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EFFECT OF ETCHING TIME ON PHOTOLUMINESCENCE AND SURFACE CONDUCTIVITY OF POROUS SILICON

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ABSTRACT

Recently, porous silicon (PS) gains a lot of research interest with its potential applications in optoelectronics, flat panel displays technology, and chemical sensor. In this work, PS was chemically etched on p-type silicon (Si) wafer by hydrofluoric acid (HF) with 40% nitric acid (HNO_3) concentration at different etching time. The PS has porosity dependent on etching time in the range (38-60) % that gives orange-red photoluminescence (PL) between 657 nm to 661 nm. The PL intensity increases and the peak wavelength shows slight blue shift as etching time increases. The energy gap obtained are higher than pure Si (1.11eV). Meanwhile, the conductivity of the PS decreases as the porosity and energy gap increase.

Keywords: porous silicon, chemical etching, photoluminescence, energy gap, conductivity

INTRODUCTION

Porous silicon (PS) started to gain a lot of interest from the scientific community when the photoluminescence of this material was reported [1,2]. PS potential applications in optoelectronics, flat panel displays technology, and chemical sensor has generated great interest since the discovery of its light emission properties in 1990 [3]. PS is a nanostructured material fabricated by various chemical and electrochemical etching method [4,5]. Electrochemical etching on silicon (Si) in HF based solution has been commonly used in developing PS, especially in the application of electroluminescence devices [6]. While chemical etching has been another method in forming PS without using external bias which is one of the effective and cost saving method.

In the etching process, the solution used was usually mixture of hydrofluoric acid (HF) and nitric acid with ethanol. Firstly, the silicon surface is oxidized by hole injection from HNO_3 and simultaneously its reduction produces NO and water [6,7]. Then silicon dioxide is etched by a reaction with HF, forming a water soluble complex, H_2SiF_6 [8]. In past studies, researcher discovered that different etching method and condition in producing PS affect the morphology and photoluminescence [9]. Thus, in this study, PS is produced by chemical etching method and the effect of different etching time on the

surface morphology, porosity, photoluminescence (PL) and electrical conductivity are studied.

EXPERIMENTAL

p-type boron doped Si wafer with orientation (100) and resistivity (0.2-0.5) ohmcm Si wafer was used in the study. The PS was prepared by chemical etching process. Before etching, the wafers were cleaned with acetone and ethanol using the solvent clean method to remove oil and organic residue from the surface [10]. The solutions were formed with mixture of concentrated HF and concentration of 40% HNO_3 in 100:1 volume proportion. Then the samples were etched from duration of 5 minutes to 25 minutes with interval of 5 minutes in the etchant. After etching, the samples were rinsed with distilled water then ethanol and were dried in air [11].

The porosity of the PS was measured by gravimetric technique. The morphology and surface element of PS were analyzed using the scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS) integrated in JEOL JSM-6360LA. The electrical conductivity of the PS surface was measured by using resistivity measurement system with four point probe technique. Besides, the PL of the PS was characterized by photoluminescence spectroscopy system, model JobinYvon HR 800 UV in the range of 500 nm to 800 nm. From the PL spectrum, the energy gap can be determined by equation (1):

$$E_g = \frac{hc}{\lambda} \quad (1)$$

Where E_g is energy gap of the PS, h is planck constant, c is the speed of the visible light and λ is the peak wavelength of the PL.

RESULTS AND DISCUSSION

The weight of the sample before and after etching was measured in order to obtain the weight loss of the sample. The porosity of the PS was then determined by gravimetric method. The porosity versus etching time is plotted in Figure 1. It shows that the porosity are linearly increased on the etching time, which is due to the longer contact time of Si with the etchant. The etching rate determined from the gradient of red fitted line is 1.0825 % min^{-1}.

The elemental composition of the PS samples was identified by Energy Dispersive X-ray spectroscopy analysis (EDX) shown in Figure2. The EDX spectrum shows one similarity that the porous silicon compositions were only consist of two elements namely silicon and oxygen. The first peak and the third peak were the indication of silicon at 0.091 keV and at 1.739 keV, respectively [12]. While the second peak at 0.5249 keV represents the presence of oxygen at the porous silicon surface. Therefore, it can be deduced that the surface of porous silicon contains Si-O and Si-Si bonds [13,14].

