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Porous Silicon: Volume-Specific Surface Area Determination from AFM Measurement Data

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Abstract: Porous silicon layers manufactured by using (100), 1-5 ohm·cm p-type (boron doped) wafer by electrochemical etching in HF etanol solution. Photoluminescence (PL) spectra of anodically etched silicon obtained for different conditions studied and surface characteristics are investigated by AFM. This study gives a simple way to determine specific surface are of porous silicon which plays a major role with porosity for explaining the blue shift in photoluminescence peak. Properties such as specific surface area, pore size, and pore size distribution, the main surface properties of layer are investigated from AFM data which are important material characteristics in many processing applications. The "specific surface area" ($S_{specific}$) generally defined as the area of solid surface per unit mass of material, solid volume or cross section area. From 3-D reconstructions of AFM data, the surface area and the volume of the porous layer can be estimated directly and volume-surface specific area is calculated. For porous silicon this feature can be defined as the total surface area per volume and given by the unit m^2/cm^3. The method is simple not need to construct a special set up for measurement and non destructive.

Key words: Specific surface area, porous silicon, porosity, photoluminescence, AFM.

1. Introduction

Most common and easiest method of manufacturing porous silicon is electrochemical anodization. The foundation of porous silicon (PS) was first discovered in 1956 by Uhlir during silicon electropolishing experiments on silicon (Si) wafer by using hydrofluoric acid (HF) as an electrolyte while trying to etch the silicon. Under approriate electrochemical conditions (current, HF concentration, dopant concentration, etc.), it was observed that the silicon is not peeled of layer by layer, it prefered to form pores on it growing in the direction of the substrate [1, 2]. Porous Si opens up exciting possibilities for creating optical devices in silicon and integrating electrical and optical devices with Si-based circuits due to their physical properties depending on anodization conditions. In order to determine the physical properties of porous silicon, the most common parameters such as shape of pores, diameter of pores, porosity, and the thickness of the formed porous layer needed to be specified.

The relation between specific surface area and porosity have great importance to define luminescent features of porous silicon where specific surface area calculated by Brunauer, Emmett and Teller (BET) analysis which is based on an absorbate gas, as the equation given below;

$$\frac{1}{W((\frac{p_0}{p})-1)}=\frac{1}{W_m C}+\frac{C-1}{W_m C}(\frac{p}{p_0}) \qquad (1)$$

here, W, weight of the absorbed gas; p/p_0, relative pressure; W_m, weight of the absorbate gas monolayer; C, BET constant.

Gas adsorbtion method is a method that gives a detailed information about the surface morphology and

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physical properities which helps to define the surface characteristics at atomic levels. The method which needs a special set up construction is based on physical adsorbtion of the gas by the layer and amount of absorbed gas is used to calculate specific surface area and the porosity.

It is known that porosity plays a major role of defining the luminescence mechanism for porous silicon. Porosity determined from the volume of the adsorbed gas and concluded that specific surface area decreases as the porosity increases [3, 4]. It is stated as porosity increases, energy band gap increases and blue shift occurres in PL spectrum [5-7].

Different to the gas adsorption method, volume-specific surface area of nanomaterials are determined by transmission electron tomography [8], they used 3-D views of tomography to calculate the volume and area of nanoparticles.

In this study, we report the change in porosity due to the etching time which causes shift in PL peak wavelengths [9-12]. We used the AFM 3-D measurements in order to calculate porosity and specific surface area that can be easily applied and also a non destructive method to derive the relationship. The specific surface area, porosity affecting luminescent properties (PL) of porous silicon included in the study.

2. Experiments

Porous silicon layers were prepared by using electrochemical anodization. The electrochemical anodization is performed at room temperature and ambient light on silicon wafers of one side polished, p-type, boron doped, (100) oriented with 1-5 ohm·cm resistivity and 381 ± 20 μm thickness. The electrolyte solution consist of 1:2 HF:Etanol from 48% HF wt. and 98% wt. ethanol. A classical teflon anodization cell is used as given in the following Fig. 1.

A Pt mesh is used as cathode during the anodization. To provide and quarantee the homogenity of the porous layer, magnetic stirring [11] is used.

