Influence of Powerful Laser Radiation on Formation of Pores in Si by Electrochemical Etching

Artur Medvid, Pavels Onufrijevs, Leonid Fedorenko, Mykola Yusupov, Edvins Dauksta

Abstract:

The influence of strongly absorbing N_2 laser radiation on pores formation on a surface of Si single crystal has been investigated using optical microscope and atomic force microscope. After irradiation by the laser and subsequent electrochemical etching in HF acid solution morphological changes of the irradiated parts of a surface of Si were observed. At the same time, pores formation on the non-irradiated parts of Si surface took place. The porous part of the Si surface is characterized by strong photoluminescence in red part of spectra with maximum at 1.88 eV. Suppression of the pores formation by laser radiation is explained with inversion of Si type condition from p to n. This fact is explained by Thermogradient effect - generation and redistribution of the intrinsic defects in gradient of temperature. It was shown that the depth of p-Si layer on n-Si substrate depends on intensity of laser radiation and it increases with intensity of laser radiation. The results of the investigation can be used for optical recording and storage of information on surface of semiconductors.

Keywords: *porous Si, laser, optical storage, chemical etching.*

1. Introduction

The discovery of clearly visible photoluminescence (PL) at room temperature from porous silicon (por-Si) in 1990 [1] has opened the way to worldwide intensive studies on its optical and transport properties and to the numerous technological applications of por-Si in microelectronics [2] optoelectronics [3] and biology [4].

There are many methods for fabrication of por-Si. The main method of fabrication of por-Si is electrochemical etching of a Si crystal in HF solution with water or ethanol [5]. In this process, on the Si surface deep channels of pores form, with depth of several micrometers and some nanometers in diameter [6]. Sometimes laser radiation (LR) is used for controlling light emission spectrum or/and for stabilizing pores' properties. It is known that in order to form the por-Si layers the sample can be 1) irradiated by Nd:YAG laser fundamental frequency before stain etching [7]; 2) irradiated by the laser after formation of pores [8]; or 3) chemically etched in situ [9]. It is known that formation of pores on n-type Si is difficult due to deficit of holes.

Formation of p-n junction by laser beam on a surface of p-Si(B) [10]-[12], p-Ge [13], p-InSb [14]-[18], InAs [19] and p-CdTe(Cl) [20] crystals have been shown. In our previous paper [11] we have shown the possibility to transform p-type Si in to n-type Si by LR which makes it possible to control the rate of chemical reaction by LR. It was shown that the use of laser for inversion of Si crystal from p-type to n-type makes possible suppression of pore formation by laser beam.

Using p-type to n-type laser inversion in Si crystal the possibility of pore formation suppression by laser beam was shown. This phenomenon can be used for optical writing. PL intensity of porous areas depends on the current density and the maximum of spectra, which is located in the range of 1.5-2.5 eV.

Si is not reacting with hydrofluoric acid (HF) if electric current is not applied. The holes play main role in the pore formation in electrochemical reaction. Usually Si surface is passivated with H atoms and acid ions have no influence on silicon structure. Reaction between Si surface and acid solution starts after electric current is applied and Si-H bonds are broken. Once H atoms are detached from Si atoms, acid ions (F^-) start to bind with the unprotected Si atoms and form SiF_6^{2-}.

In our previous paper [11] we have shown the possibility to transform p-type Si into n-type Si by LR, due to large temperature gradient. Temperature gradient effect (generation and redistribution of the intrinsic defects (interstitials and vacancies) in gradient of temperature [12] induced the drift of the vacancies to the irradiated Si surface. Therefore, it is possible to control the speed of chemical reaction, the distribution of pores and their size by LR. The aim of this study is to show the influence of powerful laser radiation on the formation of pores on a surface of p-Si exposed to electrochemical etching method.

2. Experiments and discussions

The experiments were carried out on (100) p-type Si(B) commercial wafer. At the first stage the samples were irradiated by pulsed N2 laser (λ = 337 nm, τ=5 ns) at laser intensities I_1(area 1) > I_2(area 2) > I_3(area 3) > I_4=70MW/cm^2 (area 4) as shown in Fig.1.

No morphological changes have been detected by optical microscope and atomic force microscope (AFM) studies after irradiation of the samples. At the second stage, the samples were electrochemically etched for 10 minutes at the current strength 50 mA/cm^2 in HF solution (48%) with ethanol in proportion 1:2. Electrochemical etching was carried out in ambient daylight conditions, but it's not enough to affect n-type silicon which was formed on the surface of the irradiated Si sample. The n-type Si is not reacting with HF acid ions unless holes are generated on the surface of the sample, but ambient light is not enough to generate reasonable hole concentration.

PL has been not observed on the irradiated and etched sample areas. PL spectrum of the non-irradiated surface was shifted to the red part of spectra with maximum at λ = 656 nm (1.88 eV) and PL was observed by a naked eye at room temperature under UV light as shown in Fig. 4. PL intensity is increasing along with current strength from 20 mA/cm^2 to 50 mA/cm^2, due to pores density on the sample surface. AFM study has shown the formation of pores on the etched surface except irradiated areas where n-type Si formed as shown in Fig.2.

