

Correlation between porosity of porous silicon and optoelectronic properties

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We calculate the optical constants and absorption coefficient of n-doped porous silicon (PS), by using Effective media approximation (EMA) analysis. Refractive index, n , decreases with increasing porosity in visible region. However, absorption coefficient, α , increases with increasing porosity in this region. Also energy band gap of PS has been determined using absorption spectra. Our results show that band gap of PS is quasidirect.

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1. Introduction

Porous silicon was discovered in the 1950's by electro polishing silicon in dilute hydrofluoric solutions. This material was found to consist of a network of pores. Porous Silicon was reported to have a visible photoluminescence in 1984, but another six years would pass before this important property was pointed out [1] Quantum confinement model have been used to explain the properties of PS, but some evidence suggest that the luminescence properties of PS may not simply be due to quantum confinement effects[2]. The effects of the pore morphology on the optical properties are not well understood. Extensive experimental studies indicate that the observed optical properties depend not only on the porosity but also on the way the PS sample is prepared.

One of the successful models in the calculation of the electronic structure of PS is effective medium approximation (EMA). This model provides a better description of the energy-level structure of PS and is able to incorporate the interconnectivity of the systems.

In this paper we apply EMA analysis to calculate the optical properties of PS. For the EMA analysis a FORTRAN program has been written. Also, we study behaviour energy gap of PS using absorption spectra to show that band-gap has blue shift.

2. Effective media approximation

There are many different methods that have been developed for the purpose of determining the optical constants of materials. One technique is effective medium approximation.

The effective medium approximation is a method of treating a macroscopically inhomogeneous medium, a medium in which quantities such as the conductivity σ , dielectric constant ϵ , and elastic modulus vary in space.

Many materials fall into this broad category. An example is a metal-dielectric composite, consisting of a collection of metallic and dielectric grains arranged in some ordered in random fashion. Another example is a porous rock. If this rock is filled with salt water, then it is a composite of an electrical insulator (the rock matrix) and an electrical conductor (the salt water) [3]. Yet a third example is polycrystalline sample of an anisotropic material. Each grain in that polycrystal is, in essence, a different material, since it has a different conductivity or dielectric tensor [4]. We begin by describing the EMA in the simplest case, as envisioned by Landaur and Bruggeman [5]. A random mixture of two type of grains, which denote A and B, present in relative volume fractions f_v and $1 - f_v$, and characterized by different dielectric functions ϵ_A and ϵ_B . We desire to calculate the effective dielectric function ϵ_h of this composite. To accomplish this, we imagine that each grain, instead of being embedded in its actual random environment, is instead immersed in a homogeneous effective medium of dielectric function ϵ_h which will be determined self-consistently.

The equation of Bruggeman is [5]:

$$f_v \frac{\epsilon_A - \epsilon_h}{\epsilon_A + 2\epsilon_h} + (1 - f_v) \frac{\epsilon_B - \epsilon_h}{\epsilon_B + 2\epsilon_h} = 0 \quad (1)$$

In equation (1) if we take $\epsilon_A = 1$

(The air dielectric constant) and $\epsilon_B = \epsilon$, then we have

$$f_v \frac{1 - \epsilon_h}{1 + 2\epsilon_h} + (1 - f_v) \frac{\epsilon - \epsilon_h}{\epsilon + 2\epsilon_h} = 0 \quad (2)$$

here, ϵ is complex dielectric constant for bulk silicon and ϵ_h is complex dielectric constant for porous silicon and

f_v is the void volume fraction. By using equation (2), the real part of dielectric constant, ε_{1h} , and the imaginary part of dielectric constant, ε_{2h} , are obtained.

The real and imaginary parts of refractive index can be taken in terms of ε_h :

$$\varepsilon_{1h} = n^2 - k^2, \quad \varepsilon_{2h} = 2nk \quad (3)$$

The absorption coefficient, α , is defined as:

$$\alpha = \frac{2E}{hc}k \quad (4)$$

Consequently, the optical parameters of a material are determined from EMA analysis.

3. Experimental details

PS sample was prepared by n-type silicon wafer with (111) orientation doped concentration of 10^{15} cm^{-3} and $1.5 \Omega \text{ m}$ resistivity. An ohmic contact was obtained by evaporating a thin Al film onto the back side of sample. PS films were prepared by anodization a 40% HF-ethanol solution at a constant current density of 25 mA/cm^2 for (10-25) min and then air-dried.

Porosity of the PS samples was determined by a gravimetric method and [6]. The porosity of a porous medium describes the fraction of void space in the material, where the void may contain, for example, air or water. It is defined by the ratio:

$$\Phi = \frac{V_v}{V_T} \quad (5)$$

where V_v is the volume of void-space (such as fluids) and V_T is the total or bulk volume of material, including the solid and void components. The variation of porosity in samples with various anodization times is seen in table1:

Table1. Dependence of porous silicon porosity on anodization time

| | Current Density (mA/cm^2) | Anodization Time(min) | Porosity (%) |
|---|---|-----------------------|--------------|
| 1 | 25 | 10 | 36 |
| 2 | 25 | 20 | 57 |
| 3 | 25 | 25 | 72 |

By using calculated porosity, f_v was given, and with the value of f_v and by using equation (2), optical

properties were calculated that will be scribe in more details below.

