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Structural, optical and electrical characterization of porous silicon prepared on thin silicon epitaxial layer

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ABSTRACT

Silicon-on insulator (SOI) wafers, consisting of 22 μm thick p-type silicon epitaxial layer grown on 280 μm thick n-type (1 1 1) silicon substrate, were electrochemically etched in hydrofluoric acid (HF) to produce porous silicon (PS) samples. The pores of different size and different depth were obtained by etching at different time duration, from 10 to 80 min, using the constant concentration of 48% HF in ethanol solution. The structural and optical properties of porous layers were investigated by Raman, FTIR and photoluminescence (PL) spectroscopy, and scanning electron microscopy. SEM images showed high density of micrometer-sized pores whose morphology and density depended on the etching duration. For all samples the observed PL peak is in the visible spectral range. The intensity of the PL peak was increased with the etching time. The exception was the epitaxial layer of the sample etched for 80 min. It showed the strong decrease in the PL peak intensity. For this sample the insulator layer was completely etched out and the epitaxial layer was detached from the substrate. Fine nanometer-sized pores with the strong photoluminescence were observed in the substrate layer. The fine silicon nanostructure was confirmed by the broadening and the red-shift of crystalline silicon TO(Γ) vibrational band that indicates a strong phonon confinement.

1. Introduction

When crystalline silicon (c-Si) wafers are electrochemically etched in hydrofluoric acid (HF), at specific current densities, a vast labyrinth of permeating nanosized pores is formed which is known as porous silicon (PS) layer [1]. This is an interesting material due to its unique and unusual optical and electrical properties compared to bulk Si substrate. A great interest for this material was developed when Canham, in 1990, discovered its intense photoluminescence (PL), at room temperature, in the visible light spectrum [2]. Contrary to this, bulk silicon exhibits up to five orders of magnitude weaker photoluminescence than PS, since it is a material with indirect energy band-gap [3].

In an attempt to explain the observed photoluminescence, several models have been proposed. Few models are based on surface chemistry effects [4], but nevertheless, the most promising is the quantum confinement model [5], since it can explain both the shift of the absorption edge for PS towards higher energies and the observed direct band-gap like behavior of the PS layers [4].

Structurally, porous silicon is very complicated. Some published papers indicate that PS layers consist of Si columns and pores or isolated nanocrystallites [6]. On the other hand, PS may be considered as system of interconnected quantum wells, the so-called "quantum sponge" [7]. Nevertheless, the properties of PS, such as porosity, thickness, pore diameter and microstructure of silicon, have been reported to depend on anodization conditions including the electrolyte, current density, wafer type and resistivity, anodization duration and temperature [8]. The mechanism of pore formation has not jet been completely elucidated. Different models have been suggested, all of which agree, that for the electrochemical dissolution process holes are required, and that the process starts at arbitrary nucleation sites at the surface. The pores are formed and their walls are etched until the holes are depleted [9].

In this paper we report the preparation of PS on silicon-on insulator (SOI) wafers with different time duration of etching, as well as the study of its structural, optical and electrical properties. The structural properties were studied by scanning electron microscopy (SEM), Raman spectroscopy and Fourier transform infrared (FTIR) spectroscopy, while the optical properties were studied by photoluminescence (PL). SEM images showed mostly micrometer-sized pores whose morphology and density depend on the time duration of etching. Nanometer-sized silicon structures were observed by phonon confinement effects in the Raman spectra that result in the appearance of transversal acoustic (TA) phonon band [10] and in the broadening and red-shift of transversal optical (TO)

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Table 1
The anodization conditions for sample preparation.

Sample	t/min	Current density/mA/cm^2
1	10	7
2	20	8
3	40	8
4	80	16

phonon band [11]. The FTIR spectra exhibit numerous vibration bands from Si-H_x groups, ranging from 2000 to 2300 cm^{-1}, as well as the vibration bands from CH_x groups in 2800 to 3000 cm^{-1} spectral range. Photoluminescence spectra in the visible range were observed for all samples.

2. Experimental

Home made electrochemical etching cell [12] was used to prepare PS samples from commercially available SOI wafers, consisting of a 22 μm thick p-type (1 1 1) silicon epitaxial layer grown on a 280 μm n-type (1 1 1) silicon substrate, with SiO_2 in between as an insulator layer. The bottom side of the wafers was gold coated to ensure a good electrical contact with the bottom part of the etching cell. The samples were obtained by varying the time duration of the etching process (Table 1) at constant concentration of 48% HF in 96% ethanol solution (HF:C_2H_5OH = 1:1 in volume).

