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Computational simulations of pore nucleation in silicon(1 1 1)

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Abstract

Float zone n-Si(1 1 1) was electrochemically etched in diluted NH_4F to form porous nuclei. The experimental results were compared with computational simulations of pore nucleation and growth. Electrochemical etching of silicon(1 1 1) results in pore nucleation preferentially localized on the edges of atomic terraces. The initial pore nuclei have diameter and depth of 17 nm and 0.3 nm, respectively. We find a correlation between H-terminated Si(1 1 1) atomic surface morphology and electric field distribution on pore nucleation and growth mechanism. The H-terminated surface is composed from wide (100–200 nm) atomic terraces with steps of 0.3 nm height. Electric field enhancement occurs at the terrace edges leading to focusing the holes trajectories. This leads to weakening of the Si–Si backbonds resulting in easy atom removing. The maximum electric field was observed at terrace edges and at the semispherical pore bottom.
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1. Introduction

Porous silicon is a material composed from wires and open spaces and is a widely investigated material [1–4]. The structure is formed in HF or NH_4F containing electrolyte under galvanostatic or potentiostatic conditions. For silicon dissolution a sufficient amount of holes is necessary for the etching. In the case of n-type silicon, the holes are the minority carriers and they are generated by illumination. Careful controlling of the electrochemical etching process, results in well defined structures.

The crystal orientation and prestructuring, results in porous Si with different pore size and morphology. In the case of (1 0 0) oriented wafers the pores, with high depth to diameter ratio, can growth perpendicular to the surface. In other case pores can grown randomly, forming a branched, interconnected structure, with light emitting properties. The formation of nano- meso- and micropores is strongly related with doping concentration, so the smaller pores are formed in heavily doped n-Si(1 1 1), etched without illumination [5].

Porous silicon finds some interesting and perspective applications. Because a large surface to volume ratio, up to $500\ m^2\ cm^{-3}$, porous silicon can be used in gas sensor applications [6]. The nanometer size of the pores and silicon skeleton exhibit interesting optoelectronic properties like photo- and electroluminescence [7,8]. The observed photoluminescence [7,8] is different with different porosity [9]. The anisotropic pores, grown perpendicularly to the surface, can be used as a template for particles or nanotubes growth [10,11].

The mechanism of pore nucleation and growth was studied by Beale [12,13], Zhang [14], Carstensen [15], Smith [16] and Parkhutik [17]. Beale and Zhang [12–14] consider an electric field enhancement on microstructure inhomogeneities (like doping atoms, surface with different radius of curvature).

Porous silicon prepared in wet etching processes requires a lot of time for the sufficient structures preparation. Prior to the electrochemical conditioning the

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n-Si(1 1 1) samples are prepared in the following way: (i) oxide removal in concentrated HF (1 min); (ii) cleaning in acetone and methanol in an ultrasonic bath for 10 min; (iii) successive oxidation in H_2SO_4: H_2O_2: H_2O (6:1:3) at 70 °C for 10 min; and (iv) etching in concentrated 40% NH_4F (15 min). After each preparation step, the sample was rinsed under a stream of deionised, N_2 purged ultrapure deionised water and finally dried in a stream of pure N_2 [17]. The process is called H-termination and in the case of silicon(1 1 1) results in a flat surface, composed from wide atomic terraces with 0.3 nm height steps [18]. The surface silicon atoms are passivated by hydrogen, resulting in a well stabilized surface.

In this work we present the role of the H-terminated silicon(1 1 1) wafer with flat atomic terraces on pore nucleation. The computer simulations consider the initial stage of the nanopores formation with pore diameter and depth of about few nanometers. The numerical calculations of the electric field distribution on the Si(1 1 1) surface and around the pore nuclei have been done.

2. Experimental data and results

Float zone n-Si(1 1 1) wafers with 2–12 Ω cm resistivity were experimentally investigated. Flat silicon surface with atomic terraces was formed in H-termination process [17]. The electrochemical etching was done using a 273A EG&G potentiostat/galvanostat. Surface images were recorded using a Nanoscope IIIa AFM.

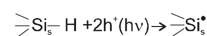
A silicon wafer was electrochemically etched in 0.1 M NH_4F, pH 4.5 electrolyte (with temperature of about 20 °C) at potentiodynamic conditions (increased by +0.1 V from the OCP with a scan rate of 20 mV s^{-1}) (Fig. 1a) and then at constant potential (+0.1 V vs. OCP) for 15 s (Fig. 1b) and 60 s (Fig. 1c). The initial stage of pore formation results in pits formation on the incisions in the atomic terraces (Fig. 1a and b). For the first time we have observed this phenomenon [18], where the initial pore nucleation on (1 1 1) surface is localised. After 15 s etching (Fig. 1b), the initial average diameter and depth of the pits is about 17 nm and 1 atomic layer (0.3 nm), respectively. After 60 s etching (Fig. 1c), the diameter and depth increases up to 28 nm and 2–3 atomic layers (0.6 and 0.9 nm), respectively. The next grown pits are formed along edges of the atomic terraces. After 60 s we have observed remnants of the atomic terraces, but most of the surface is corroded.

3. Computational simulations

It is commonly known, that any surface inhomogeneities result in changes of the electric field [11–13]. In the case of silicon atomic terraces morphology, the electric field should be enhanced at the edges and incisions of V-shapes atomic terraces, as well as on zigzag tongues (Fig. 2a and b). We propose, that the surface irregularities result in localization of the electric field, focusing trajectories of the holes in the inner edges of the atomic terraces (Fig. 2c and d) and resulting in localization of the charge flow. From the second point of view, a high electric field results in weakening of the bonds between surface silicon atoms, which facilitates their removing.

The suggested pore nucleation and growth mechanism connected with local surface irregularities of the H-terminated Si(1 1 1) have two aspects

- the electric field enhancement leads to focusing of the holes generated by light (Fig. 2) and the holes trajectories are directed towards the surface irregularities,
- atoms at the edges of the atomic terraces, with a smaller number of backbonds can easily to removed from the lattice. The holes consumed by surface atoms result in surface radicals with strongly weakened backbonds, which then react with F^- ions



The pits observed on Fig. 1 can be explained by electric field enhancement. Solvated F^- ions are electrostatically attracted toward incisions of the atomic terraces (Fig. 2). The photogenerated holes are deflected towards these sites, where the Si surface atoms can be oxidized by the holes from the valence band. This leads to weakening of the Si–Si backbonds. The locally enhanced electrolytic counter charge results in pit formation. The localized charge results in nucleation of the nanometer size pores (Fig. 1).

The assumptions of numerical calculations of the electric field distribution on the Si(1 1 1) surface and around the pore nuclei are presented below.

The Si atoms have not permanent dipole moments. These moments can be induced by placing the silicon wafer in the external electric field, thus resulting in electron cloud distortion. The dipole generates the electric field in the surrounding space. The external field moves the electron cloud from the equilibrium position and weakens the atom bonds, facilitating atoms removing.

A model Si crystal is a three-dimensional repetition of some unit of cubic cell. These simulations were made on a crystal consisting of 10^6 atoms. The silicon wafer has been numerically formed with the active (1 1 1) plane. In the wafer the pores with semispherical bottom were numerically generated (Fig. 3). Cells are repeated periodically and the summation procedure is used to calculate the dipolar field. The effective electrical field in any point is the superposition of the external electrical field and stray electrical field from induced dipoles.

We have developed and applied a computer algorithm that generates realistic models of silicon with periodic boundary conditions. As starting parameters expected crystallographic data such as unit cell and lattice parameter.

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