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Short Communication

Effect of Surface Morphology on Electrical Properties of Electrochemically-Etched Porous Silicon Photodetectors

N. Naderi[*], *M.R. Hashim*

Nano-Optoelectronics Research Laboratory, School of Physics, Universiti Sains Malaysia, 11800
USM, Penang, Malaysia
*E-mail: naderi.phd@gmail.com

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In this communication, porous silicon samples were prepared by pulsed photo-electrochemical etching using HF based solution. The porosity of silicon substrate was changed by applying electroless chemical etching process prior to photo-electrochemical anodization. A novel parameter of delay time (T_d) was described in the shape of current, besides cycle time (T) and pause time (T_{off}) of pulsed current which could influence the morphology of pores. Our results showed that applying the delay time can produce uniform porous layers. A coplanar structure of Ni was evaporated on porous layers in order to fabricate Schottky contacts for studying the I–V characteristics of the metal–semiconductor–metal (MSM) photodetectors. For improving the quality of electrical contacts, all of the samples were subjected to the annealing in a conventional tube furnace under flow of nitrogen gas. By considering the quantum confinement theory, it was found that electrical characteristics of porous samples measured in dark (I_d) and under illumination (I_{Ph}) can be fitted well by the equations of thermionic emission. From this point of view, Schottky barrier height (SBH) and ideality factor (n) of fabricated photodetectors were calculated. The results showed that surface morphology of porous silicon can affect the electrical properties of fabricated photodetectors if the quality of electric contact is optimized. As an overall view ideal electric contacts on porous silicon can improve the sensitivity of devices even for PS with micro-sized porous surface.

Keywords: Porous silicon; Photo-electrochemical etching; Schottky barrier height; MSM photodetectors.

1. INTRODUCTION

Porous silicon (PS) has become the material of favor for sensing applications recently, because of the low cost, low power consumption, and its compatibility with silicon-based technologies. Beside optoelectronic applications [1], PS layers have been used in environmental sensors like gas detectors [2] and humidity sensors [3]. It has been proven that the sensitivity of PS depends upon the morphological characteristics of pores, including the pores diameter and uniformity, regularity of the surface and the layer thickness [4].

Several investigations show that electrical and optical characteristics of porous semiconductors can be considerably changed upon the alterations in their surfaces [5]. Electrochemical anodization method is an attractive technique for fabrication of uniform pores on the surface of silicon [6]. There are several parameters used to optimize the surface characteristics of porous layer, such as current density, time of etching, light with several frequencies, shape of current and electrolyte. PS is mostly formed by constant current electrochemical anodization of silicon in HF–based electrolyte [7]. A fixed current-based etching process is suffered from the creation of hydrogen bubbles in pores. This phenomenon decreases the speed of etching and results in shallow pores [8]. The solution to this problem is by applying discontinuous current with combination of cycle time (T) and pause time (T_{off}) in order to eject the H_2 bubbles and allow fresh HF react with substrate [9]. The pulsed-current method which can be controlled by changing the cycle time (T) and pause time (T_{off}) of current during the etching process has been introduced [10]. In this communication the optimization of porous layers has been developed by applying an initial delay time (T_d) in order to prepare samples prior to pulsed electrochemical etching.

Photodetectors are used for accurate measurement of light intensity in science and industry [11]. Among several types of photodetectors like p-n junctions, p-i-n diodes, p-π-n diodes, schottky barrier detectors and metal–semiconductor–metal (MSM) photodetectors, the advantages of MSM devices such as simplicity of fabrication, high response speed and reduction in noise are unique [12]. It can also facilitate the application of sensors in photodetectors and gas sensors [13].To achieve a large Schottky barrier height on n-type silicon, several metals with high work functions are available, such as nickel (Ni), gold (Au), and platinum (Pt). However Ni makes a stable Schottky contact. The growth of metal thin films on high-porous surfaces with micro-sized pores is complicated and needs optimization of experimental procedure. The sensitivity of photodetectors will decrease if the electric contacts become non-uniform or non-stable. From the other side, increasing the porosity of surface will improve the absorption of light by increment in the specific surface area of porous semiconductor. Thus if the quality of coated metals on high porous materials is improved, ideal diodes with high sensitivity can be constructed.

In this paper, the evaporation and annealing of Ni contacts were carried out in order to achieve a high quality and stable electric contact on optimized PS. The MSM photodetectors were fabricated based on Ni/PS/Si structures. The electrical parameter of Schottky contacts like Schottky barrier height (SBH) and ideality factor (n) were investigated as a function of porosity. To the best of our knowledge there is no report on simultaneous optimization of surface porosity and electrical contact to control the ideality of photodetectors.