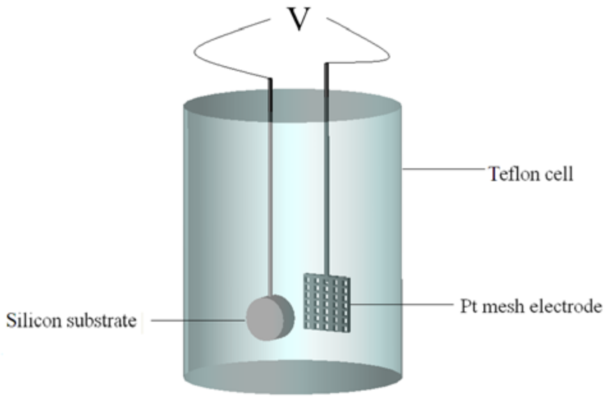

Fig. 1 Schematics of etching cell.

Etching times and anodization current were 20; 30 and 40 min and 11 mA/cm^2, respectively. After the anodization, the samples were rinsed in DI and 5 × 5 min DI water ultrasonic cleaning was done. Then the samples were dried by Argon.

3. Results and Discussion

Specific surface area in porous silicon is defined by the total surface area per volume with the unit m^2/cm^3. As Ref. [13], the volume of pores are calculated considering the pores as a cone and the volume of the pores were calculated from the AFM measurement of pore diameter and pore depth. Since the porosity can be calculated by gravimetric technique which needs to remove the porous layer from the wafer with KOH solution, destructs the sample and does not allow to use the samples for further studies.

With the assumption, the pore shapes are conic and number of pores within the etching area is “n”, the total area and the total volume of the pores are calculated in this section.

Total area of the empty space (pored surface) will be used for specific area calculation, which can be calculated as the sum of total pore area (A_{Tpore}) and the area of the electro polished depth ($A_{Telectropolish}$). Also the total volume will be defined as the sum of the total pore volume (V_{Tpore}) and electro polished volume ($V_{Telectropolish}$).

The etched surface area is a circle in the study with area “S” which has the radius of “r_a”. Since the etched surface area is known, the radius of the etched area is:

$$r_a = \sqrt{\frac{S}{\pi}} \tag{2}$$

Defining the parameters in Fig. 2;

d_1 = wafer thickness before anodization;

h = depth of pores;

d = thickness of the porous layer.

m_1, m_2, m_3 masses are written by using the measured radius of the pores (r), depth of the pores (h), number of the pores (n), area of the etched surface (S), silicon wafer density (ρ) and the thickness of the porous layer (d);

$$m_1 = \rho d_1 S \tag{3}$$

$$m_2 = d_1 S\rho - (d-h)S\rho - \frac{n}{3}\pi r^2 h\rho \tag{4}$$

$$m_3 = \rho d_1 S - \rho d S \tag{5}$$

The porosity equation from gravimetric measurement is:

$$P(\%) = \frac{m_1 - m_2}{m_1 - m_3} \tag{6}$$

The porosity can be calculated from Eq. (6) with the masses given in Eqs. (3)-(5):

$$P(\%) = \frac{(d-h)S + \frac{n}{3}\pi r^2 h}{dS} \tag{7}$$

In Fig. 2, electropolished part depth can be written as d – h. And the electropolished surface area is:

$$A_{Telectropolish} = (d-h)2\pi\sqrt{\frac{S}{\pi}} \tag{8}$$

and:

$$A_{Tpore} = n\pi r\sqrt{r^2 + h^2} \tag{9}$$

Area of the surface except pores:

$$A_{remaining} = S - n\pi r^2 \tag{10}$$

Related volumes which will be considered in specific surface area can be written as:

$$V_{Telectropolish} = (d-h)S \tag{11}$$

and:

$$V_{Tpore} = \frac{n}{3}\pi r^2 h \tag{12}$$

specific surface are can be written as given below ;

$$S_{spesific} = \frac{(d-h)2\pi\sqrt{\frac{S}{\pi}} + n\pi r\sqrt{r^2 + h^2} + S - n\pi r^2}{\frac{n}{3}\pi r^2 h + (d-h)S} \tag{13}$$

In order to determine the relation between specific surface area and porosity, denominator of Eq. (7) can be written in terms of specific surface area and the porosity and the specific surface area can be given as:

$$\%P = \frac{(d-h)\sqrt{4\pi S} + n\pi r\sqrt{r^2 + h^2} + S - n\pi r^2}{S_{spesifik} dS} \tag{14}$$

From the Eq. (14), it can be seen that with increasing porosity, specific surface area decreases.

Fig. 3 shows the AFM measurement data for the prepared samples and they are used to calculate porosity and specific surface area.

