data.

3. Results

3.1. Dark current

The etching of the SiO_2 on n-Si produces a well-known dark current transient [1, 3] with a pronounced maximum when the etching front reaches the interface. The typical

dark current we present here (figure 2) shows an additional feature. Before the current starts to rise to the main transient there is a long flat plateau, where the current is about 1/100 of the maximum current. This plateau showed up in all experiments and we named it 'precursor'.

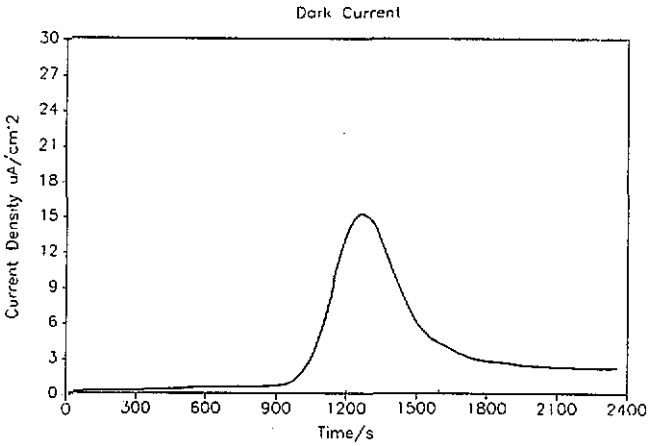

Figure 2. Dark current during etchback of thermal oxides.

3.2. Ellipsometry

In situ experiments were carried out with different levels of probe light intensity. Two sets of recorded data are shown in figures 3(*a*) and (*b*). The sample with 7 nm of oxide in figure 3(*b*) was etched under illumination with 100 nW of probe light. This value was chosen because it was far below any intensity level causing large changes in the transient current in the dark and under illumination. In figure 3(*a*) the results are given for a sample with 13 nm of oxide under DC-biased illumination of 100 μW. This sample will be referred to as high-intensity probe.

The linear increase of Delta in the beginning for both sets of data is consistent with a decrease of the oxide thickness. This increase stops at the rising edge of the transient current. Thickness calculations with a constant refractive index of 1.46 for SiO_2 yield still 4 nm of oxide at this point. As the current approaches its maximum, large differences between the high- and low-intensity probe turn up. The high-intensity probe shows the already-known excursion-like behaviour of Delta and Psi [3]. The sharp decrease in Delta by 40° contrasts to 1.5° for the low-intensity case. Together with the decrease of the reflected intensity the major part in this dramatic change must be from roughness. The light intensity of a few mW used in a seperate experiment with a conventional ellipsometer left a black spot at the surface in a several microns deep hole. The spot where the beam hit the surface began to glow, reflecting large amounts of light away from the specular direction.

The signature of the electrochemical current diverges for the two data sets from the onset of the precursor regime. While the low-intensity probe reproduces exactly the dark current, the precursor in the high-intensity case is no longer a plateau and the current maximum degenerates into a slow increase to a level controlled by the DC photo current. The AC photo-current changes in phase and magnitude for both

