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MORPHOLOGY OF SILICON (111) DURING ELECTROCHEMICAL ETCHING IN NH$_4$F ELECTROLYTES

ABSTRACT

The n-type silicon with (111) orientation and resistivity of 8-12 Ω·cm was electrochemically etched. The results obtained by electrochemical etching of silicon in 0.1M NH$_4$F (pH4.5), 0.1M NH$_4$F (pH4.0) and 0.2M NH$_4$F (pH4.0) electrolytes, indicates that slight increase of the NH$_4$F concentration by 0.1M results in faster silicon dissolution. In slightly reactive 0.1M NH$_4$F (pH4.5), we can observe initial stage of silicon dissolution on the inside edges of atomic terraces. Flat atomic terrace under electrochemical etching undergoes to mesa-type structures surrounded by strongly corrugated areas. The diameter and heights of the mesas are 150-200 nm and 5-7 nm, respectively. The mesa-type structures are the remnants of the atomic terraces and theirs formation proceed independently on the electrolyte concentration. The mesas appear faster at higher concentration and faster disappear by pits formation. During increase of etching time, increase of pore size, more in the case of diameter than depth, because pits coagulation appears.

Key words: *porous silicon, electrochemical etching*

INTRODUCTION

In the last years porous silicon was intensively investigated due to its interesting properties, like photoluminescence [1-3].

Porous silicon can be prepared by electrochemical etching in electrolytes containing fluorine, usually under a constant current density of 10 mA·cm^{-2} [1]. The electrolyte usually contains hydrofluoric acid as the etching factor, water and ethanol with ratio of HF:H$_2$O:C$_2$H$_5$OH (1:1:2) [1]. Due to the hydrophobic character of clean silicon surface, the C$_2$H$_5$OH is necessary to improve the wettability of porous silicon [2]. Ethanol is the surface active agent and its presence facilitates removing the bubbles of hydrogen formed during etching.

Formation of porous silicon [3] can be controlled by current or potential. In practice, current density is more accurate in controlling of porosity and reproducibility of the porous layer. HF concentration and the current density usually are in the range of 15-40 wt.% and 1-100 mA·cm^{-2}, respectively. Beside the HF, also NH$_4$F can be applied for silicon etching [4]. Porous silicon formation takes place at a potential range between open circuit potential and critical potential, where electropolishing starts [4].

Different morphologies and size of the pores reflects a difference in etching conditions. The more important parameters are the type and the level of doping atoms, crystal orientation, electrolyte composition, conditions of anodizing, design of etching chamber, preparation of silicon surface before and after electrochemical etching. These factors cause that samples prepared in different laboratories can be no comparable, even at comparable experimental conditions [3].

Electrochemical etching results in selective removing of bulk silicon. In the process the presence of the electronic holes at the semiconductor surface is necessary. Low holes density (in n-type silicon, where holes are the minority carriers) results in low current flow. To support the electrochemical reaction, an external source of holes is necessary. Increase in holes quantity results in increase of the current density and etching [5]. For the holes generation most effective way is an illumination. During illumination, electrons in the valence band take the photons energy and are exciting into the conductive band, leaving the holes in the valence band. Density of holes depends on the light intensity. Positive holes react on the surface with negative solvated ions F^-, which results in dissolving of the surface [6]. Formation of porous silicon includes both oxidation and etching of silicon atoms [7]. Removing of the silicon atoms from the surface proceeds through fluoride formation.

The aim of the research was the study of the effect of the etching conditions (time, molarity, pH) on surface changes in silicon (111).

EXPERIMENTAL PROCEDURE

Microstructural changes were generated by electrochemical method with application of potentiostat/galvanostat 273A EG&G. Silicon was an anode and hence underwent selective dissolution. Float zone single crystal n-Si (111) with resistivity of 8-12 $\Omega \cdot$cm was etched. Surface morphology was investigated by AFM using the Nanoscope IIIa (contact mode operation).

Before electrochemical etching, chemical cleaning was applied. The chemical etching [8] reveals atomic terraces and passivates silicon surface atoms by hydrogen atoms (H-termination).

In electrochemical setup, silicon was the anode, Pt was the counter electrode and saturated calomel electrode (SCE) was the reference electrode. Ohmic contact of silicon electrode was provided by Ga-In eutectic on Ag sheet. Single electrochemical cell was applied.