2. EXPERIMENT

The PS layers were made by anodizing of silicon wafer in HF based electrochemical bath at room temperature under illumination of 100W tungsten lamp placed at 30 cm above the samples. The electrochemical bath was a Teflon container of 10 mm diameter and 25 mm height. The solution was containing a mixture of hydrofluoric acid (HF 49%), ethanol (95%) and hydrogen peroxide (H_2O_2) with the ratio of 1:2:2 by volume.

A pulsed current with peak density (J_{max}) of 20 mA/cm^2 and period time (T) of 14 ms containing pause time (T_{off}) of 4 ms was connected to the electrochemical system and the etching last for 30 minutes. By applying (T_d= 2 min) a uniform porous silicon was fabricated called PS** which was compared to the sample without delay (PS*). As-prepared PS samples were dried in room temperature (RT) under nitrogen flow for ~ 1 h to ensure that all the solution has evaporated. For metallization of samples in order to fabricate MSM diodes, finger shaped electrodes of Ni (figure 1) with the thickness of 204nm, and dimension of 3300×3950 µm containing finger spacing of 400µm [14], were deposited onto all porous substrates by thermal evaporation of pure nickel in vacuum chamber at pressure of 3.8×10^{-5} mbar. In order to reduce the atomic mismatch, for a high quality Schottky contact, samples were annealed in tube furnace at temperature of 450 °C under nitrogen gas flow for 10 min. For SEM measurements a Jeol (JSM-6460 LV) microscope was used for morphology analysis. The I-V measurements were carried out at room temperature with a Keithley (2400) sourceMeter.

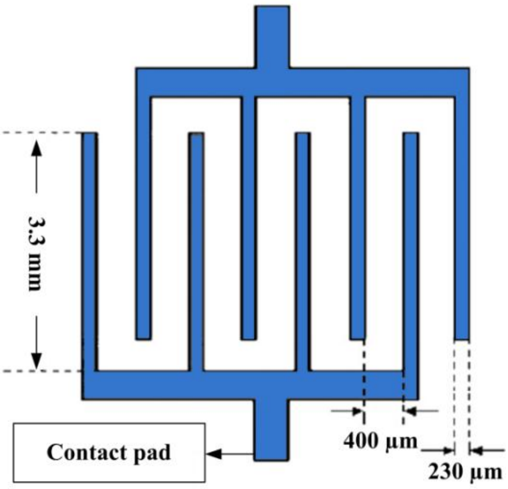

Figure 1. Schematic diagram of the metal pattern used for the fabrication of the MSM photodetectors.

3. RESULTS AND DISCUSSION

A gravitational method was used to calculate the percentages of porosity for PS* and PS** samples which were 71% and 83% respectively [15]. We can see that overall porosity of PS can change by applying T_d. During the delay time, the electroless chemical etching of silicon will take place. The surface of crystalline silicon will be affected by exposure to oxidant and etchant chemicals in the solution in absence of current. The electroless etching of silicon in the fluoride solution occurs by local coupling of redox reactions [16]. The points on the Si surface randomly become oxidation or reduction sites [17]. A localization of primary pores in crystalline silicon happens as random points are resolved [18]. During the chemical process, the entire silicon surface has equal etching parameters, for example, the concentration of acid and oxidants, which leads to homogeneous pore fabrication by random localization. During electrochemical etching, the flow of electrons is not uniform for all parts of the surface and causes non-uniform sub-micrometer pore fabrication. Thus, electroless etching can be assumed as a chemical method to fabricate shallow but uniform holes on a silicon surface for use as a template to fabricate deep and homogeneous pores by extending them through the electrochemical etching process. The oxidation and dissolution of silicon occurs more favorably at the pore crystallites than at the pit walls [19]. This occurrence implies that longitudinal etching is more favorable than lateral etching for forming deep pores. Figure 2 shows the planar and cross-sectional SEM image of porous samples.

