Regarding the Optical Properties of Porous Layers Prepared on Si Substrates

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Abstract: The paper deals with the complex refractive index and photoluminescence in the IR-VIS light region of two sample types (i) black p-type silicon (BSi) produced by the surface structure chemical transfer method using Pt catalytic mesh, and (ii) porous p-type silicon prepared by standard electrochemical etching. We present, compare, and discuss the values of the IR-VIS complex refractive index obtained by calculation using the Kramers-Kronig transformation and the photoluminescence properties thereof. The results indicate that differences between the optical properties of the BSi and the porous Si are given by (a) the oxidation procedure of BSi, (b) the thickness of the formed black and porous Si layer, and by (c) the porosity of both layer types. We assume that the photoluminescence signal generated by oxidized BSi structures can be mainly related to the quantum confinement effect, while the photoluminescence of the porous p-type Si is caused by the optical activity of the SiOxHy compounds covering its surface region.

Key words: Black silicon, porous silicon, complex refractive index, photoluminescence.

1. Introduction

Black silicon structures are currently used in the development of new-type Si-based solar cells that do not have anti-reflection coatings. The anti-reflection properties of black silicon structures enable the formation of solar cells with conversion efficiencies of over 19% on large areas. Such efficiency of corresponding solar cells can be increased by the suitable passivation of defects created during the etching procedure. The oxidation of prepared black silicon structures is one of the most suitable passivation procedures. Si nano-crystallites covered by SiOxHy create one of the basic elements of BSi structures used for the development of corresponding high-efficiency solar cells.

The SSCT (surface-structure chemical transfer) method can produce a nano-crystalline Si black color layer on c-Si with a thickness range of ~50 nm to ~300 nm by the contact of c-Si immersed in HF + H2O2 solution with a catalytic Pt mesh. Formation and properties of porous Si structures are reviewed in Ref. [1]. The second type of porous Si structures was formed by the standard electrochemical manner in a solution of HF and methanol under the influence of the electric field between the Si sample (+) and Pt electrode (-).

Researchers at ISIR Osaka University have developed a fabrication method of low reflectivity Si surfaces in which a mold with catalytic Pt layer is contacted with Si-immersed H2O2 + HF solution. The
PL maximum of a black silicon layer prepared on polycrystalline Si wafer at room temperature had the position ~1.85 eV [2]. A similar method was also applied for the preparation of the BSi samples in this contribution. An additional alternative technological approach was developed in the same Japanese laboratories by M. Takahashi et al. [3].

In the contribution [4] we presented an analysis of the photoluminescence properties of as prepared thin (~100 nm thick) multicolor silicon structures.

In this paper we will present, discuss and compare values of the calculated complex refractive index and the photoluminescence properties of oxidized p-type BSi structures and porous p-type Si.

2. Experiment

2.1 Preparation of Samples, Measurements and Evaluation

The p-type (100) Si has been treated using Pt mash in the solution 15 wt% HF + 25 wt% H₂O₂, and produced with the help of Pt mash. After the formation of a black layer, the structures were dried and oxidized at ~900 °C. A set of the following three samples was prepared: (a) reference sample, (b) Si treated by etching solution for 20 seconds, and (c) Si treated by etching solution for 240 seconds.

The standard porous Si was prepared in an electrochemical manner using a solution of HF and MeOH. Electrical voltage (6-11 V) was applied between the Si sample (positive potential) and the Pt negative electrode localized in the solution outside the Si sample. A constant current of 30 mA-cm⁻² was maintained during the etching. The following two samples were prepared: (i) with etching time of 1 minute, and (ii) with etching time of 10 minutes.

For the calculation of the complex refractive index of structures, we used IR reflectivity measurements under the angle 30° and recorded by a Digilab Excalibur FTS 3000 MX spectrometer with the following FTIR spectroscopy software: Resolutions Pro 5.2.0, Agilent with Kramers-Kröning transformation. A PIKE Technologies Specular Reflectance Accessory was used at an angle of 30°. The diameter of the measured area was 10 mm, used resolution: 4 cm⁻¹, number of scans: 60.

Real and imaginary parts of the complex refractive index can be expressed from the following equations:

\[
n = \frac{1 - r^2}{1 + r^2 - 2r \cos \theta}
\]

\[
k = \frac{-2r \sin \theta}{1 + r^2 - 2r \cos \theta}
\]

where \(n\) and \(k\) are the real and imaginary parts of the refractive index \(\hat{n} = n - i \cdot k\), \(R = r^2\) is the experimentally-measured reflectance, and \(\theta\) is the phase difference between the incident and reflected waves. This can be calculated as Ref. [5]:

\[
\theta_c = 2 \frac{\omega_c}{\pi} \int_0^{\infty} \frac{\ln r(\omega) - \ln r(\omega_c)}{\omega^2 - \omega_c^2} d\omega
\]

where \(\theta_c\) is the quantity \(\theta\) for the given \(\omega_c\), \(\omega_c\) and \(\omega\) are the frequencies.