After irradiation and etching, the area 4 peals to pieces with peace thickness of 1 µm and porous Si is found below the n-Si layer. Further experiments show that the next area 3 start to peel off after subsequent electro chemical etching of the sample used in the earlier experiments. The thickness of the intact Si layer is up to 1.5 µm. These results show that n-type silicon is formed on surface layers in depth less than 1.5 µm. It means that n-type Si thickness depends on laser radiation intensity.

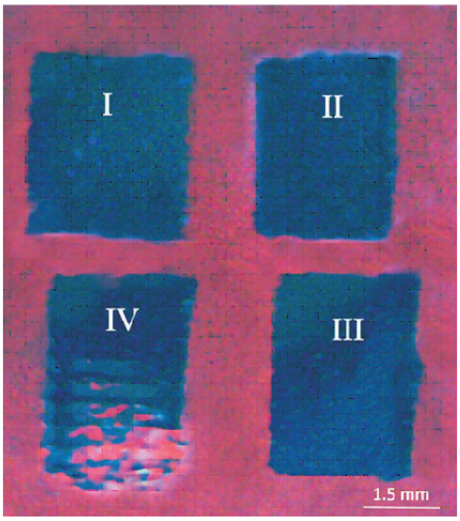

Fig. 1. Irradiated areas with laser intensities at I_1(area 1) > I_2(area 2) > I_3(area 3) > I_4=70MW/cm^2 (area 4).

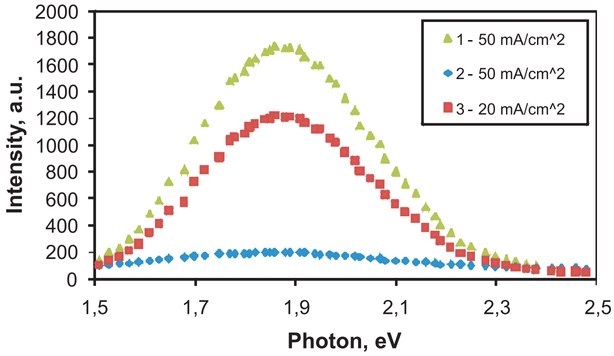

Fig. 3. PL spectrum of the irradiated (2) and non irradiated (1, 3) areas.

3. Conclusion

The possibility to control the electrochemical activity by laser beam has been shown. The depth of formation of p-n junction at the surface of p-Si crystal can be controlled by intensity of laser radiation. One more proof of p-type Si transformation into n-type Si by the Nd:YAG laser beam has been provided. Possibility of optical information recording and storage on p-Si surface by the Nd:YAG laser beam has been shown.

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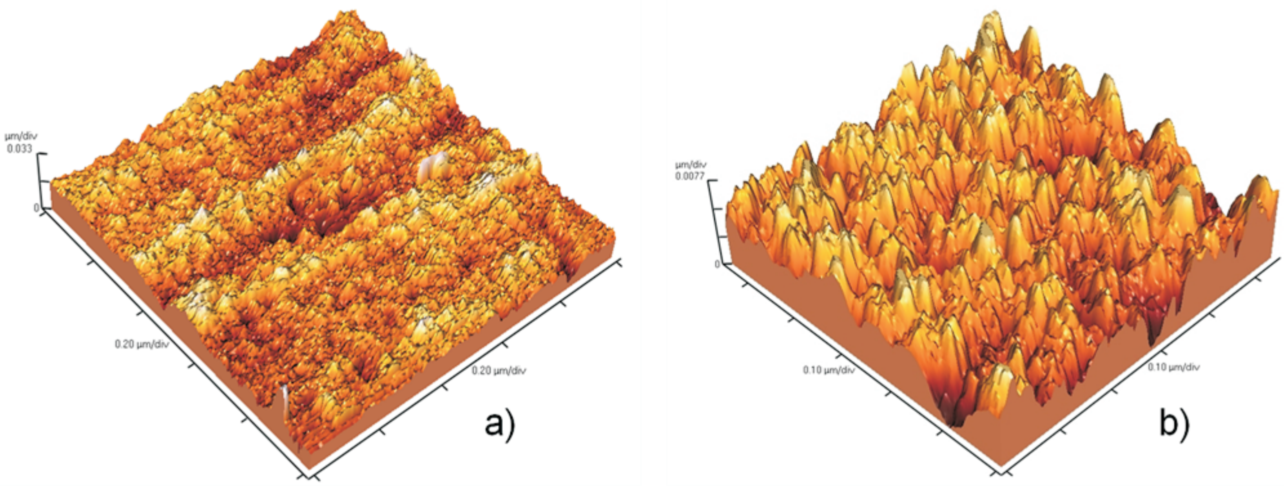

Fig. 2. 3D AFM image (a) por-Si formed by N2 laser at in-tensity I = 20.0 MW/cm^2 and subsequent electrochemical etching in HF acid solution, (b) the surface of por-Si for-med by electrochemical etching in HF acid solution.

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