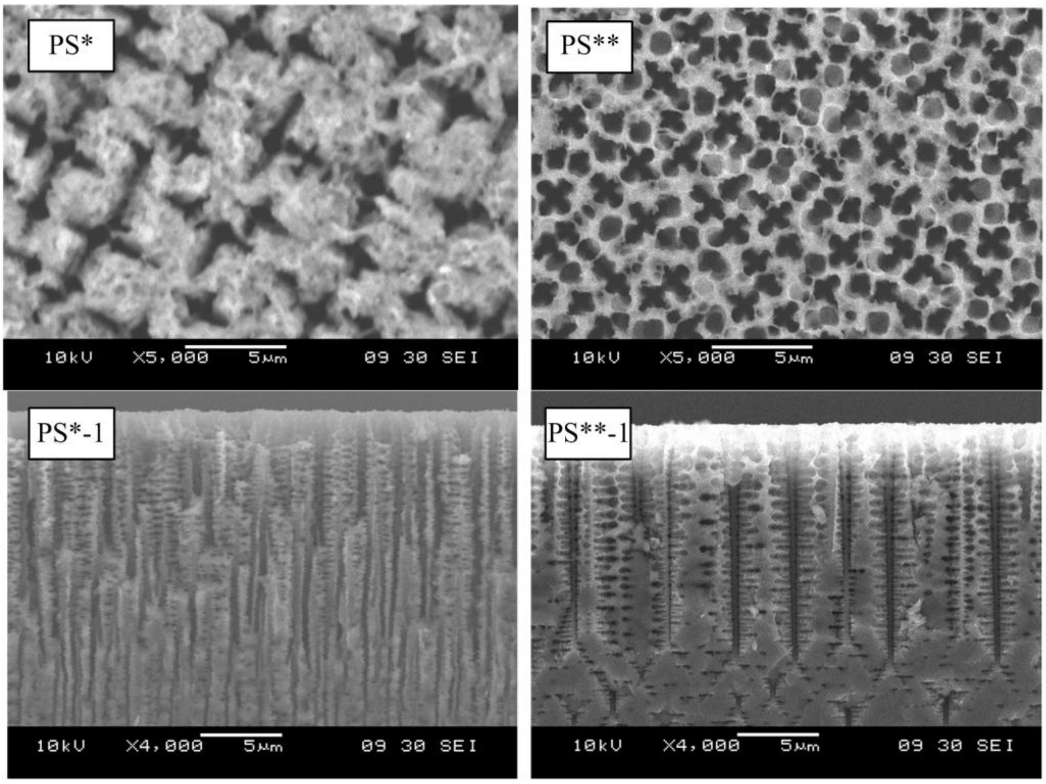

Figure 2. SEM images of PS* (without delay time) and PS** (with delay of 2 min). Cross sectional micrographs are shown by PS*-1 and PS**-1 respectively.

The electron micrograph of PS* shows evidence of non-uniform pores which decreased pore density of this sample. Cross sectional image related to this substrate demonstrates non–parallel and partially cracked silicon walls which caused narrow and asymmetrical holes in between them. The planar view of PS** reveals its high porous nature with substantially wider pores which are uniform across the whole surface. The silicon walls can be distinguished from the sharp pin-shape holes which have the length of up to 20 μm inside the silicon substrate.

From the morphology of the pores, it can be concluded that the delay time of 2 min before applying the current could prepare a unique electroless process which was followed by a homogeneous electrochemical etching and created a uniform porous surface. Figure 3 shows the current-voltage (*I*-*V*) characteristics of MSM photodetectors with Ni electrodes, measured in dark (I_d) and under illumination (I_{Ph}) for fabricated photodetectors on PS* and PS**. The Schottky detectors presented very low dark current (I_d) due to the high material resistivity and Schottky barrier height. PS** showed higher increase in photocurrent comparing to PS* due to the differences in morphology of pores between these two substrates.

The gain of sensors (the ratio of photocurrent to dark current) which is a fundamental factor for the accuracy and efficiency of them is shown in the inset of figure 3. PS** showed the higher current gain indicating highly photo-responsive porous structures. In addition it is interesting to note that the PS** indicated an increasing current gain even at 5 volts while PS* showed saturated values at high voltages.