For the measurements of the photoluminescence properties of the BSi and porous Si structures, we used the same equipment as published in Ref. [4].

2.2 Experimental Results and Discussion

Fig. 1 illustrates the IR dispersion characteristics of the refractive index \(n\) of reference Si, and two oxidized BSi structures prepared with Pt catalytic mesh. We assume that in both records of oxidized BSi structures in the region 500-1,200 cm⁻¹, the increased absorbance of structures caused by Si-O and Si-OH bonds modifies the calculated values of refractive index \(n\).

Fig. 2 illustrates the corresponding IR dispersion characteristics of extinction coefficients \(k\) of all three samples presented in Fig. 1.

Fig. 3 shows the photoluminescence signal obtained from the oxidized BSi sample at room temperature and at 6 K.

Fig. 4 presents the photoluminescence signal measured on p-type porous Si structure at 40 K.
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Fig. 1  IR dispersion characteristics of refractive index $n$ of reference Si (ref) and two BSi structures (2, 3).

Fig. 2  IR dispersion characteristics of extinction coefficient $k$ of reference Si (ref) and two BSi structures (2, 3).

Fig. 3  Photoluminescence signal obtained from the oxidized BSi sample at room temperature and at 6 K.
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Fig. 4 Photoluminescence signal measured on p-type porous Si structure at 40 K.

Table 1 Positions of maxima of photoluminescence signals presented in Figs. 3 and 4.

<table>
<thead>
<tr>
<th>No.</th>
<th>BSi (eV) 6 K</th>
<th>BSi (eV) RT</th>
<th>Δ Energy BSi (eV)</th>
<th>Porous Si (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.86</td>
<td>1.57</td>
<td>0.29</td>
<td>1.53</td>
</tr>
<tr>
<td>2</td>
<td>2.09</td>
<td>1.71</td>
<td>0.38</td>
<td>1.67</td>
</tr>
<tr>
<td>3</td>
<td>2.24</td>
<td>1.88</td>
<td>0.36</td>
<td>-</td>
</tr>
</tbody>
</table>

Fig. 5 IR dispersion dependences of extinction coefficient $\kappa$ of p-type porous Si structures prepared with etching time: (a) 1 minute (3/2/1), (b) 10 minutes (3/2/4).

Table 1 shows the positions of maxima of photoluminescence signals presented in Figs. 3 and 4. They were determined by the fitting procedure.

Figs. 5 and 6 show the IR dispersion dependences of extinction coefficient $\kappa$ and refractive index $n$, respectively, of two porous p-type Si structures prepared with etching time: (i) 1 minute (3/2/1), (ii) 10 minutes (3/2/4).

The results indicate that small differences between the optical properties of thermally-oxidized BSi and standard p-type porous Si is given by the oxidation procedure of BSi, the thickness of the formed black and porous Si layer, and the porosity of both types of formed layers. The utilization of catalytic metal in BSi
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Fig. 6  IR dispersion dependences of refractive index \( n \) of p-type porous Si structures prepared with etching time: (a) 1 minute (3/2/1), (b) 10 minutes (3/2/4).

does not strongly influence the observed IR optical properties in comparison with standard porous Si. The optical properties of the reference Si (see Fig. 1) are influenced by the surface native oxide, and/or by the mechanically-damaged surface region of crystalline Si wafers. We assume that the photoluminescence of the BSi structures (Fig. 3) is related to the quantum confinement effect. A blue shift of the photoluminescence signal of standard porous Si (see Fig. 4, Table 1, and Ref. [6]) with decreasing temperature was not observed. We relate the generation of the photoluminescence signal of standard p-type Si to the \( \text{SiO}_x\text{H}_y \) compounds covering the structure after its formation and drying.

3. Conclusions

This contribution deals with the complex refractive index in the IR light region of two sample types (a) thermally-oxidized black p-type silicon (BSi) nano-crystalline specimens produced both by the surface structure chemical transfer method, and (b) standard porous p-type Si.

We present and compare (i) the values of the IR complex refractive index obtained by calculation using the Kramers-Kronig transformation, and (ii) their photoluminescence properties. Small differences were observed in the values of the complex refractive index between thermally oxidized BSi and standard p-type porous Si when they have similar porosity. On the other hand, the photoluminescence signal generated by oxidized BSi structures is related to the quantum confinement effect, while the photoluminescence of porous p-type Si is caused—most probably—by the \( \text{SiO}_x\text{H}_y \) compounds covering its surface region.

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