Electrolyte was prepared by dissolution of NH_4F salt in deionized water and pH was adjusted by addition H_2SO_4. Molarity was changed from 0.1M to 0.2M NH_4F and pH was in the range of 4-4.5. The following electrolytes were investigated: 0.1M NH_4F (pH4.5), 0.1M NH_4F (pH4.0) and 0.2M NH_4F (pH4.0). Silicon surface area was 0.2 cm^2. Electronic holes were generated by halogen lamp illumination with intensity of 10 $mW \cdot cm^{-2}$.

The etching was performed potentiodynamically and potentiostatically according the same scheme: increase of potential with scan rate of 20 $mV \cdot s^{-1}$ by 0.1 V from the OCP and then sample was kept at constant potential -0.5 V in time of 15s (Fig. 1) and 60s (Fig. 2).

RESULTS AND DISCUSSIONS

Relatively slightly reactive electrolytes were applied, which results in slow changes of surface morphology. The slow etching results in easy identification of the initial dissolution process and results (images and respective cross sections) of etched n-Si (111) are presented on Figs. 1 and 2.

Short etching time in 0.1M NH_4F (pH4.5) (Fig. 1a) does not significantly change the surface morphology. However, on the surface we can observe pits, with diameter of some nanometers (15-20 nm), localized on the inner edges of atomic terraces (kink sites). These places

