Optical properties of porous silicon surface

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Abstract

The optical characteristics (transmission and reflection, absorption and scattering coefficients) of the Si nanowires obtained by electrochemical treatment of Si wafers were studied experimentally in spectral range 350-750 nm, using the different angles of incidence and measuring the angular distribution of the reflected (scattered) light. Theoretical treatment made on the basis of the Mie theory and some original modeling explains the characteristics determined and gives a simple method of estimation of refractive index of porous semiconductor layer created above the bulk specimen. The main conclusion is that the integrated light reflection from the P-Si surface is essentially smaller than the reflection from the bulk crystalline Si. Both theory and experiment show that the porous surface layer, although non-homogeneous and thus possessing the light scattering, acis as antireflection coating for Si and could be used, in particular, in solar cells made from Si as well as from the other semiconducting materials.

Keywords: Porous silicon, Optical properties, Reflection, Scattering

1. Introduction

Porous dielectrics or semiconductors were never considered as good optical materials, and for obvious reasons: their inhomogeneity creates the light scattering and therefore the dissipation of optical energy. In particular, the traditional antireflecting coatings for solar cells, as any other antireflecting layers, are optically homogeneous and made of materials with the refractive index lower than that of a cell semiconductor (see, for example, [1-3]). However, the development of science and technology of the nanostructured materials (i.e. materials with the structural details smaller than the light wavelength and thus characterized by the averaged optical constants), the new approach to the mentioned problem appeared [4,5] based on the use of nanostructured materials with the components having the different refractive indexes, which gives a possibility to tune an average index to the necessary value. This paper presents investigation of one of the types of nanostructural antireflecting layers—namely, the nanoporous one. The results obtained show that these layers, although exhibit some light scattering, could essentially reduce the reflection and therefore are promising to be used in solar cell engineering.

2. Samples and methods

The nanoporous (P-Si) layers on Si crystalline samples were prepared by electrochemical etching of (100) oriented p-type silicon wafers. The HF-ethanol solution was used (HF:H₂O:CH₃OH=1:1:2), anodization current density between 5 and 75 mA/cm² and the fixed etching time 10 min. An example of the surface structure of a sample thus obtained is shown in Fig. 1 (AFM image showing the details of quasi-pyramidal shape with the size of 20–60 nm). Depending on the etching current, the details of the surface relief varied in size: an average dimension increases from approximately 40 nm at 5–20 mA/cm² to about 300 nm at 50–75 mA/cm² (for the detailed description of experimental conditions, see [6-8]). The total thickness of the P-Si layer was around 0.5 μm.

Optical absorption and reflection spectral measurements were carried out in UV–VIS Lambda 2 Perkin-Elmer Spectrophotometer. The spectra of some samples were
The photoluminescence (PL) in the range 1.5-2.2 eV which is typical for porous Si (squares in Fig. 2). The same figure presents the PL excitation spectrum (circles). The detailed analysis of this latter spectrum (in particular, its dependence upon the etching time and sample ageing (see [7-9])) well agrees with the assumption about the optical generation of electrons of the upper valleys of the Si c-band, which structure in the samples studied is practically the same as in the bulk Si. The PL is excited by these hot electrons, the luminescent centres are situated either in the sample surface, or in oxide surface layer. These important points are beyond the scope of the present paper: what is essential here is the luminescent transformation of the photons energy from UV to visible region.

It is evident that the average refractive index in the porous layer varies gradually between the vacuum value of 1 at the outer surface to that of the bulk Si (3.94 at wavelength 600 nm [10]; see also Table 1), so it is natural to investigate the possibility of its use as an antireflecting coating on the bulk Si (on Si solar cell, in particular) with an additional advantage of the photon energy transformation from the higher to lower energy region, which makes the photons more suitable for the photovoltaic action in the solar cell (due to smaller thermalization losses and lower absorption coefficient, therefore the smaller surface recombination).

3. Results and discussion

The data of reflection measurements from the P-Si layer on c-Si surface made at normal light incidence are presented in Fig. 3. The upper spectrum (squares) refers to the specular reflection; the specular reflection for other angles of incidence is not much different, having the same order of magnitude (between 5 and 8%). It is necessary to remind that reflection of the visible light from pure c-Si surface is of
order of 35% due to large refractive index of the material (varies from 5.5 at 400 nm to 3.75 at 700 nm).

The lower curve on Fig. 3 (circles) is experimentally measured at detection angle 60° the scattered light intensity; its wavelength dependence approximately follows the $\lambda^{-4}$ law (triangles in Fig. 3) typical for the Kayleigh scattering which proves its nature. The scattered light intensity integrated over all scattering angles and averaged over the spectral region studied gives about 2% of the incident intensity, thus not adding much to the reflection losses shown by the upper curve.

Fig. 4 presents the angular dependence of reflected (scattered) light intensity obtained at angle of incidence 60°; correspondingly, the signal detected at angle 60° gives specular reflection in arbitrary units, whereas the rest of the points give the scattered light intensity (upper curve) is for the wavelength of 350 nm, and the lower curve—550 nm. In agreement with Fig. 3, the scattered light intensity quickly decreases with an increase of the wavelength.

The layer of porous Si (P-Si) could be modelled in its interaction with electromagnetic waves as a homogeneous film with its real thickness (of order of 500 nm), having the refractive index averaged over the layer thickness, for the following reasons: (a) electromagnetic wave penetrates the reflecting material by the length comparable with the wavelength which is about the same as the layer thickness and much larger than the transversal size of the surface details, (b) the classic reflection by Fresnel law is proportional to $(\Delta n)^2$ where $\Delta n$ is the difference in refractive indexes of the adjacent layers, so reflection between the different parts of the P-Si layer separated by small distance $dx$ will be proportional to $(dn)^2$, i.e., is negligibly small.