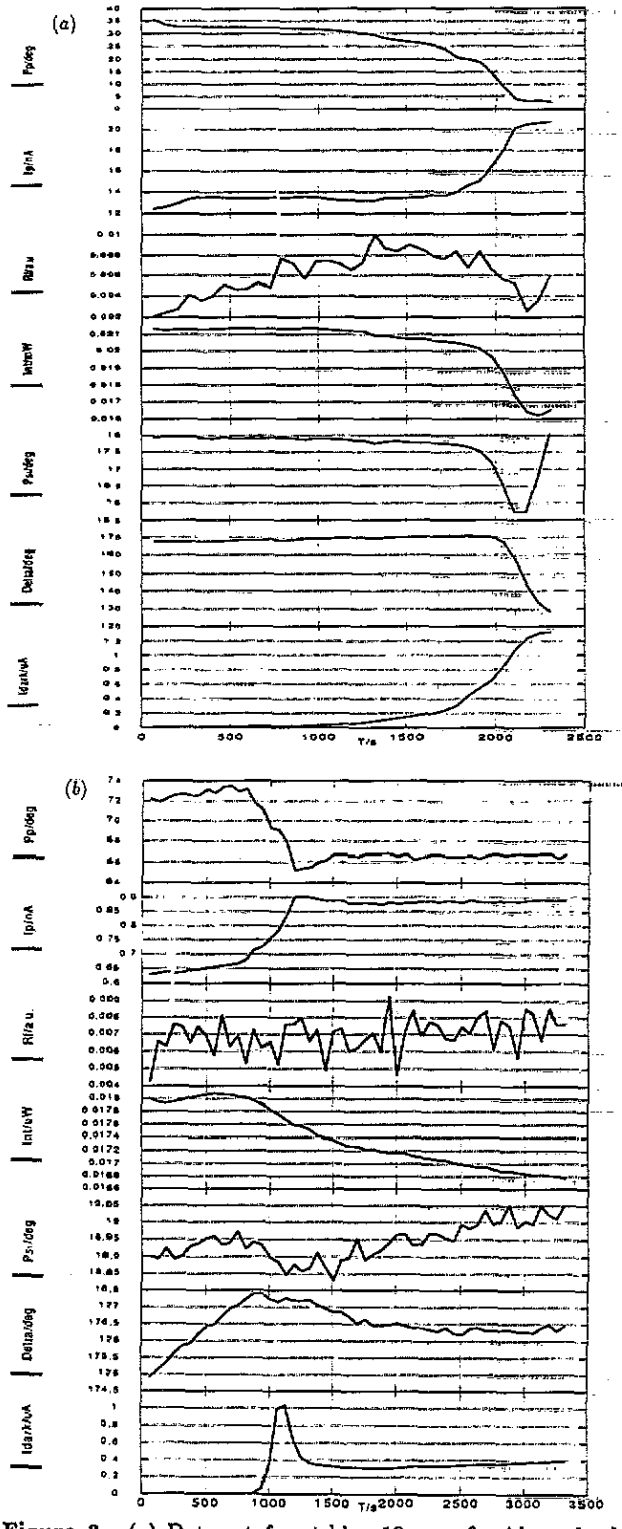

Figure 3. (*a*) Data set for etching 13 nm of oxide under low-level illumination (100 nW). (*b*) Data set for etching 7 nm of oxide under illumination with 100 μW.

samples from the beginning of the precursor to the maximum of the electrochemical current.

3.3. STM

STM measurements were made in a vessel filled with dry nitrogen. Figures 4(*a*) and (*b*) show STM pictures of a high- and low-intensity probe equivalent to those of figure 3. Both samples were removed from the electrochemical cell directly after the current maximum. Figure 4(*a*) shows what we believe is an atomically flat silicon surface terminated with rows of hydrogen atoms. We obtained this picture from a probe practically etched in the dark. The distance between the rows were evaluated to be 0.34 nm and the inter-atom spacing to be 0.21 nm. This is contrasted by the scan of a surface with roughness on a much larger scale given in figure 4(*b*). Pictures on an atomic scale could not be taken from the high intensity probe.

4. Discussion

The presence of the photo-generated holes in n-silicon seems to be the source of surface roughening by a corrosion reaction of the type

$$Si + 2H_2O + 4h^+ \rightarrow SiO_2 + 4H^+ .$$

This reaction governs the process after the maximum of the transient current is reached and enough holes are generated.

The STM picture of the hydrogen-terminated silicon surface shows that the highest value of Delta corresponds to a residual oxide film of 4 nm. Even an additional monolayer coverage of hydrogen cannot explain this difference. It is possible that the effect is due to a semimacroscopic roughening where the structure is made of atomically smooth terraces.

Several models for this interfacial region can account for some of the recorded data. A model using growing pores in the oxide near the interface can describe the existence of a precursor, the form of the transient current and the photo-current behaviour [3]. Another candidate is surface roughening and strain close to the interface due to formation of the oxide [8, 9]. This model was developed to account for differences in ellipsometric and XPS thickness determination of thin oxide films. Dense films of strong polarized ions replacing step by step the last patches of insulating oxide could also be a solution.

5. Conclusions

Ellipsometry with low probe light intensity allowed us to trace *in situ* the etching of SiO_2 on n-doped silicon wafers avoiding roughening and other probe light effects. Aqueous solutions of NH_4F turn out to be perfect wet etchants for n-doped wafers in the dark, if they are emersed shortly after the maximum of the transient current. On the other hand a controlled roughness of n-silicon surfaces can be produced by applying a certain level of illumination.