From the measurements of AFM (pore depth, layer thickness, pore radius, etc.) and by using the equations derived for porosity and specific surface area, porosity

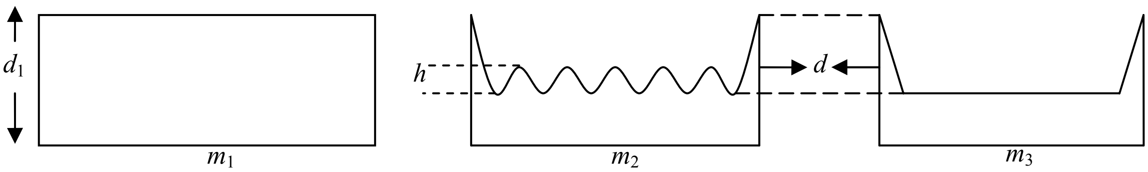

Fig. 2 Schematic view of masses m_1, m_2, m_3, before anodization, after anodization and the remove of porous surface with KOH.

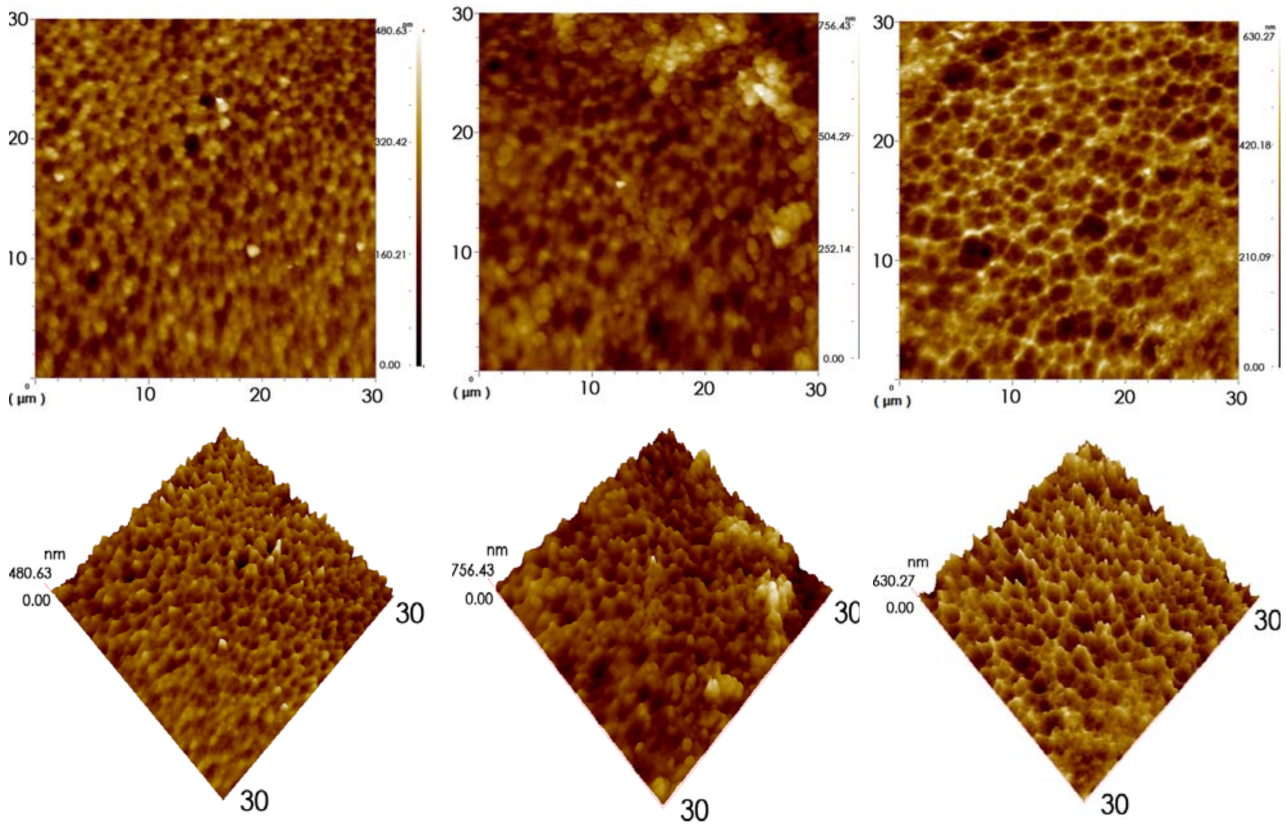

Fig. 3 2D and 3D (30 μm × 30 μm) porous silicon samples anodization times are 20, 30 and 40 min, respectively.

and specific surface area can be calculated and the relation is given below with the Fig. 4. It is obvious that the pore size increases with anodization time as seen from the AFM views. As the pore size increases the porosity increases depicted from Eq. (7).