Thus, we consider the light reflection by P-Si layer with thickness $L$ and average refraction index $n^*$. Having from one side vacuum or air ($n = 1$), and from the other—c-Si ($n = n_o = 3.94$). We assume that the surface details in the P-Si layer (Fig. 1) has the optical properties of the bulk Si [6–9], so the dependence of $n(x)$ in the P-Si layer is determined by the geometry of these details (columns, wires, etc.).

To find the $n^*$, we use two approximations: (1) the thickness of the columnar details ($r$) increases linearly with the distance $x$ from the outer layer surface ($r = kL$), so $n^*$ will increase with $x$ by quadratic law (the conical surface details), and (2) $r$ is proportional to square root of $x$ ($r = k \times \sqrt{x}$), so $n^*$ should have a linear coordinate dependence (this case corresponds to parabolic shape of the surface details). In each case, the value of $n^*$ at a given distance from the surface is defined by a material layer between coordinates $x$ and $x + dx$, which contains a cylindrical cross-section of a P-Si columnar detail having area $\pi r^2$ surrounded by air with refractive index approximately 1 and area of $(D^2 - \pi r^2)$, where $D$ is an average distance between the surface details. Thus, the general $n(x)$ dependence has a form

$$n(x) = [n_o \pi r^2 + (D^2 - \pi r^2)]/D^2 = 1 + (n_o - 1)\pi r^2/D^2.$$  \tag{1}

Besides, we must take into account that at the Si—P-Si interface ($x = L$), the column diameter will be equal to the intercolumnar distance: $r(L) = D/2$.

On the basis of (1), we get for the two cases mentioned above:

(1) $r = kL$, $kL = D/2$, $k = D/2L$. Then $n(x) = 1 + (n_o - 1)\pi x^2/4L^2 = 1 + C x^2$. $C = (n_o - 1)\pi 4L^2$. The average refractive index

$$n^* = \left[ \frac{\int_0^L n(x)dx}{L} \right] = 1 + CL^2/3 = 1 + (n_o - 1)\pi L/12.$$  \tag{2}

(2) $r = k \times \sqrt{x}$, $k \times \sqrt{L} = D/2$. $n(x) = 1 + C^* x$. $C^* = (n_o - 1)\pi 4L$. The average refractive index

$$n^* = \left[ \frac{\int_0^L n(x)dx}{L} \right] = 1 + C \times L/2 = 1 + (n_o - 1)\pi L/8.$$  \tag{3}

It is seen that the average refractive index, in both approximations, does not depend upon the layer thickness.

Reflection coefficient at the outer layer surface is

$$R = \left( \frac{n^* - 1}{n^* + 1} \right)^2.$$  \tag{4}

Taking the value of $n_o$ for the wavelength of 600 nm given above, we get for the first case (Eq. (2)) the value of $n^* = 1.77$, and for the second case (3) $n^* = 2.15$, which gives for the reflection coefficient $R$ values of 7.7 and 13.40% correspondingly. These values roughly agree with the reflection coefficients experimentally observed; the observed
spectral dependence of the reflection could be, in first approximation, attributed to the spectral dependence of $n_e$.

To account for scattering and to give the more complete description of optical properties of the porous layer, we use the Mie theory (for the mathematical treatment, we follow the procedure described in [11]). In this theory, each scattering particle is characterized by the scattering and absorption coefficients $q$ and $q^*$ described with the following expressions:

$$q = \text{Re} \left( \frac{8}{3} \frac{m^2 - 1}{m^2 + 2} \right),$$

$$q^* = \text{Im} \left( \frac{8}{3} \frac{m^2 - 1}{m^2 + 2} + \frac{4}{15} \frac{m^2 - 1}{m^2 + 2} \right) \frac{m^4 + 27m^2 + 38}{2m^2 + 3}.$$

where $\text{Re}$ and $\text{Im}$ are the real and imaginary parts, respectively, $x = 2\pi aN/\lambda$, $a$ is a particle radius, $N$, is the host material refractive index, $\lambda$ is the wavelength, and $m = (N - iK)/N_p$, $i = (-1)^{1/2}$. Correspondingly, $N$ and $K$ are the real and imaginary parts of refractive index of the scattering particle material (Si, in our case). The theory was designed for round particles; we assume that the back scattering from the P-Si surface details could be, in first approximation, described by this approximation since the details shape is close to hemi-sphere (see Fig. 1, with an account that the horizontal and vertical scales are five times different), with the radius $a \approx 20$ nm. The values of $N$ and $K$ for Si were taken in [12]. $N$, in our case is 1.

The contribution of the coefficients $y$, $y^*$ into effective extinction coefficient $Q$ is given by expression $Q = 2\pi a^2 L(q + q^*)$, where $Z$ is the density of scattering particles, and $L$ is a sample thickness. It gives the corresponding effective absorption coefficient $\alpha = Q/L$. To estimate the value of $Z$ in our case, we take the total amount of the scattering surface details for surface area $S$ as $S/D^2$, and having divided by the volume $SL$, we get $Z = (D^2L)^{-1}$.

All the data used for calculation as well as the results obtained are given in Table 1. The last column gives the effective absorption coefficient which includes both absorption and scattering effects. For the values obtained, the total losses of the light beam after passing the layer with the thickness $L = 1$ $\mu$m will be around 1%. This estimation agrees with the experimental data on the scattering losses mentioned above.

4. Conclusions

Simple method of estimation of the optical parameters of porous semiconductor layer on the bulk material of the same kind is given. The results of calculation and measurements show that the classical approach to optical materials as highly homogeneous ones might be questioned on the basis of the achievements and ideas of the nanotechnology, which give opportunities to tailor the material up to the specific needs and applications.

References