Determination of free standing porous silicon energy gap by absorption coefficient

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Porous silicon (PS) nano crystals were made from p-type Si wafer by electrochemical anodization at etching times of 10, 20, 30, and 40 min. SEM images of samples from top and cross section showed that porous layer thickness and porosity increase with increasing etching time. PS layers were lifted off from Si wafer by mechanical method and put on glass lamel. Free standing structures are interesting because absorption spectra can be measured on the samples. Absorbance (ABS) of the samples were measured by spectrophotometer and showed it decreases with increasing etching time. Absorption coefficient calculated from absorbance by α=ABS/(dloge) relation, where d is PS layer thickness. Energy gap of the samples has been obtained from $(\alpha h v)^{1/2}$ and $(\alpha h v)^2$ curves versus $h v$ which they confirm that free standing porous silicon (FPS) has quasi-direct energy gap like porous silicon. Also extinction coefficient of the samples were calculated from α equation and showed that it decreases with increasing porosity.

1. Introduction

Silicon, being the investigated dominant material of electronics, has been investigated like no other material and its technology has been pushed to a very high level. Unfortunately silicon is an indirect semiconductor which means that is a poor light emitter. Electrons in the conduction band minimum ready for recombination with holes in the maximum valence band have to wait a long time in order to get the necessary momentum transfer. During its long life time in the conduction band the electron travels quite a distance through the crystal and scans it for non-radiative recombination centers. Typically before the event of a photon emission (phonon-assisted), a recombination path at surface or volume defect is followed and hence light emission is quenched quite efficiently-unless silicon is made porous. In 1990, Canham reported the discovery of significant light emission from porous silicon under UV illumination [1].

There have been different attempts to explain the light emission from PS. At the moment there are two promising models explaining the mechanisms involved in the luminescence process. One of them emphasizes the quantum confinement effect and the other suggests the essential participation of the localized surface states in the silicon nanostructures. Both approaches strongly depend on the geometry of the silicon skeleton created during the anodic dissolution process [2].

Porous silicon is a material which has been intensively investigated in respect of its potential applications in its various forms. It is used in powder form for applications including medical applications in the photography of cancer cells, in the thin layer form there are applications in optoelectronics as optical filters, in the form of layers it is used as linings in capacitors, and it is used as thin porous gas absorbing layers in gas detectors [3].

Many investigations of porous silicon have been done; although there are only a few works have investigated optical absorption spectra [4-5]. This is related to the fact that a porous silicon layer has energy gap bigger than the energy gap of silicon. In this case, it is difficult, or rather impossible, to obtain optical absorption spectra of porous silicon using the standard transmission method. However, there are other methods for calculation of porous silicon band gap such as; photoluminescence [6], ellipsometery [7], effective media approximation [8], and Kramers-Kronig [9]. Free standing porous silicon films are of great interest, because they offer the possibility to study PS properties using techniques which cannot be applied to the PS film on Si substrate. However, the fabrication of free-standing films of sufficient size is a delicate procedure, due to their poor mechanical strength. High porosity light-emitting material makes the task even more complicated. As a result, the number of publications devoted to PS separated from substrate is much less than that for PS layers on Si [3].

In this paper, absorbance of FPS samples is measured and then absorption coefficient (α) is obtained. Energy gap of samples is calculated from α versus $h v$ curve. Also

$(\alpha h v)^{1/2}$ and $(\alpha h v)^2$ curves versus hv are plotted and behavior of energy gap is studied through them. Results showed that free standing porous silicon samples have quasi-direct energy gap and confirmed quantum confinement model.

2. Experimental details

PS samples were made from p-type Si with (100) orientation and 600 $\Omega/\square$ sheet resistance. Ohmic back contact was produced by Al deposition under vacuum evaporation method followed by vacuum annealing process at 450 ˚C for 30 min. Then it covered with an acid-proof wax for protection. Anodization process took part at a Teflon cell. Electrolyte concentration of samples is HF(40%):C_2H_5OH with ratio of 1:1. Positive electrode is connected to Si with 1.5 x 1.5 cm^2 area and negative to a Pt plate with 4 cm^2 area. Current density is chosen 20mA/cm^2 with etching times of 10, 20, 30, and 40 min. Table 1 is shown characteristics of our samples.

Table 1. Characteristics of PS samples.