Fig 1 shows typical scanning electron microscopy (SEM) images of PS samples with different porosity. It shows porosity increases with increasing anodization time.

4. Results and discussion

4.1 Optical properties

In this study, we calculated optical properties of PS by EMA. In this method, we should know the real and imaginary of dielectric constant of bulk silicon. The complex of dielectric constant porous silicon was calculated with equation (2), by using optical constant bulk silicon [7] and given f_v from experimental method. Index refraction and absorption coefficient were calculated by equations (3), (4); the results of calculation, will be explained in the following:

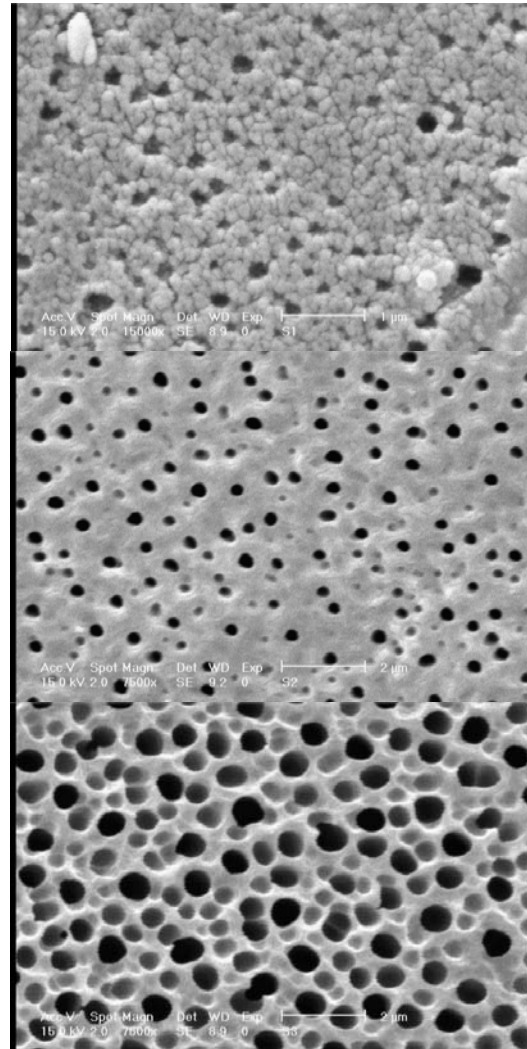


Fig. 1. The top view SEM images PS at different porosity (top) 36%, (mid) 57%, (bottom) 72%

For showing the excellent agreement between experimental optical data and EMA modeling, we show plot n, k versus photon energy (E) for experimental data bulk silicon [7] (solid lines) and the value of n, k were calculated by EMA (dashed line) in Fig 2 it shows that EMA modeling has good agreement with experimental data. Therefore our numerical solving has good accuracy.

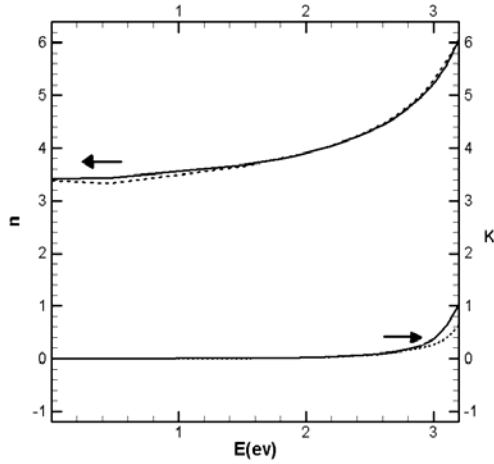


Fig. 2. Curve n, k versus photon energy (E) for experimental data bulk silicon [7] (solid lines) and the value of n, k were calculated by EMA (dashed line).

From Fig. 3, we see that the refractive index decreases with the increase of porosity. This may be attributed to the variation of the packing density. The film packing density [8,9]. The relation between refractive index n and packing density p can be illustrated by [10]:

$$n = pn_s + (1 - p)n_v$$

Where n_s and n_v are the refractive index of the solid part of the film and the voids, respectively. The packing density of films decreases with the increase of porosity. Therefore, we know that the refractive index of film decreases as packing density decreases or porosity increases, which has good agreement with others [11].

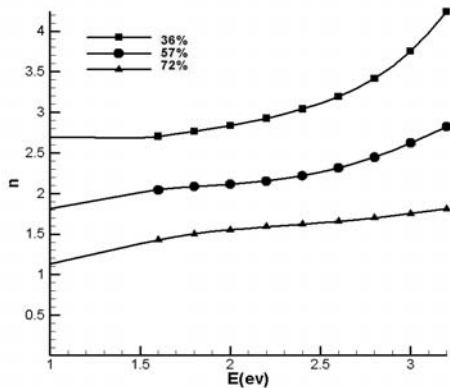


Fig. 3. Refractive index of PS samples for different porosity

Fig. 4 shows absorption coefficient curves of samples. We can see that the absorption edge will be shifted to a higher energy with increasing porosity in visible region. With increasing porosity, due to decreasing size silicon, the absorption edge appears blue shift, which this result confirm quantum confinement model.