As etching time increases, the void volume increases leading to increase of porosity [15,16]. Figure 3 shows the SEM images of PS samples prepared with different etching time at magnification of X10000. There were only slight differences on the surface morphology for these samples. Big hillock crystallite structures and small pores population were formed on the PS surface produced at 5 minutes etching time. The pores size was estimated in range of (50-100) nm and the hillock structure size ~500nm. At 10 minutes etching time, the PS surface contains small grain structure with the size ~400nm as shown in Figure 3(a). The small grains are the residue left over from the etched layer of silicon after the chemical etching.

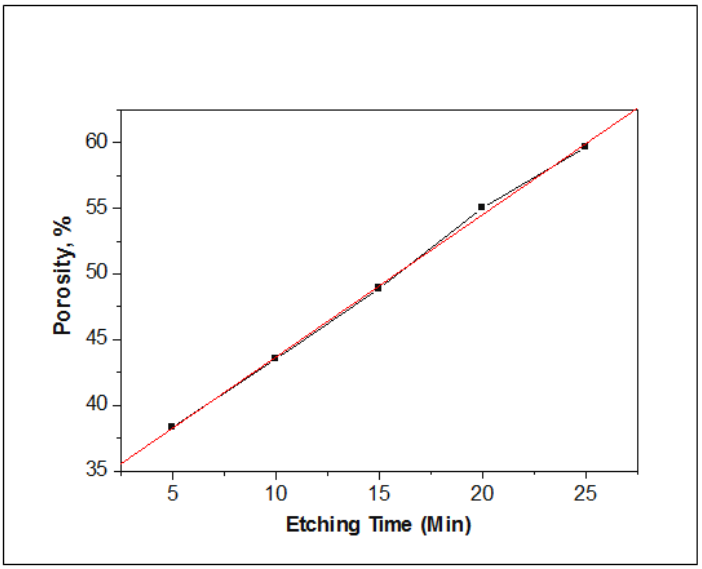


Figure 1: The porosity versus etching time

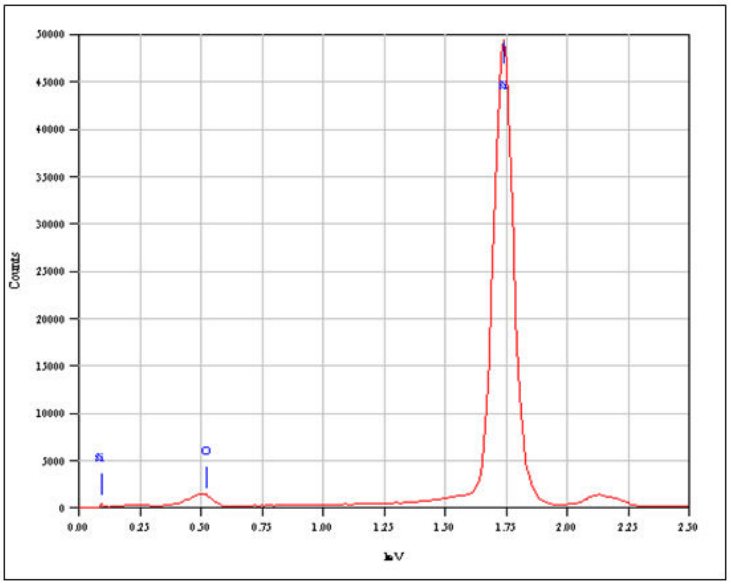


Figure 2: The EDS spectra for PS

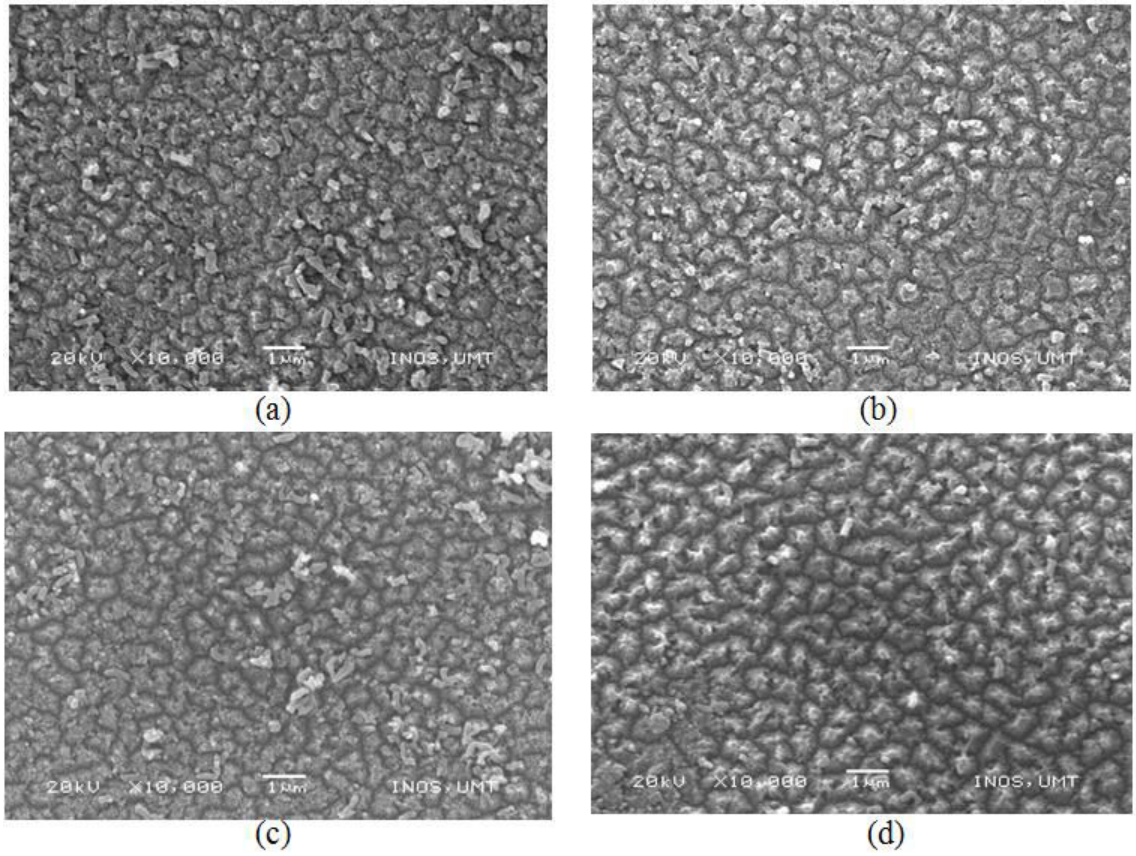


Figure 3: SEM images of PS produced at etching time (a) 10 minutes, (b) 15 minutes, (c) 20 minutes and (d) 25 minutes with magnifications X10000

The grains structures become smaller and lesser in PS at 15 minutes etching time as depicted in Figure 3(b). Besides, the roughness of surface reduces with wider pores. The surface morphology of PS with 20 minutes etching time (Figure 3(c)) formed hillock crystallite, slightly more pores and fewer grain structures as compare with those etched at lesser etching time. As shown in Figure 3(d), the surface morphology for PS prepared at 25 minutes etching time contains more proper formed hillock crystallites and more pores (~100 nm) resulting to higher surface area as compares to others.

The PS was further analyzed by PL spectroscopy and the PL spectrum were Gaussian-like spectrum which almost similar in Vasquez et al. studies [13]. The PL spectrum obtained from the PS at different etching time is shown in Figure 4. The PS are able to illuminate orange-red visible photoluminescence with the PL peak wavelength fall in the range of (657-661) nm.

