Optical Reflectance of Nanostructured Silicon Fabricated by Metal-assisted Chemical Etching at Ammonia Adsorption

Conference Paper · October 2013

DOI: 10.1364/FIO.2013.FTu3A.23

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Abstract: The optical reflectance of various nanosilicon structures after ammonia adsorption were investigated. It was shown that increasing of ammonia concentration in the measurement chamber leads to an increase of the reflectance.
OCIS code: (240.0240) Optics at surfaces; **(**040.5110) Photodetectors.

1. Introduction.

Porous silicon (PS) technologies have many applications in semiconductor technology, optoelectronics, chemical, biological sensors and other fields of science [1-3]. Changes in electrical and optical properties of the porous silicon under gas adsorptions are well-known and it is still under attentive investigation [4-6]. Porous silicon exhibits a great potential in optical sensor applications due to the possibility to change its reflectance index and luminescence properties after adsorption of molecules. The sensitivity of an optical sensor depends on the adsorption properties of the measured substances and the interaction of the specific analyte with the porous silicon, which can be adjusted and improved by proper fabrication parameters.

Porous silicon, obtained conventionally by anodisation of crystalline p-type silicon (electrochemical method), is a potential platform for high efficiency gas sensors mainly due to its very large surface to volume ratio, which enhances adsorption of the sensing gas, a primary step for gas sensor. Also the high chemical reactivity of PS with the environment and the possibility of porosity control by the variation of the formation parameters further create an interest in sensing applications. Recently, a new method, termed metal-assisted chemical etching, has been developed, which is relatively simple compared to the electrochemical method. The method does not need an external bias and enables a formation of uniform PS layers more rapidly than the conventional methods. Thin metallic films or particles (Au, Pt, Al, Pd, etc.) are generally deposited directly on a silicon surface prior to immersion in an etchant composed of HF and an oxidizing agent [7, 8]. Metal-assisted chemical etching is essentially a wet etching method yet produces anisotropic high aspect ratio semiconductor micro and nanostructures without incurring lattice damage. In present paper, we report on the formation of porous p-type silicon using H_2O_2 as an oxidizing agent and silver (Ag) as deposited metal. We discuss the reflectance properties of obtained PS layers after adsorption of NH_3 molecules.

2. Experimental and Results.

During the experiment, we obtained samples with different surface morphology. At a low concentration of oxidizing agent - H_2O_2, there were pores that had a conical form, like a crater, having approximately the same size and uniformly distributed over its surface. The approximate diameter of pores ranged from 1 to 1.6 um in diameter (samples No 1). For samples series no. 2, that had higher concentration of $AgNO_3$ in immersion solution (10^{-3} M), we have obtained macro porous silicon structure. The approximate diameter of pores ranged from 10 to 20 um in diameter (samples No 2).

Instead of a conventional spectrum analyzer which is expensive and hard to miniaturize a cost-effective and transportable evaluation system was developed. In the proposed system the light sources are three different LEDs (red, green and blue). The total reflection is detected by a photodiode.

Figures 1and 2 show reflectance spectrum at different concentrations of ammonia in the chamber. Figures demonstrate a shift in the reflectance before and after ammonia exposure for different concentration of ammonia. An increase of ammonia concentration in the measurement chamber leads to an increase of the reflectance for all samples having different porous structure. Notice that samples having macro porous structures are most sensitive to ammonia exposure compared to samples with micro and nanoporous structure for all wavelengths. Adsorption of ammonia in porous silicon layer affected the reflectance magnitudes appreciably. The reflectance is changing after removal of the ammonia molecules to ever decreasing reflectance values.

A possible explanation for this behavior is the change in surface area due to the rough textured surface of the porous silicon. The results seem to indicate that ammonia molecules are diffusing further and further into the pore cavities changing the reflectance index. On the other hand, it is possible that ammonia molecules are adsorbed mainly on surface of wires and in the pore cavities. Adsorption of ammonia molecules creates new surface levels. A re-charging of levels and electrical micro fields close to polar ammonia molecules can affect on recombination rates of electron-hole pairs changing the charge concentration and thus changing the local dielectric constant of the medium (ε) and refractive index ($n = \sqrt{\varepsilon}$).

Next we looked at how porous structure evolves in time. The reflectance after NH_3 exposure is observed to slowly increase with time. Saturation occurs after about 30-150 minutes depending on the silicon structures.

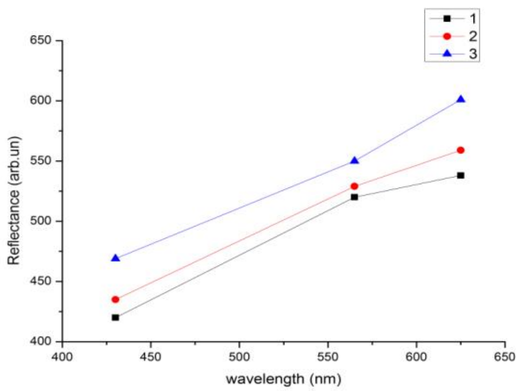

Fig.1. Dependences of maximal magnitudes of reflectance for samples No 1 under nitrogen (curve 1) and different concentrations of ammonia (curve 2 – 20 ppm, curve 3 – 60 ppm).

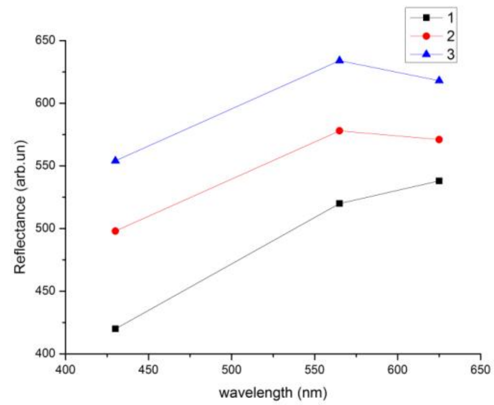

Fig.2. Dependences of maximal magnitudes of reflectance for samples No 2 under nitrogen (curve 1) and different concentrations of ammonia (curve 2 – 20 ppm, 3 – 60 ppm).

3. Conclusion.

Reflectance and surface morphologies of porous silicon prepared by metal-assisted chemical etching using H_2O_2 as an oxidizing agent have been studied. Depending on the metal-assisted chemical etching conditions, the macro- or microporous structures could be formed. The optical reflectance changes significantly when exposed to ammonia gas. The PS is most sensitive for pores having approximately size 10-15 μm. A response of porous silicon on the adsorption of ammonia molecules may be used for development of new sensors. This is an interesting result and an area for further investigation.

4. References.

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