

CURRENT OSCILLATIONS IN NH₄F ELECTROLYTES AND AFM STUDY OF *n*-Si (111)

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Abstract: During electrochemical etching of silicon in HF or NH₄F solutions, at higher anodic potentials (>3 V *versus* saturated calomel electrode – SCE) current oscillations appears and silicon oxides are formed and then dissolved. Oscillations take place due to the competition between oxide formation and its dissolution. Cracks and pores due to a lattice mismatch between silicon and silicon oxides are formed and the presence of defects results in faster etching. Consequently, the silicon oxides are removed faster than bulk silicon. Current oscillations on *n*-Si (111) with doping level 10^{15} cm⁻³ at higher anodic potentials in NH₄F solutions were investigated. The character of the current oscillations depends from the potential, electrolyte composition, illumination and type of silicon. The oscillations can be sustained or dumped. Sustained oscillations were observed in a narrow potential range of 4÷6 V and electrolyte pH 4÷4.5. In this work sustained oscillations were studied. The changes in surface microtopography as well as roughness were studied by atomic force microscope. The roughness R_a of the surface, changes with the current oscillation cycle, resulting in maximum R_a slightly before maximum current peak and smoothening of structure at the bottom of the oscillation. The removed amount of materials during etching increase with increasing of the potential as well as number of oscillations.

1. INTRODUCTION

Electrochemistry of silicon is an important part of semiconductor technology. Silicon is an basic material for electronic applications. During electrochemical treatment in NH₄F solutions, at relatively low potentials (slightly positive from open-circuit potential up to a first maximum current peak) and currents, can be prepared porous silicon [1-3]. At higher anodic potentials (>3 V *versus* saturated calomel electrode – SCE) the silicon oxides are formed and then dissolved [4, 5] resulting in current oscillations. The cyclic nature of oscillations results in cyclic increase and decrease in amount of SiO₂ on Si surface [6]. The formation and growth of the oxide on *n*-Si depends from a number of light-induced holes, potential and solution composition. Oscillations take place due to the competition between oxide formation and its dissolution. Such prepared oxide layer is usually less than 10 nm thick [4]. Due to a lattice mismatch between silicon and silicon oxides, cracks looks like pores are formed. The presence of defects results in faster etching [7]. Consequently, the silicon oxides are removed faster than bulk silicon.

In this work the formation of oscillations in the *n*-Si (111) was presented and microtopography study of silicon at different points of the oscillation peak were studied by atomic force microscope (AFM).

2. EXPERIMENTAL DETAILS

Electrochemistry experiments have been done in a three-electrode electrochemical cell (Pt-counter, saturated calomel electrode (SCE)-reference and Si-working electrode). The experiments were done under potentiostat control using a 273A (EG&G Princeton Applied Research). The sample surface area was about 0.2 cm². For imaging the Nanoscope IIIa AFM (Digital Instruments) in the contact mode operation was applied. Standard Si₃N₄ tips were used.

Phosphorus doped *n*-Si (111) wafers with specific resistivity 2±12 Ωcm (10¹⁵ cm³ doping level) have been used in the experiments.

Prior to electrochemical treatment and AFM measurements, clean, smooth H-terminated silicon substrates were prepared in the following way: (i) the native oxide removal in concentrated HF (1 min), (ii) cleaning in acetone and methanol in an ultrasonic bath for 10 min, (iii) oxidation in H₂SO₄:H₂O₂:H₂O (6:1:3) at 70°C for 10 min and (iv) etching in concentrated 40% NH₄F (15 min). After each preparation step, the sample was rinsed under a stream of deionised N₂ purged Millipore water (18 MΩcm) and finally dried in high purity N₂.

The 0.1 M NH₄F electrolytes with different pH used in the experiments have been prepared from high quality NH₄F salt diluted in deionised Millipore water. The pH of the solution was adjusted by adding H₂SO₄ and was controlled with a calibrated pH meter. In aim to remove the oxygen, the solution as well as water has been purged by high purity nitrogen.

Electrochemical treatment was performed at constant potentials under halogen lamp illumination with light intensity 10 mWcm². Backside contact of the Si sample was ensured by Ga-In eutectic. Etching depth was found when a part of the sample was covered and not immersed in the electrolyte.

3. RESULTS AND DISCUSSION

Figure 1 shows current oscillations of *n*-Si (111) in 0.1 M NH₄F pH 4.0 electrolyte for different potentials *versus* SCE. The applied illumination intensity of 10 mWcm² bringing sufficient number of holes for electrochemical reactions. In the potentials range of 4÷7 V the current oscillations were observed and sustained oscillations appears in the range of 4÷6 V. At relatively low potential (4 V) the initial maximum current peak is relatively low (3.1 mAcm²) and oscillation period and amplitude are 26 s and 1.3 mAcm², respectively. The increase of the potential changes the character of oscillations. At 5 V the oscillation period is 33 s and amplitude is 0.71 mAcm². The initial current peak is 4.1 mAcm². At 6 V the oscillation period still increases and is estimated to 63 s, the amplitude is 0.9 mAcm² and initial current peak is 6.9 mAcm². At higher potentials current oscillations are different from the previous cases. At 7 V, after first high initial current peak (8.3 mAcm²), the oscillations tends to damping and after 300 s the current is constant without distinguish changes.

