Ammonia detection using optical reflectance from porous silicon formed by metal-assisted chemical etching

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Ammonia detection using optical reflectance from porous silicon formed by metal-assisted chemical etching

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ABSTRACT

An impact of morphology on reflectance of porous silicon was investigated. Depending on the metal-assisted chemical etching conditions the macro- micro structures could be formed. The reflectance properties of various porous silicon 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. The most sensitive structures for ammonia detection are porous silicon having approximately size of pores - 10-15 μm. A fast response of porous silicon on the adsorption of ammonia molecules may be used for development of new sensors.

Keywords: porous silicon, adsorption, reflectance, metal-assisted chemical etching, ammonia

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 [4-8]. 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 [9, 10]. 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.

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2. EXPERIMENTAL

2.1 Porous silicon formation and morphological investigation

Metal-assisted chemical etching (MaCE) is fundamentally a wet etch technique. MaCE was first used as an electroless etching technique to produce porous Si and porous III–V compound semiconductor by Li et. al. in 2000 and 2002, respectively [11,12], in contrast to the conventional anodic etching method for porous semiconductor formation. Details on the MaCE mechanism and development can be found elsewhere [13].

The metal-assisted chemical etching processes were applied to p-type Si wafers Czochralski-grown (100) 1-4 Ohm·cm. After standard RCA cleaning the wafers were cleaned with acetone and deionized water via ultrasonic cleaning. A thin oxide layer was formed and the surface became hydrophilic. This oxide layer was removed by dipping the samples into a dilute HF solution. The silver particles, which act as catalysts to assist the etching of silicon, were deposited on Si samples by immersion in 0.23 M HF and 5×10^{-5} M $AgNO_3$ (samples series No 1) and in 0.23 M HF and 10^{-3} M $AgNO_3$ (samples series No 2) metallization aqueous solutions. The time of immersion was varied between 0.5 to 30 minutes. After the electroless metallization, the wafers were etched in aqueous solutions containing HF (40%), H_2O_2 (30%) and ultra-pure H_2O at different concentration ratios and for etching times varied from 1 to 30 minutes. After etching, the samples were rinsed with deionized water. The etching and immersion procedures were performed at room temperature.

Structural properties of porous silicon prepared by metal-assisted chemical etching have been investigated by Atomic Force Microscope (AFM) NT-206. AFM studies were done at atmospheric conditions. Using AFM we could characterize the shape and sizes of isolated particles, their distribution depending of the chemicals conditions

2.2 Reflectance measurement system

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. Fig. 1 shows the schematic setup of a simple optical system. The implementation of the developed system and determination of the suitable application areas with the corresponding resolutions is actually in evaluation.

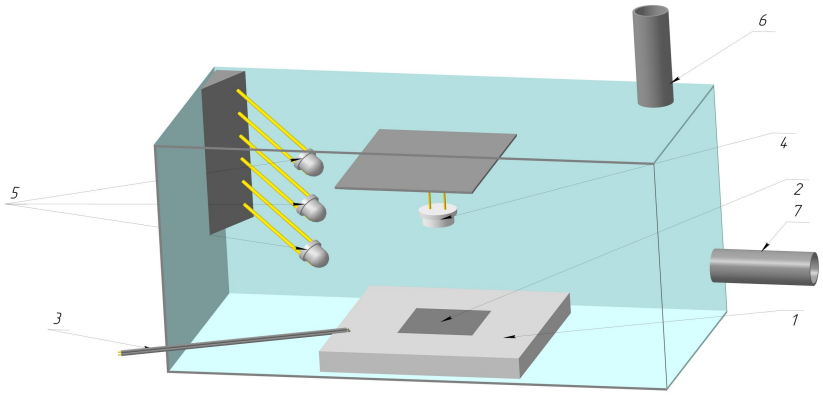

Figure 1. Experimental setup: 1 – Peltier Module; 2 – Sample; 3 – Thermoresistor; 4 – Photodiode; 5 – LED's; 6, 7 – Inlet/Outlet gas.

3. RESULTS AND DISCUSSIONS

3.1 AFM studies of porous silicon

During the experiment, we obtained samples with different surface morphology. Fig. 2 displays an AFM image of the porous silicon surface (samples series No 1). At a low concentration of oxidizing agent - H_2O_2 ($H_2O_2/H_2O/HF=10/80/40$), as seen from this image, 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.