Sample	Current density (mA/cm^2)	Etching time (min)	Porosity (%)	Thickness layer (μm)
PS1	20	10	7	4
PS2	20	20	12	7.5
PS3	20	30	18	14
PS4	20	40	25	18

SEM images of the sample from cross section are shown in Fig. 1. Porosity and thickness of the samples are obtained from SEM images (Table 1). The measurements have done by a computer program called microstructure measurement.exe applied to SEM cross section view images. The computer program has ability to measure sample thickness and porosity by using SEM cross section view images. The figure shows that porosity and thickness of the sample increase with increasing etching time which are agreed with previous results [10]. According to our previous paper [11], the porosity of samples after removing the PS layer is slightly higher than before.
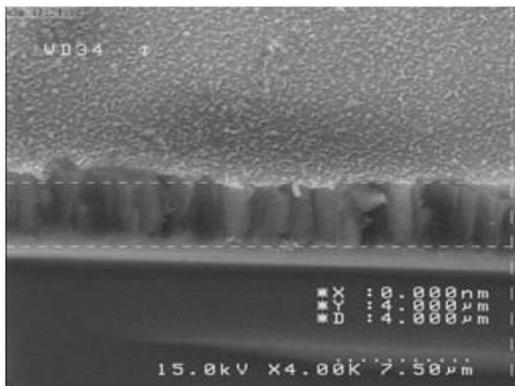
PS1
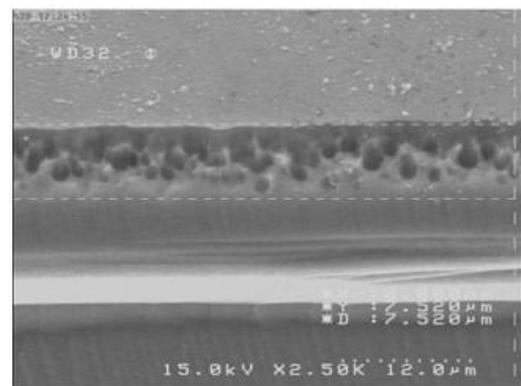
PS2
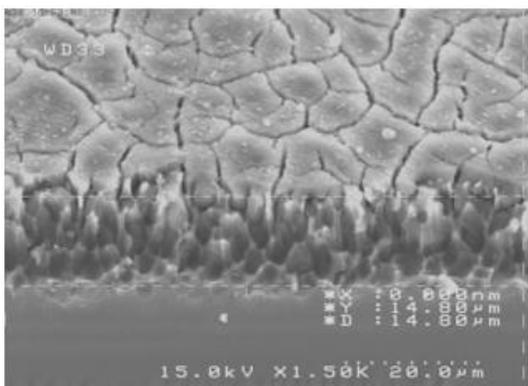
PS3
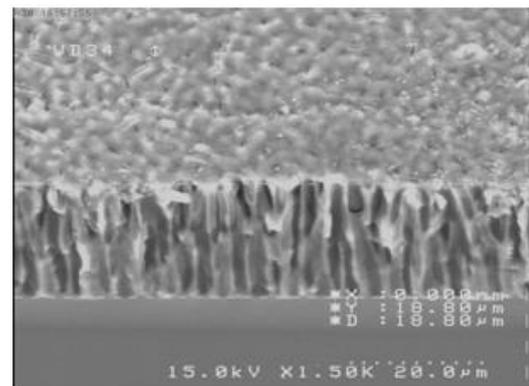
PS4

Fig. 1. SEM images from cross section view of PS samples.

PS layer were removed by mechanical method [1] and placed in a glass substrate. Take care have been made to avoid any damage to porous media during the lift-off step. Since FPS are fragile, therefore sticky band put carefully on the samples. Absorbance (ABS) of sample is measured by a Spectrophotometer Ocean Optics; HR4000CG-NIR model. In all measurements, the absorbance of glass has been illuminated from total result of glass/PS. The absorbance (also called optical density) of a material is a logarithmic ratio of the radiation falling upon a material, to the radiation transmitted through a

material. For majority of samples, absorbance has linear relation with sample concentration. Spectrophotometer calculates absorbance of FPS samples by following equation:

$$ABS = - \log_{10} (S_\lambda - D_\lambda)/(R_\lambda - D_\lambda) \qquad (1)$$

where S_λ is transmission light from sample, D_λ is dark reference, and R_λ is light reference at wavelength of λ. Fig. 2 shows absorbance of the samples versus wavelength. The figure shows absorbance of the samples decrease with increasing porosity due to reduction of PS concentration. Also Fig. 2 shows that absorbance peak is gradually moving to blue shift with increasing porosity.
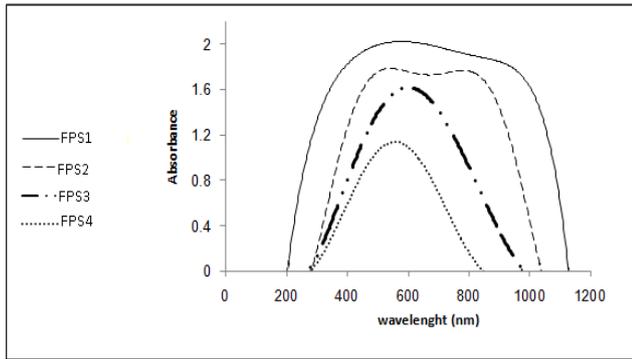
Fig. 2. Absorbance of FPS samples versus wavelength.