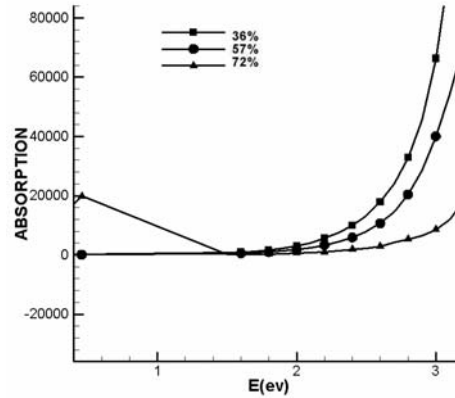


Fig. 4. Absorption coefficient of PS samples for different porosity. the left curve shows absorption coefficient in visible region.

4.2 Energy band gap of PS

The value of the absorption coefficient near the band edge provides key information about the films band structure. The energy gap E_g can be found from the well known relation [12-14]:

$$\alpha h\nu = A(h\nu - E_g)^m$$

Where A is the edge width parameter representing the film quality, E_g is optical energy gap of materials and m determines the type of transition. When $(\alpha h\nu)^{1/m} = 0$ for certain ν_0 , then $E_g = h\nu_0$. Parameter m has the value $1/2$ for the direct allowed transition and the value 2 for the indirect allowed transition. The usual method for the determination of the value of E_g involves a plotting of $(\alpha h\nu)^{1/m}$ versus $h\nu$. The value of the energy gap E_g is determined from the intercept of extrapolation to zero absorption with the photon energy axis.

The aim of my work is to show energy band gap porous silicon is quasi-direct, that it will be explain with more details in following:

Fig. 5(a) shows the plot $(\alpha h\nu)^{1/2}$ versus $h\nu$, which is used to calculate the energy band gap, considering an indirect allowed transition of PS for samples with different porosity. It is easy to observe that the indirect energy band

gap increases from 1.5 to 2 when porosity increases from 36% to 72%, Nevertheless when direct allowed transition for PS is taken into account, as shown in Fig 5(b) for a $(\alpha h\nu)^2$ versus $h\nu$, a smaller increase in the direct band gap value from 1.4 to 1.6 eV is found as the film porosity increases, which has good agreement with experimental results others [15-17]. These results confirm that PS, has a quasidirect band gap [18]. The obvious blue shift of the optical energy gap is seen in both figures.

The blue shift in absorption band edge has been claimed as a consequence of exciton confinement with increasing porosity and decreasing partial size in Si (the so-called quantum size effect)

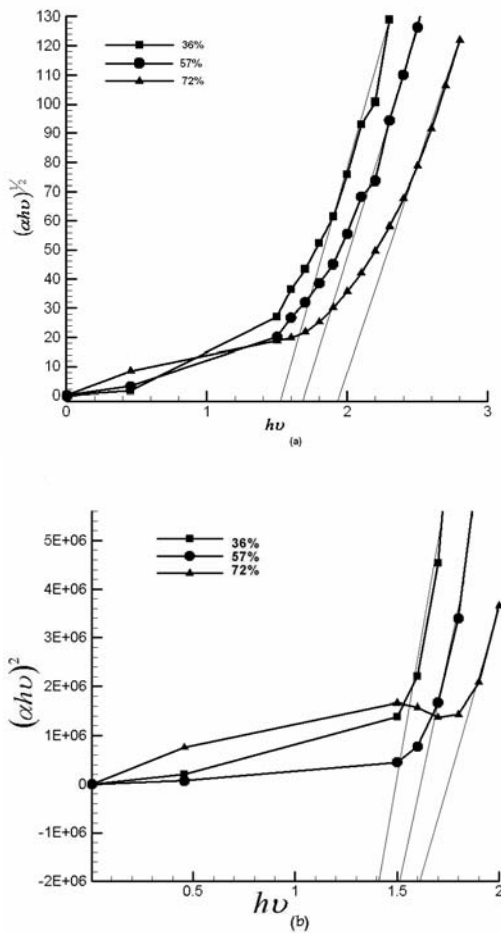


Fig. 5. Calculation of the energy band gap using (a) $(\alpha h\nu)^{1/2}$ versus $h\nu$ for indirect and (b) $(\alpha h\nu)^2$ versus $h\nu$ for direct allowed transition in PS samples with different porosity.

5. Conclusion

We have studied optical properties and energy band gap of porous silicon with the increase of porosity. Refractive index and absorption coefficient were determined by effective media approximation. Also energy band gap was measured using absorption spectra.

Our results showed that refractive index decreases with increasing porosity in visible region and edge absorption coefficient increases with the increase of porosity.

We found that the absorption edge of PS samples exhibits a blue shift with increasing porosity. Also we have observed that porous silicon has a quasidirect band gap.

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