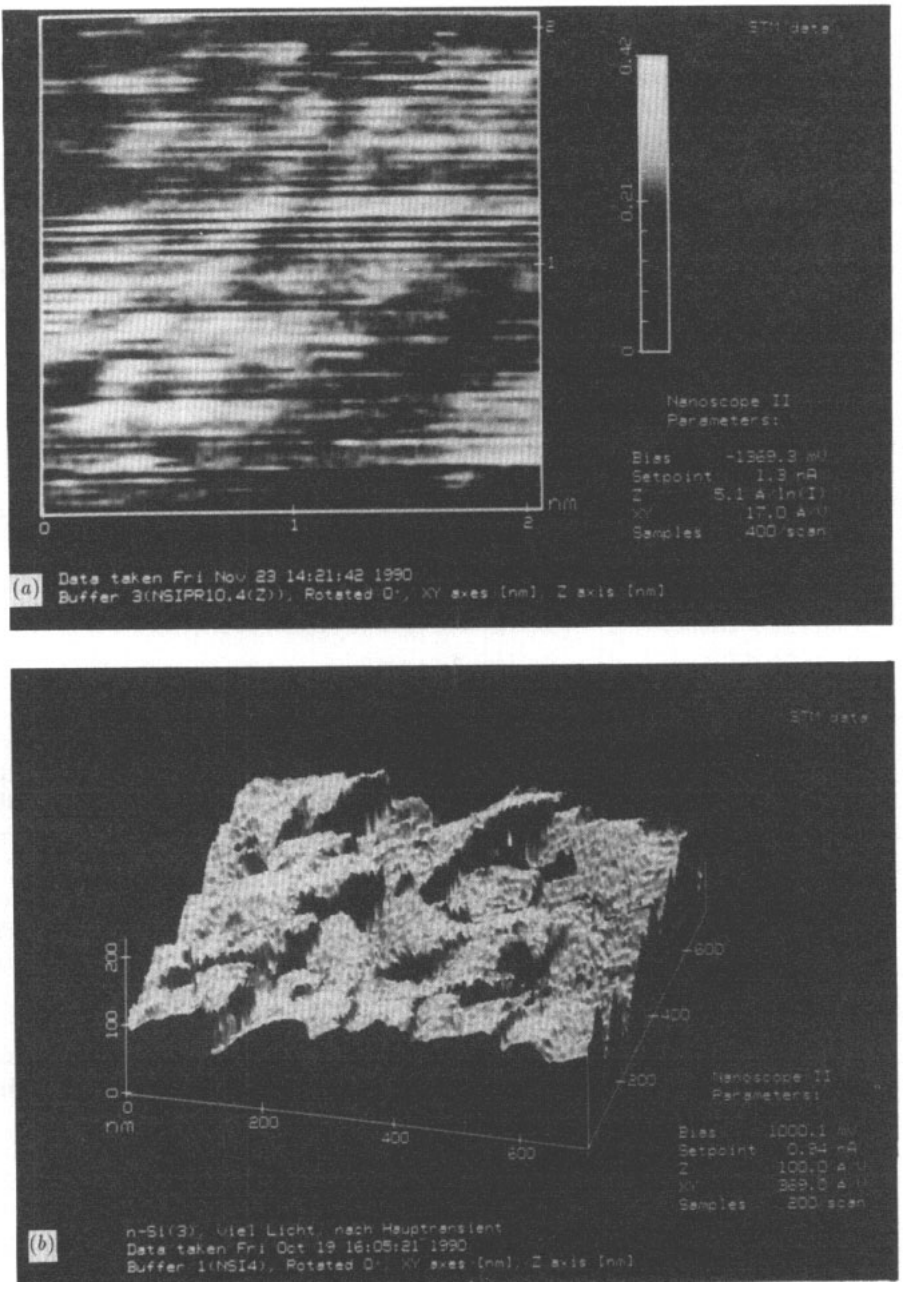

Figure 4. STM of n-Si (100) sample (*a*) etched under 100 nW of illumination showing atomic resolution; (*b*) etched under 100 nW of illumination. Large scale roughness caused by photo-corrosion.

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