If the current oscillations are relating to changes in amount of the oxide on Si surface, at shorter oscillation period (at lower potentials, 4 V for instance) the oxides should be formed faster and faster disappears than at higher potentials (6 V for instance). It can be possible that thickness of oxides is different at lower and higher potentials.

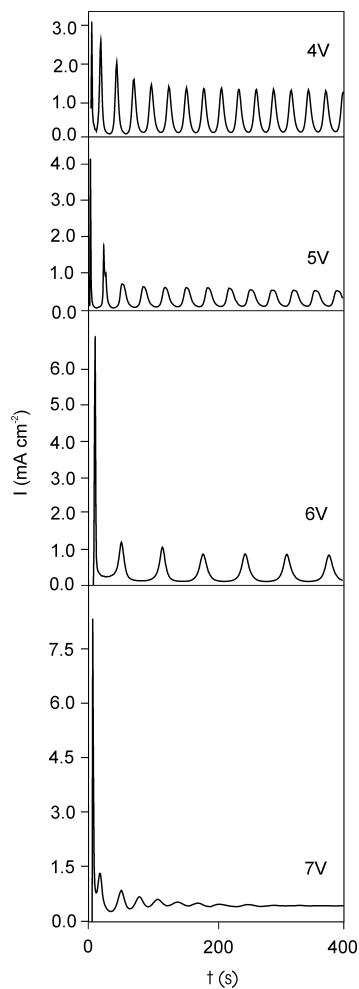


Fig. 1. Current oscillations of $n\text{-Si}$ (111) at 4 V, 5 V, 6 V, 7 V in 0.1 M NH_4F pH 4.0 electrolyte

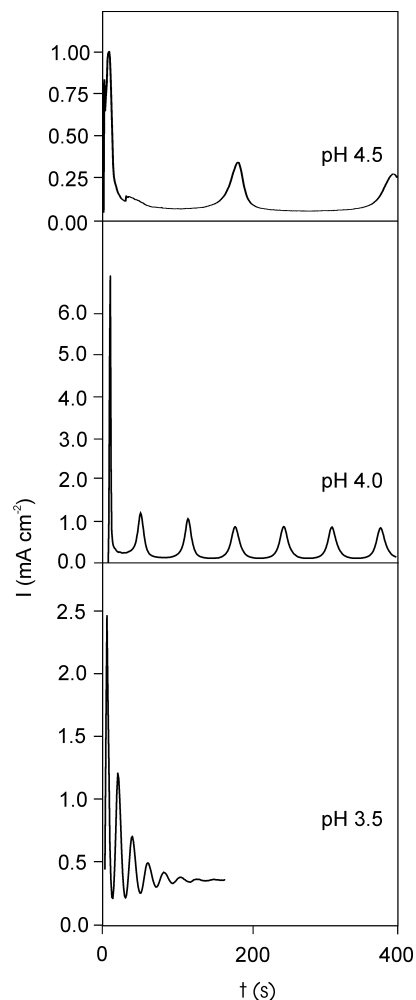


Fig. 2. Current oscillations of $n\text{-Si}$ (111) at 6 V in 0.1 M NH_4F with pH 3.5, pH 4.0, pH 4.5

Figure 2 shows current oscillations for different pH (at 6 V). The current also depends from the pH of the electrolyte. In this case, the oscillations can be sustained or damped, also. For pH 4.5, the oscillations have long period 190 s and low amplitude 0.27 mAcm^2 . The initial current peak is 1 mAcm^2 . At pH 4.0 of the solution, the initial current peak is 6.9 mAcm^2 , amplitude is 0.9 mAcm^2 and oscillation period is 63 s. In these two cases the oscillations are sustained. For lower pH 3.5, after 170 s the oscillations completely disappears. The sustained oscillations at experimental setup were observed only at the potentials of 4÷6 V and pH 4.0÷4.5. When a part of the sample was immersed and another one not immersed in electrolyte, the border between the etched and unetched part of the sample was localised, respectively. This way, the etched depth was precisely determined and samples AFM image

with cross section of the etched step after 15 cycles of oscillations at 6 V in 0.1 M NH_4F pH 4.0 is presented on Fig. 3. The etching depth was estimated on 70 nm. The dependence of the etching depth of the silicon as a function of number of the current oscillations at 6 V in 0.1 M NH_4F pH 4.0 is presented on Fig. 4. The etching rate (dissolution rate) is linear and was estimated to 5.0 nm oscillation⁻¹. After 21 current oscillations, the etching depth is equal 107 nm.