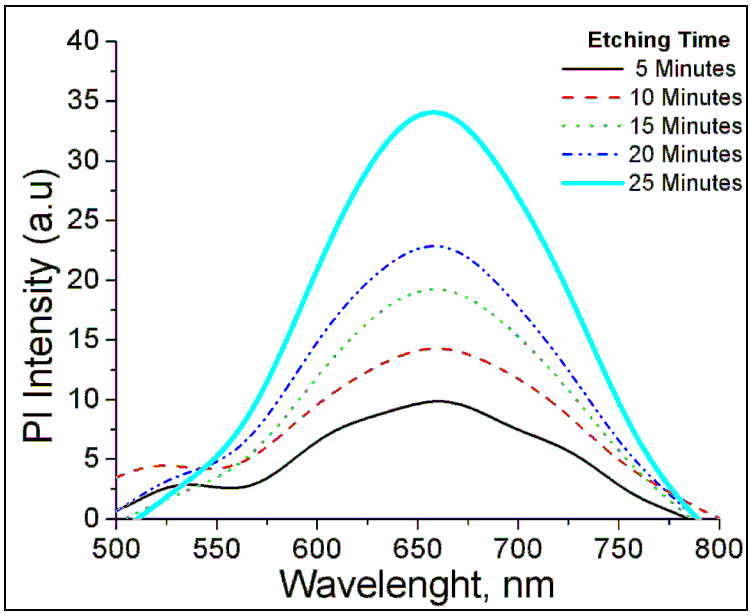
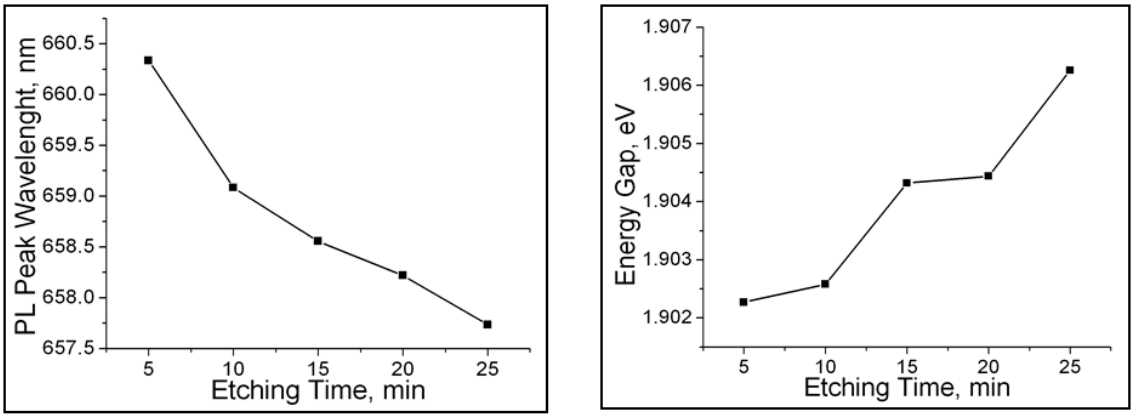


Figure 4: Photoluminescence Spectrum of PS prepare at different etching time

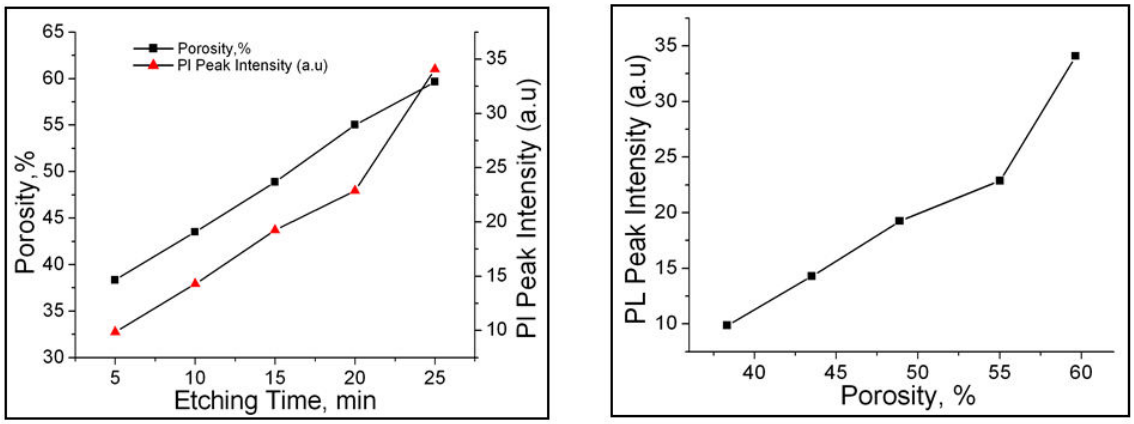
The PL peaks wavelengths plotted in Figure 5(a) shows slight blue shift effect in the range 658 nm to 661 nm as etching time increases. This effect is due to the decreases of the pore population and crystallite structure size as reported by previous researchers [17-20], which consequently resulting in increasing of energy gaps. The shift was small because there were only slight changes on the crystallites and pore size as etching duration varies. The energy gaps of the samples were calculated and plotted in Figure 5(b) where it ranges from 1.9023eV to 1.9063eV. The energy gap of PS is higher compare to Si (1.11eV) and it increases with etching time and porosity, which can be ascribed to quantum confinement effect [21-23].