are privileged for porous silicon formation. At this stage the pits quantity was estimated to be 3×10^9 cm^{-2}. The flat atomic terraces, produced during H-termination, have width of 100-150 nm and as we see no pits are observed on these planes: terraces are free from the pits. Increasing of etching time, results in defragmentation of atomic terraces and increasing of the pits quantity and size (Fig. 2a). Remnants of atomic terraces are well visible (Fig. 2a).
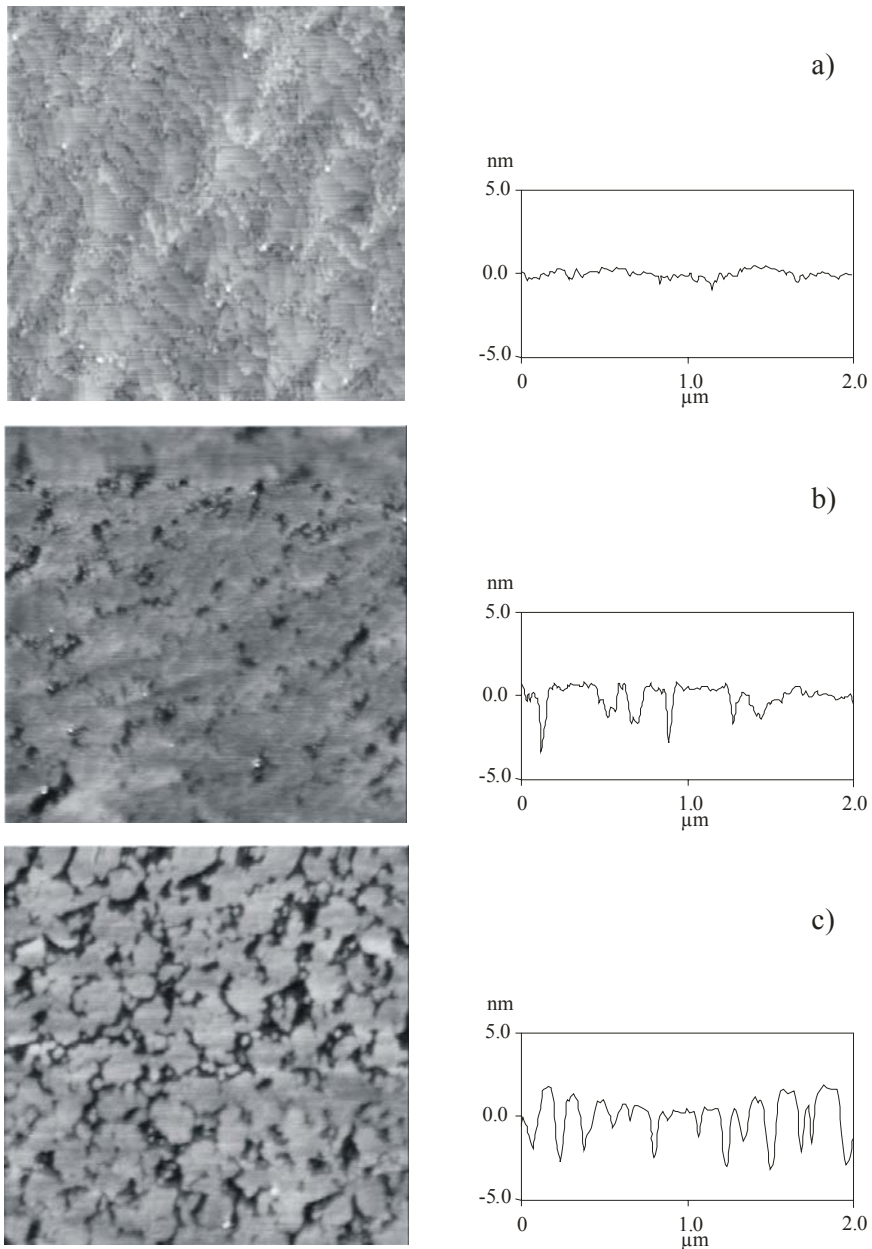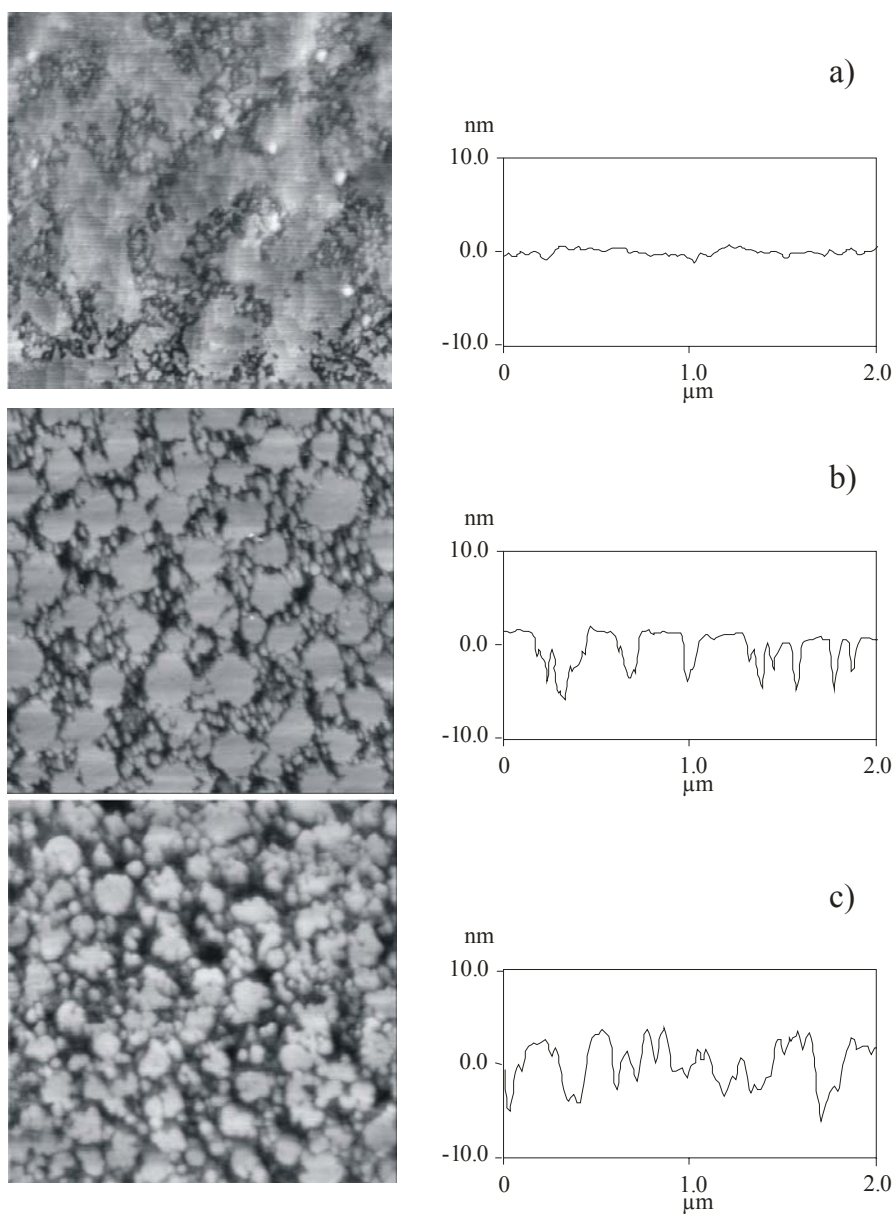