Absorption coefficient (α) is a quantity that characterizes how easily a material or medium can be penetrated by a beam of light, sound, particles, or other energy or matter. α is calculated from following relations [12]:

$$I = I_0 10^{-ABS} \rightarrow ABS = \log_{10} (I_0/I) \qquad (2)$$

where I_0 is incident light intensity and I is transmission light intensity.

$$I = I_0 e^{-\alpha d} \rightarrow \alpha = ABS/(d \log e) \qquad (3)$$

where d is sample thickness. The thickness of each sample is taken 0.1 mm by scratching a few the same samples. Fig. 3 shows α versus energy curve for the samples. The figure shows that absorption edge shifts to higher energy with increasing porosity. This is a blue shift and has good agreement with quantum confinement model [13]. Energy gap of the samples can be calculated from following equation [14]:

$$\alpha h v = A(h v - E_g)^m \qquad (4)$$
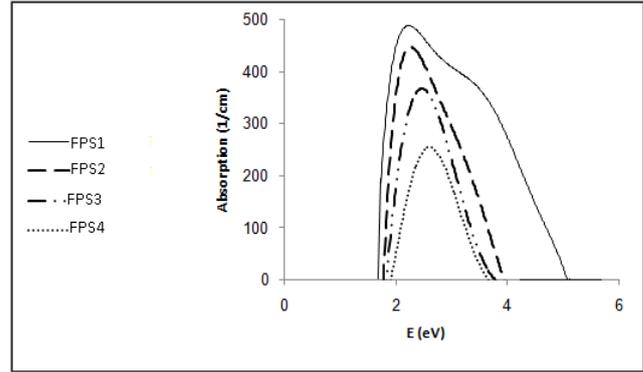
Fig. 3. Absorption coefficient of FPS samples.

where A is the edge width parameter representing the film quality, E_g is optical energy gap of material, hv is photon energy, and m determines the type of transition. When m is 1/2, E_g is direct transition and when m is 2, E_g is indirect transition. E_g is determined from extrapolating the straight line portion of this plot to the energy axis. Figs. 4 and 5 show $(\alpha h v)^{1/2}$ and $(\alpha h v)^2$ curves versus energy where can be used for calculation of energy gap for indirect and direct transitions at different porosities, respectively.

The Figures show the dependency of energy gap to porosity in terms of direct and indirect transitions for FPS samples. The figures show energy gap of FPS samples increases with increasing porosity. The dependency shows a good agreement with quantum confinement model [15]. Also, blue shift clearly has seen for both transitions. The blue shift in absorption coefficient has been claimed as a consequence of exiton confinement with increasing porosity and decreasing partial size in Si which is so-called quantum size effect.
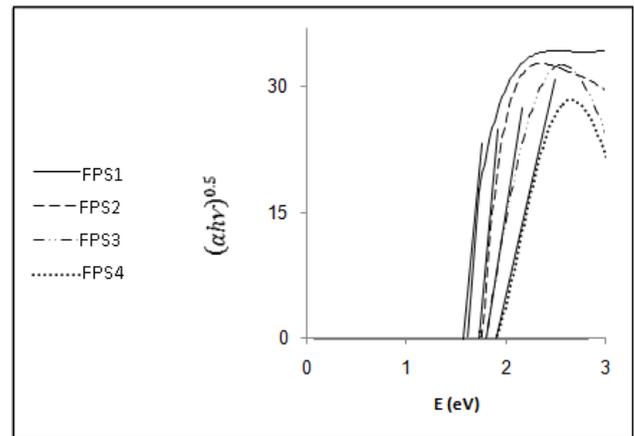
Fig. 4. Energy gap calculation of samples with different porosities for indirect transition.
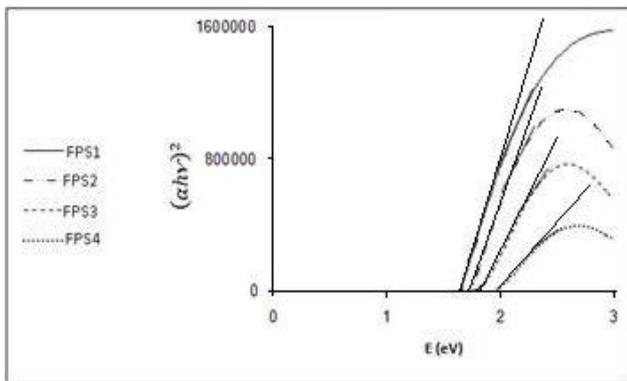
Fig. 5. Energy gap calculation of samples with different porosities for direct transition.