During the etching process of samples 2 and 3 the voltage was gradually increased until the current reached 100 mA which produced 8 mA/cm^2 current density. For sample 1 the maximum current was 85 mA, while for sample 4 the voltage was gradually increased until it reached 30 V and than was kept constant until

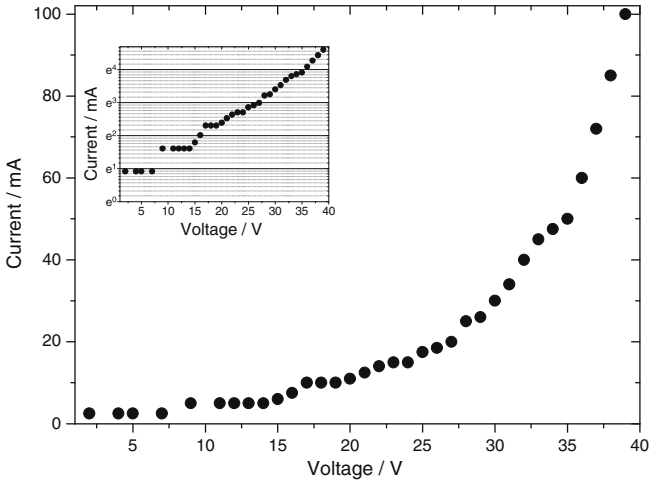

Fig. 1. The i–V curve for silicon. The inset shows the same graph in logarithmic scale to confirm exponential dependence.

the current reached 200 mA, where it was kept constant. The samples were then rinsed twice in ethanol and twice in pentane to prevent the breakage of fine porous silicon structures, since pentane reduces the capillary tension without any chemical interaction with PS [13]. After rinsing, all samples were dried in the air. The Raman spectra were recorded with Jobin Yvon T64000 triple spectrometer using 514.5 nm argon-ion laser line for excitation. The spot diameter was 6 μm and the laser power was 20 mW. FTIR spectra were recorded in transmission mode with Perkin-Elmer GX spectrometer equipped with DTGS detector. One hundred scans

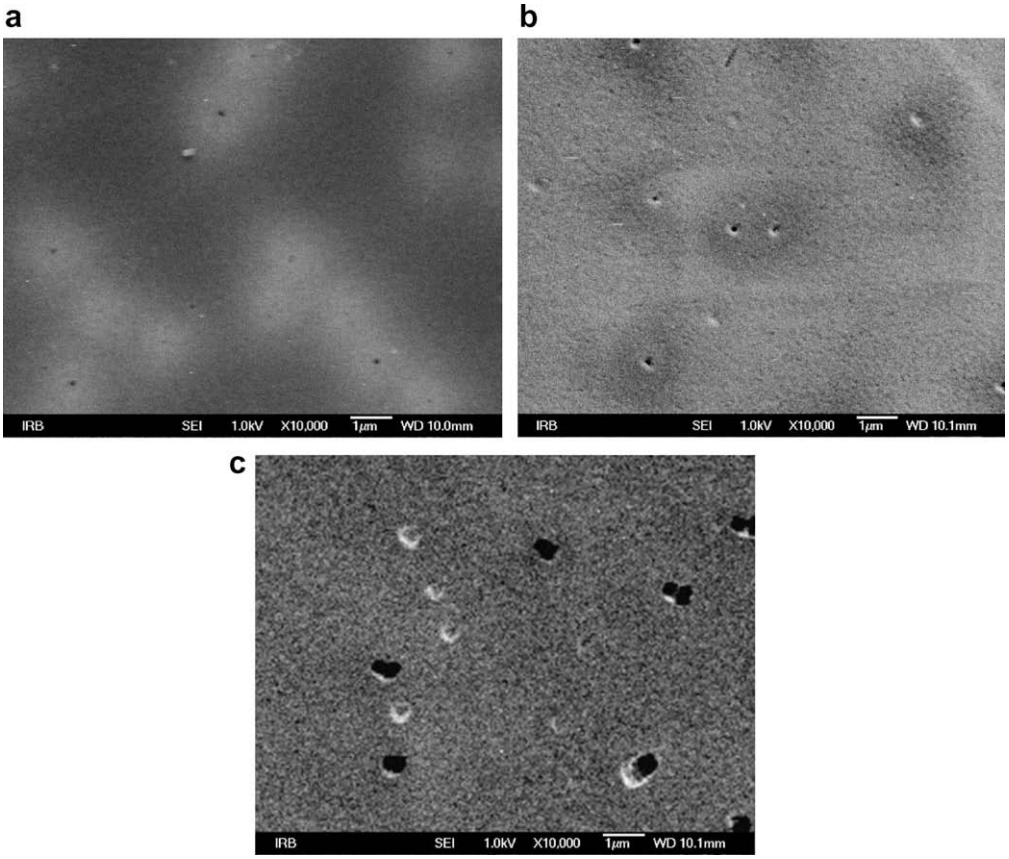

Fig. 2. SEM images of the top side of prepared samples – (a) sample 1 (10 min), (b) sample 3 (40 min), (c) sample 4 (80 min). The images were taken at 10,000X magnification.