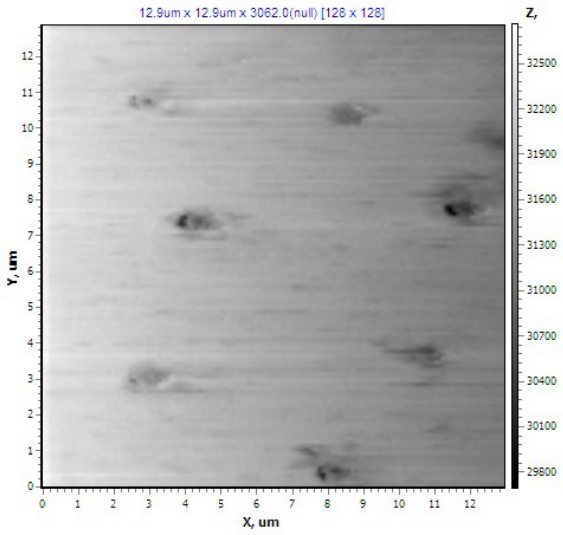

Figure 2. AFM image of Si(100) with a resistivity of 4 Ohm cm after 10 minutes etching in solution—$H_2O_2/H_2O/HF$ = 10/80/40. Ag particles were deposited before etching in solution 0.23 M HF and 5×10^{-5} M $AgNO_3$ within 15 min.

The next step was to figure out how the increasing of oxidant concentration affects surface morphology. The increase of oxidant concentration ($H_2O_2/H_2O/HF$ = 25/80/40) leads to a change in the surface structure of silicon from microporous to highly porous structure. We have observed highly porous structure with the dimensions of the pores having an approximate size of 50–200 nm depending on the deposition time (Fig. 3). For both concentrations of H_2O_2, the prolonged etching time induces an increase of pore depth. The changing of surface morphology due to increasing of H_2O_2 concentration could be explained by the theory proposed by Chartier et al. [14]. Charties et al. have shown that as the composition varies from high to low HF/H_2O_2 ratio, mesopores, cone-shaped macropores, craters could be obtained. This change occurred because of fast dissolving of the silicon surface.

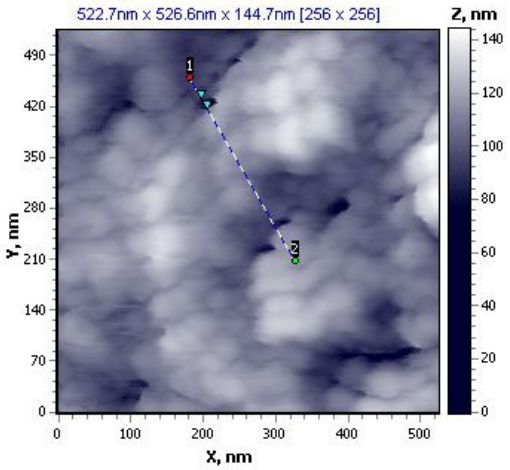

Figure 3. AFM image of Si(100) with a resistivity of 4 Ohm cm after 10 minutes etching in solution—$H_2O_2/H_2O/HF$ = 25/80/40. Ag particles were deposited before etching in solution 0.23 M HF and 5 × 10−5 M $AgNO_3$ within 15 min.

For samples series no. 2, that had higher concentration of $AgNO_3$ in immersion solution (10^{-3} M), we have obtained more remarkable experimental results. The color of the silicon surface after etching has been almost black (1–15 minutes

of immersion time) or light brown (15–30 minutes of immersion time) depending on the immersion time. First, we supposed that it is similar to "black" silicon having a needle-shaped surface structure where needles are made of single-crystal silicon and have a height above 10 microns and diameter less than 1 micron [15]. However, AFM investigation showed an absolutely other morphology (Fig.4) having macropores.

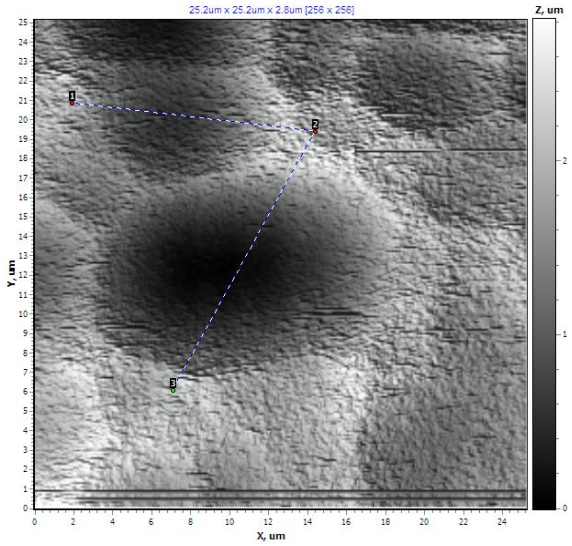

Figure 4. AFM image of Si(100) with a resistivity of 4 Ohm cm after 10 minutes etching in solution—H_2O_2/H2O/HF = 15/80/40. Ag particles were deposited before etching in solution 0.23 M HF and 10^{-3} M $AgNO_3$ within 5 min.