The thickness increases with increasing anodization time which is given by "*d*" in Fig. 2 and it directly contributes to porosity and specific area calculations. The relation between porous layer thickness and the etching time is as given in Fig. 5.

Since the porous layer thickness increases with increasing anodization time as given in Fig. 5, the porosity calculated by using Eq. (7) increases and the variation of porosity with respect to anodization time is as given in Fig. 5.

In order to examine the blue shift in PL spectrum data PL measurements were taken by using the Jobin Yvon Florong-550 PL system with a 50-mW He-Cd laser (λ = 325 nm) as excitation light source at room temperature and the related results are given in Fig. 6.

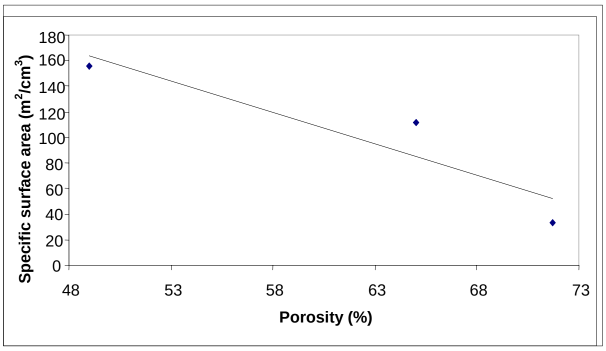

Fig. 4 specific surface area as a function of PS layer porosity.

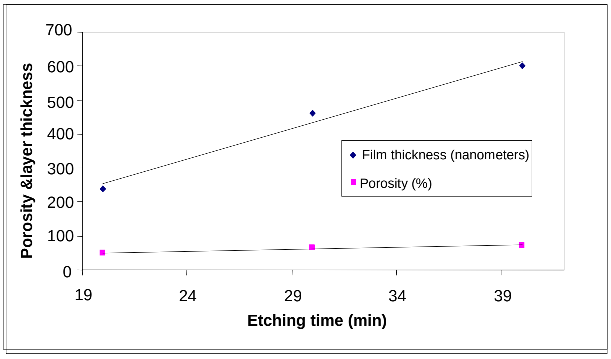

Fig. 5 thickness of porous layer and porosity with respect to anodization time.

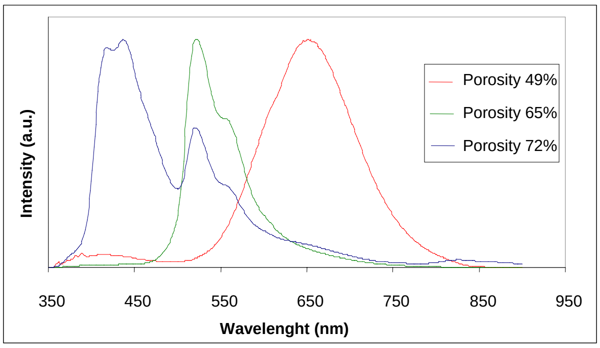

Fig. 6 PL peak shift with porosity.

In Fig. 6, as the porosity increases, energy band gap increases and blue shift occured in PL spectrum which is complient with many studies [5-7].

As etching time increases [9, 11], and due to prosity increase [5, 6, 12] blue shift in PL .Specific surface area decreases with increasing porosity [3, 4] as as concluded in many studies.

Porosity increase with decreasing specific surface area as derived in Eq. (14), which leads to blue shift in photoluminescence peak complient with the studies [5, 6, 14, 15].

4. Conclusions

Electrochemically prepared porous silicon samples pore related properties were examined by AFM which and the specific surface area calculated by modelling the pores using their depth and diameter from AFM data. The method is fine to determine the specific surface area and porosity relevance without use a special set-up.

From the equations derived in results and discussion part the porosity calculated and as the porosity increases, specific surface area decreases.

From the AFM measured data the pore diameter and layer thickness determined from the 3-D views and it is observed that the pore diameter and porous layer thickness increased due to increasing anodization time which results an increase in porosity.

For the porous samples manufactured obtained PL data show that due to the porosity increase photoluminescence peak wavelenght shifts to blue region.

Acknowledgments

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