The aim of this work is to show that energy gap of free standing porous silicon is quasi-direct transition like porous silicon [13]. Fig. 4 shows that for indirect transition, energy gap increases from 1.5 eV to 1.9 eV with increasing porosity from 7% to 25%. On the other hand, figure 5 shows that for direct transition, energy gap increases from 1.67 eV to 1.95 eV with increasing porosity from 7% to 25%. A small enhancement of energy gap is seen for direct transition with increasing porosity which has good agreement with others experimental results [16-17]. However, this does not by any means prove that the material is direct gap. In a direct gap semiconductor, the luminescent decay time is typically not more than a few nanoseconds. In porous silicon, however, this life time can be several tens of microseconds, which raises the possibility that this is an indirect transition [18]. Also from figs. 4 and 5, we can realize that the difference between the minimum position of the conduction band and that of the maximum position of the valence band is not large, i. e. the energy band structures of the wires along the wire direction are approximately those of a direct-gap-like semiconductor. Therefore, we can consider the transition of FPS as a quasi-direct transition.

It is generally accepted that the blue shift of the absorption curves with increasing porosity or decreasing the size of the nanometer silicon particle is due to the quantum size effect. According to the quantum confinement effect, the energy gap associated with each crystallite should increase with the decrease in the size of the nanometer silicon particles, and thus absorption curve should be blue shifted.

In our experiments, we have three distinct evidences which confirm that our samples show blue shift with increasing porosity. Firstly, fig. 3 shows that absorption coefficient peaks is moving to blue shift with increasing porosity. Secondly, figure 3 also shows that absorption edge is moving to blue shift with increasing porosity. Thirdly, fig. 5 shows that Eg of the samples is moving to blue shift with increasing porosity.

We propose an explanation as follows: the energy gap only associated with crystallite sizes. Our results confirm that free standing porous silicon has similar quasi-direct transition like porous silicon. It shows that the size of the nanometer silicon particles has major role for the energy gap and no matter it is on Si substrate or in any other substrate. Only the important issue is to lift off carefully from Si wafer without any damage to nanometer silicon particles during the lift-off step.

When light passes through a medium, some part of it will always be absorbed. This can be conveniently taken into account by defining a complex index of refraction (N = n + ik). Here, the real part of the refractive index indicates the phase speed, while the imaginary part indicates the amount of absorption loss when the electromagnetic wave propagates through the material .k is often called the extinction coefficient. That k corresponds to absorption can be seen by inserting this refractive index into the expression for electric field of a plane electromagnetic wave traveling in the z-direction (Eq. 5) [17].

We have measured extinction coefficient by following equation [12]:

$$K = \alpha\hbar c/(2E) \tag{5}$$

Fig. 6 shows extinction coefficient versus E curve for our samples. The figure shows extinction coefficient decreases with increasing porosity which is in agreement with Ref. 19.
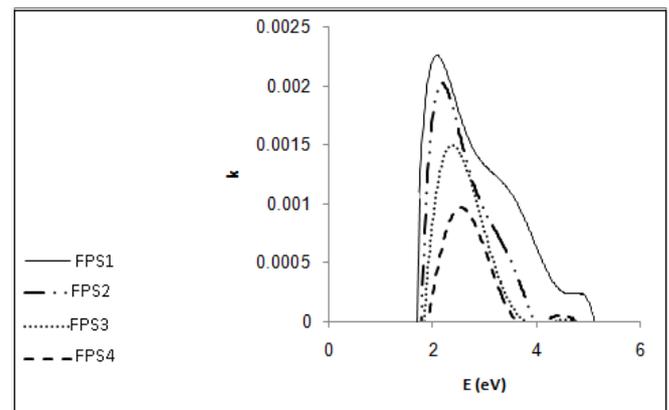
Fig. 6. Extinction coefficient of FPS samples.

3. Conclusion

Porosity and thickness of PS sample increase with increasing porosity. Absorbance and absorption coefficient of samples decrease with increasing porosity. Absorption edge has a blue shift with increasing porosity that is in good agreement with quantum confinement. E_g of FPS samples increase with increasing porosity and has a quasi-direct transition. Extinction coefficient reduces with increasing porosity.

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