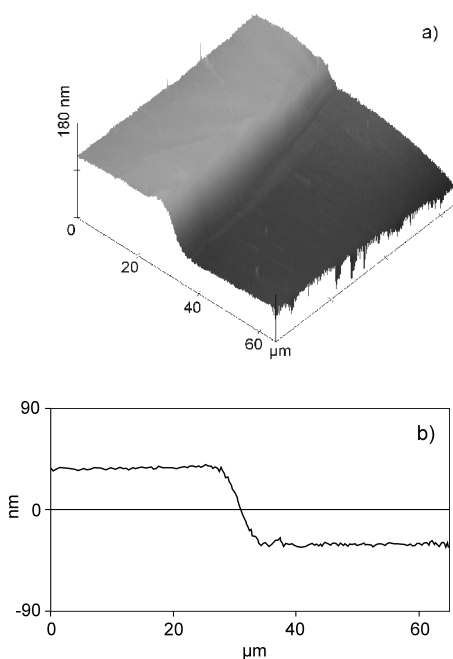


Fig. 3. AFM image (a) and cross section (b) of etching depth of $n\text{-Si}$ (111) at 6 V in 0.1 M NH_4F pH 4.0 electrolyte after 15 cycles of the current oscillations

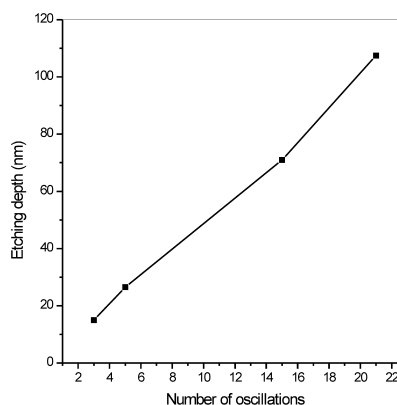


Fig. 4. Etching rate, measured as an etching depth as a function of number of the current oscillations for $n\text{-Si}$ (111) at 6 V in 0.1 M NH_4F pH 4.0

The changes in roughness of silicon during formation of the oscillation peak are presented on Fig. 5a, which include also the current curve (dashed line). The maximum roughness 0.95 nm occurs slightly before maximum current peak. Changes of the current results in distinguish changes of the surface roughness. The microstructure was determined before, during and after current passed through the peak at 6 V in 0.1 M NH_4F pH 4.0. These conditions ensure sustained character of oscillations. The current oscillations are accompanied by cyclic increase and decrease in amount of SiO_2 covering the Si surface as well as opening and closing of the pores during current oscillations. During increase of the current the silicon oxides are etched. The SiO_2 has dielectric nature and during its formation the current decreases. Due to the lattice mismatch between silicon and silicon oxide, it should be expect, that during oxide formation, cracks should appears and etching proceeds faster into the bulk

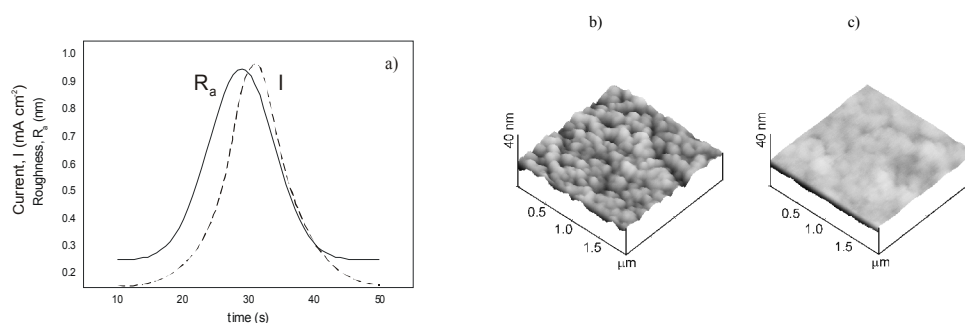


Fig. 5. Changes of roughness R_a (a) of n -Si (111) at 6 V in 0.1 M NH_4F pH 4.0 electrolyte during the current oscillation peak (dashed line) and AFM images microstructure with highest (b) and lowest (c) roughness

silicon. When the current reach the minimum, then the oxide thickness is maximum and surface undergoes to smooth. The roughness maximum correspond to oxide coverage minimum and strong increase of the current. Maximum in roughness $R_a = 0.95$ nm was observed slightly before current reach the maximum and oxides have domains (like islands) structure (Fig. 5b). At the bottom of the current peak surface is smooth (Fig. 5c) with $R_a = 0.28$ nm, without distinguish cracks.

4. CONCLUSION

Current oscillations in the electrolyte – n -Si (111) occurs at higher anodic potentials. Character of these oscillations depends from the electrolyte composition as well as voltage applied to the electrode in the electrolyte. Sustained oscillations were observed at 4÷6 V in 0.1 M NH_4F pH 4.0 and for pH 4.0÷4.5 at 6 V. Oscillations are connected with oxide formation and its dissolution. During oscillations the removed amount of materials increase with increasing the potential as well as number of oscillations.

References

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