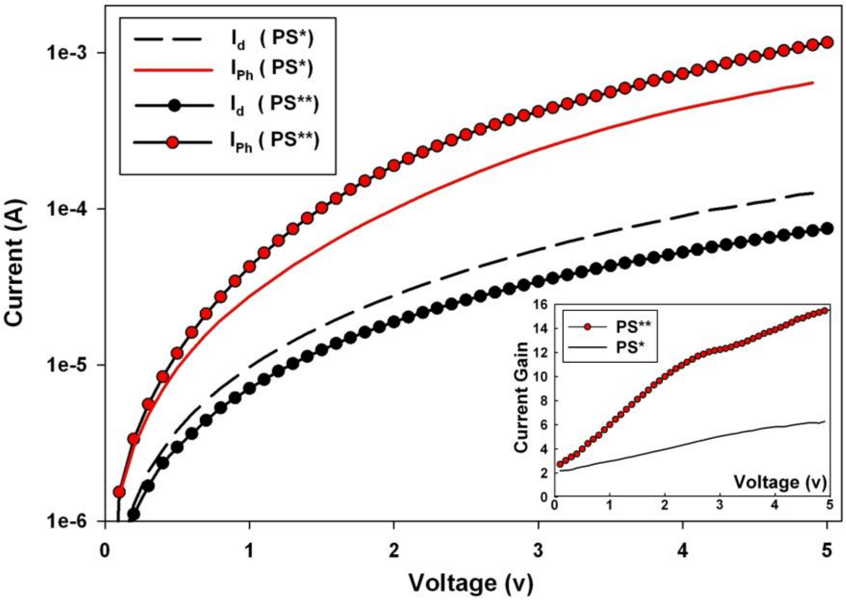

Figure 3. The I–V characteristics of the fabricated MSM photodetectors based on PS* (without delay time) and PS** (with 2 min delay) measured in dark (I_d) and under illumination (I_{Ph}). The gain values are shown in the inset.

It was found that these characteristics curves can be fitted well by the following equations of thermionic emission theory [20].

$$I(V) = I_{\circ}\left[\exp\left(\frac{qV}{nKT}\right) - 1\right] \qquad (1)$$

Where *V* is the voltage across the device, *n* is called the slope parameter or ideality factor, *K* is the Boltzmann constant and I_o is the saturation current which is given by equation (2).

$$I_{\circ} = A^{**}T^{2}W \times \exp\left[\frac{-q\varphi_{B\circ}}{KT}\right] \qquad (2)$$

In Eq. 2, q is the electron charge, W is the junction area, A^{**} is the modified Richardson constant and φ_{Bo} is the Schottky barrier height. The slope parameter (n) for ideal devices is equal to 1. For the ordinary schottky devices, n is a parameter which can show the ideality of fabricated devices.

For determining the ideality factor and Schottky barrier height of fabricated devices, a linear line was obtained by plotting the logarithm of current verses voltage from the I-V characteristics data. From equation (2) the slope of this line is q/nkT and y-intercept is lnI_0. The theoretical value of A^{**} is 96 $Acm^{-2}K^{-2}$ based on equation ($A^{**} = 4\pi q\, m^* k^2/h^3$) which m* is the effective mass of electron in n-type silicon. The ideality factor, Schottky barrier height (SBH) and the maximum current for schottky diodes fabricated on PS* – without delay time – and PS** – with 2 min delay time – are summarized in table. 1. The current contrast ratio at 5 volts for PS* and PS** was found to be 5.04 and 15.54 respectively, this degree of sensitivity of porous sample to light can be seen in changing of SBH. The related parameter for both under dark and illuminated samples were observed to be higher for the diode based on PS** compared to that one on PS*. Under illumination, the barrier height of both samples became smaller. This led to the higher photocurrent of detectors.

Table 1. The characteristics of fabricated photodetectors in dark and under illumination

Sample	Ideality Factor (n)	φ_{Bo} (eV)	Current at 5V
PS* – Dark Current	2.91	0.70	$1.2701\times10^{-4}\,A$
PS* – Photocurrent	1.98	0.68	$6.4130\times10^{-4}\,A$
PS** – Dark Current	3.19	0.74	$7.4504\times10^{-5}\,A$
PS** – Photocurrent	2.12	0.69	$1.1583\times10^{-3}\,A$

Moreover, it should be noted that the change of SBH in PS** is more noticeable than PS* which did not experience the effect of delay time. Ideality factor was found to be influenced by both illumination and porosity. A slight difference can be seen in calculated ideality factor of PS* and PS** compared to an ideal diode (n=1).

As an overall view, the presented method for evaporation and annealing of Ni has improved the quality of sensors by offering a reasonable ideality factor. The results showed that fabrication of ideal contacts on porous silicon can improve the sensitivity of photodetectors even for PS with micro-sized porous surface (PS**).

4. CONCLUSIONS

The sensitivity of photodetectors based on porous silicon has been improved by optimization of etching process and metallization method. By introducing a novel parameter (T_d) in pulsed-current photo-electrochemical etching of silicon, PS** with uniform pores was fabricated. The lack of stability of metal contacts on porous surfaces because of micro-sized pores was resolved by evaporation of Ni thin film (thickness of ~200nm) and annealing at 450 °C for 10 min. The results show that the ideality factors for PS** is comparable to PS*, indicating that this sample can show a good Schottky behavior under exposure of light. The rising amount in Schottky barrier height (SBH) after applying light is more intensive for PS** than PS* which is due to the high sensitivity of fabricated photodetectors based on this sample.

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