3.2 Reflectance of porous silicon after NH_3 adsorption

Reflectance measurements were conducted with the optical system mentioned above (fig.1). Figures 5and 6 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. Notice that samples No 2 (macro porous structures) are most sensitive to ammonia exposure compared to samples No 1 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.

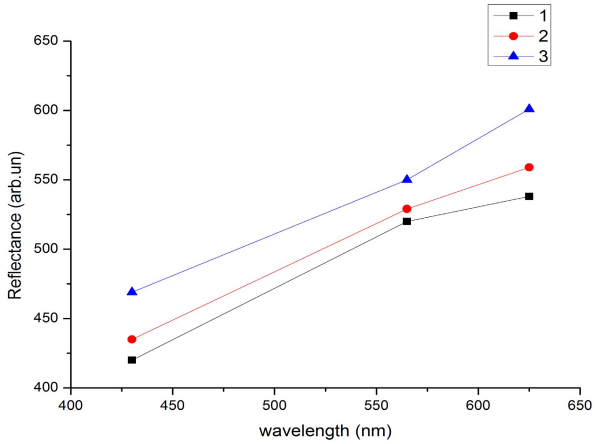

Figure 5. Dependences of maximal magnitudes of reflectance for samples No 1 under nitrogen (curve 1) and different concentrations of ammonia (curve 2 – 20 ppm, curve 3 – 60 ppm).

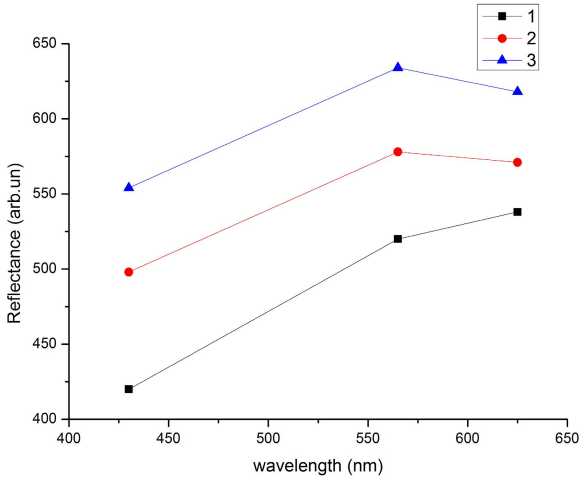

Figure 6. Dependences of maximal magnitudes of reflectance for samples No 2 under nitrogen (curve 1) and different concentrations of ammonia (curve 2 – 20 ppm, 3 – 60 ppm).

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 ammonia exposure is shown in fig.7. Here, the reflectance after NH_3 exposure is observed to slowly increase with time. Saturation occurs after about 3-5 minutes for all samples. Research has shown that increase in concentration of ammonia increases the saturation time. Such fast response of porous silicon on the adsorption of ammonia molecules may be used for development of new sensor's structures.

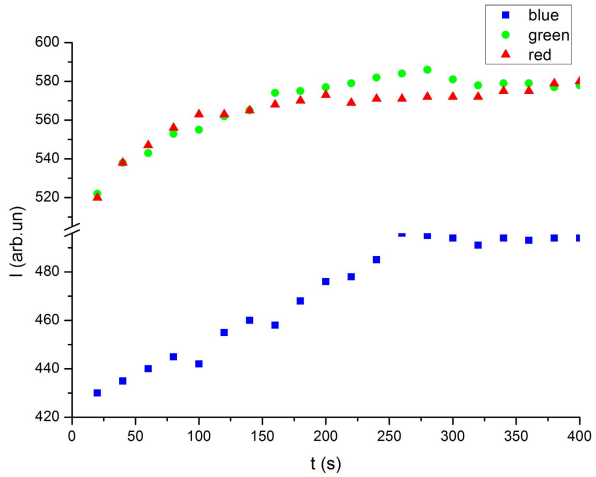

Figure 7. The reflection after ammonia exposure of samples No 1; ammonia concentration 20 ppm.

4. 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 fast 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.

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