Fig. 1. Change of silicon morphology during increase in potential from -0.6 V to -0.5 V (20 mV·s^{-1}) and at constant potential (-0.5 V) for 15s in 0.1M NH$_4$F pH4.5 (a), 0.1M NH$_4$F pH4.0 (b), 0.2M NH$_4$F pH4.0 (c); (2x2 μm scan size)

Fig. 2. Change of silicon morphology during increase in potential from -0.6 V to -0.5 V (20 mV·s^{-1}) and at constant potential (-0.5 V) for 60s in 0.1M NH$_4$F pH4.5 (a), 0.1M NH$_4$F pH4.0 (b), 0.2M NH$_4$F pH4.0 (c); (2x2 μm scan size)

Etching in more acid 0.1M NH$_4$F (pH4.0) distinctly accelerates the rate of pores nucleation and growth (Fig. 1b after 15s and Fig. 2b after 60s). The pores have larger depth and width. After 15s the large atomic terraces are still visible and after 60s the remnants of atomic terraces are still visible. The mesa-type structures (remnants of atomic terraces) have diameter of about 150-200 nm and height of 5-7 nm (Fig. 2b). Between them, pores are visible with depth and width up to 7 nm and 10-50 nm, respectively.

Increase of molarity up to 0.2M NH$_4$F (pH4.0) results in more effective silicon dissolution. Microstructure after 15s of etching (Fig. 1c) looks very comparable to microstructure obtained after 60s in 0.1M NH$_4$F (pH4.0) electrolyte (Fig. 2b). Increase in time up to 60s results in increase of pores dimensions and decay of the remnants atomic terraces. The pore depth measured by AFM reaches 10 nm and theirs width increase due to coagulation.

At the intermediate dissolution, the characteristic mesa-type structure is visible (Fig. 1c, Fig. 2b). These polyhedral islands have flat surfaces which are the remnants of the atomic terraces. The walls of the mesa-type structures lies at the angles multiplied by 30° (mainly 90°, 120°, 150°) [6]. The mesa-type stuctures are formed from {110}, {111}, {113} planes [9]. The features are relatively resistant on dissolution, which is attributed to the passivation by hydrogen atoms, resulting in higher stability.
The factor which is more important in silicon dissolution is the molarity than pH. Increase of NH$_4$F concentration, distinctly increase of silicon dissolution.

On the base of the AFM cross-sections (Fig. 1, Fig. 2) an average pore dimensions were measured. The relationship between the pore width and depth is shown on Fig. 3 and as we see it is a linear dependence. The pore depth is expressed in number of removed atomic bilayers (1 atomic bilayer = 0.3 nm). For the depth of 1 atomic bilayer, the width of initial pits is equal 17 nm and for 10 bilayers increases up to 80 nm. When etching time increases a part of pores coagulate to larger structures.
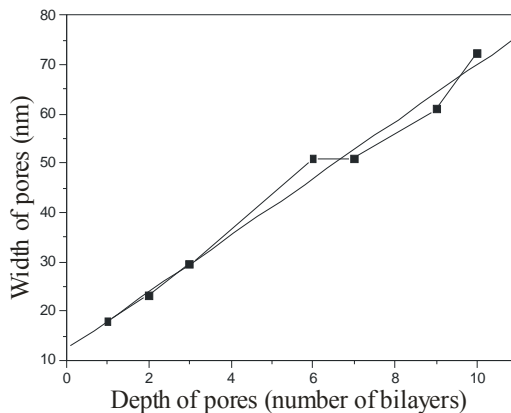

Fig. 3. Increase of pore depth and width during electrochemical etching

SUMMARY

The change of the silicon surface morphology due to the etching in electrolytes with slightly different molarity and acidity has been presented. In the initial stage of dissolution, the pit nucleation density has been observed to be of 3×10^9 cm^{-2}. Application of electrolyte with lower pH and/or higher molarity results in the acceleration of dissolution and in the formation of larger pores. In the intermediate stage of dissolution, the mesa-type structures were observed with diameter of 150-200 nm, which were surrounded by pores. In the last stage of silicon surface dissolution, the mesa-type structure dissolves and forms the pores.

Acknowledgements

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