Figure 6(a) depicts that PS porosity and PL peak intensity increases with etching time. These trends were due by the increase of total surface area because high surface area contained more amount of the surface species that illuminate light. Furthermore, the PL peak intensity also shows that it directly proportional with porosity as display in Figure 6(b). There was a sharp increase in PL peak intensity at 25 minutes etching duration when the porosity only had a slight increased. This phenomenon can be due to the high surface area of the studied sample.



(a) (b)

Figure 5: Relationship between (a) PL Peak Wavelength, and (b) Energy Gap with etching time



(a) (b)

Figure 6: Relationship between (a) Porosity and PL Peak Intensity with etching time, and (b) Porosity with PL Peak Intensity

The surface conductivity of PS prepared with different etching time lies in the range of $(3.113\times10^{-5} - 0.015)$ $(\Omega \cdot cm)^{-1}$. Figure 7(a) shows the conductivity versus porosity for the PS samples. From the figure, the conductivity reduces as porosity and etching time increase. When the porosity increases, some of the carriers at the surface might be etched away and the porous surface with increase surface roughness had reduced the density and mobility of the carriers [24].

Besides, electrical conductivity of semiconductor is also influenced by the energy gap as given in Equation 2

$$\sigma = \sigma_0 \exp(-\frac{E_g}{2kT}) \qquad (2)$$

where σ is electrical conductivity, σ_o is pre-exponential factor, E_g is energy gap. K is Boltzmann constant and T is temperature.

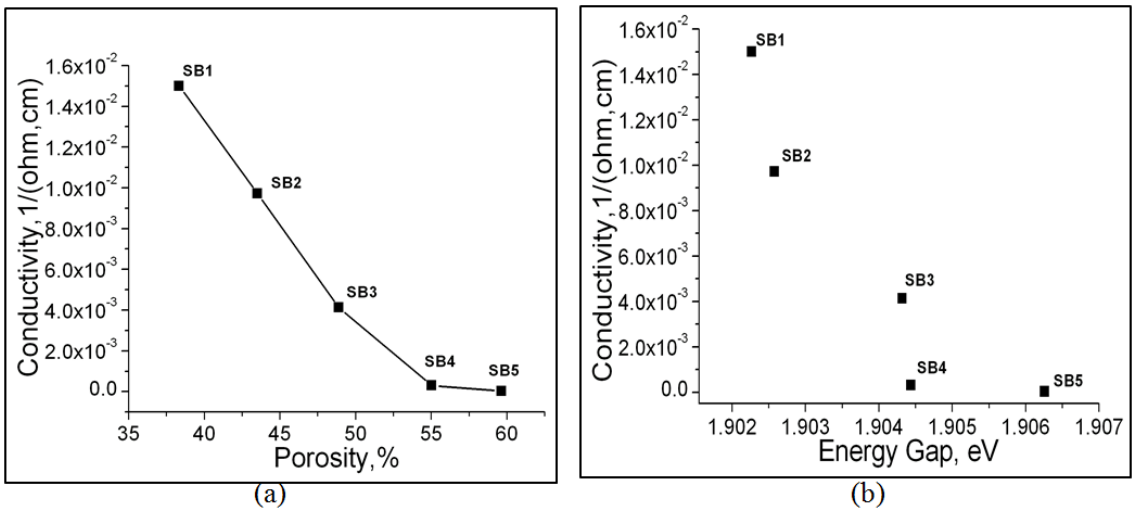


Figure 7: Relationship between Conductivity with (a) Porosity and (b) Energy gap

From the equation, it shows that the conductivity decreases when the energy gap increases. This is because the minimum energy required to excite an electron from valence band to the conduction band has increased causing less carrier available in the conduction band [25]. This effect can also be evidenced in the plot of conductivity versus energy gap in Figure 7(b), in which as the energy gap increases, the PS conductivity decreases from 0.015 $(\Omega.cm)^{-1}$ to 3.113×10^{-5} $(\Omega.cm)^{-1}$.

CONCLUSION

The PS has been successfully fabricated by chemical etching. The results show that the PL and the electrical conductivity has dependent on etching time and porosity. The porosity is in the range of (38-60) % and increases linearly with etching time. The surface morphology of PS shows that it has crystallites structure surrounded with pores on the surface. The PS able to illuminate orange-red luminescence because of the surface contained species of Si-O bonds as confirmed by EDX analysis. Blue shift effect towards higher energy was observed on PL peak and band gap, which is due to the confinement effect from the reduction of the crystallite size as etching time increases. The conductivity of PS decreases as the etching time, porosity and energy gap increases.

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