Temperature Dependence of Photoluminescence of Porous Silicon

Róbert Brunner¹, Emil Pincik¹, Michal Kučera², Pavel Vojtek³ and Zuzana Zábudlá³

1. Institute of Physics, SAS, Dubravska cesta 9, Bratislava 84511, Slovak Republic
2. Institute of Electrical Engineering SAS, Dubravska cesta 9, Bratislava 84104, Slovak Republic
3. Faculty of Mathematics, Physics, and Informatics of Comenius University, Mlynska dolina, F2, Bratislava 84228, Slovak Republic

Abstract: The photoluminescence (photoluminescence) spectra of PS (porous silicon) prepared via electrochemical etching are presented and analysed. The PL of samples was measured at various temperatures. The corresponding parameters of peaks (energy, intensity and FWHM) were calculated using a fitting procedure, where the PL spectrum was approximated by a set of Gaussian peaks. This model is based on the presumption that the emission of photons in the PL process represents independent events. The optimal number of peaks used in the model was estimated, where the residuum of the approximation was used as a criterion. The low thermal dependence of energies in the PL spectra (blue shift) indicates the strong influence of defects on the position of corresponding PL maxima. The observed increase of energies of peaks with temperature requires additional explanation.

Key words: porous silicon, Gaussian peaks, photoluminescence peak position.

1. Introduction

PS (porous silicon) based structures have promising applications in the electronics (LED, sensors, etc.) and power industry (new types of solar panels with antireflection coating—based on “black silicon”, fuel elements, etc.) sectors. Hence, the importance of investigating the parameters of PS structures increases accordingly. PL (photoluminescence) spectroscopy is a selective and extremely sensitive method of probing discrete electronic states in PS, while varying PL intensity with temperature can be used to characterize underlying electronic states.

In the quantum confinement model proposed by Canham [1], visible emissions originate from the electron-hole recombination between the discrete energy levels inside the quantum wells formed by the bulk silicon regions that are separated by nanoscale silicon particles (nanocrystallites). Si luminescence is often interpreted as resulting from the presence of Si nanostructures of scale size 1-2 nm. The theoretical calculations of luminescence spectra for Si₄ nanocluster (a planar rhombus) showing two major peaks at 530 nm and 650 nm (2.34 and 1.91 eV) are reported.

Wu et al. [2] investigated the fundamental bandgap of InN grown by molecular epitaxy, using transmission and PL spectra as a temperature function. The authors have ascertained that band edge absorption energy and its temperature dependence are controlled by doping level. The energy of the PL peak was affected by the emission from localized states, and was not suitable to determine band gap energy. The structural and luminescence characteristics of porous silicon produced by chemical etching were studied by Korsunskaya et al. [3]. It was shown that the luminescence band of porous silicon produced by chemical etching represents the superposition of two bands—one band was attributed to excitonic recombination in amorphous Si nanoclusters smaller than 3 nm; while the second band—prevalent at room temperature—corresponds to the recombination of charge carriers via defects in silicon oxide. Smirnov et
al. [4] elaborated a mathematical model to describe the temperature dependence of the PL spectrum of self-ordered arrays of quantum dots with regard to the electron-phonon interaction and different transfer processes in the quantum dot—wetting layer—barrier system. This model enables the effects of various mechanisms of excitation transfer in the PL spectra to be separated, and for the observed dependences of the spectra to the structural features of the quantum-dot array to be related. Yoo et al. [5] investigated the PL spectra of lightly boron-doped crystalline p-Si under 488 Ar ion laser excitation in the 22-290 K temperature range. The authors determined the parameters of PL peaks (height, position, peak area, FWHM). They found that the direction of peak position shifts with the sample temperature to be in good agreement with bandgap temperature dependence. All measured PL spectra were fitted using combinations of modified Gaussian function(s) and standard Gaussian function(s). Liu et al. [6] investigated the temperature dependence of PL spectra for green light emission from InGaN/GaN multiple wells—it was found that when the In component increases, the PL spectral bandwidth may anomalously decrease with increasing temperature. This reduction may be ascribed to the enhanced non-radiative recombination process, which may lower the light emission efficiency of localized luminescent centres with shallow localization energy in high-In-content InGaN quantum wells, and also cause reduced integrated PL intensity. Tynishtykbaev et al. [7] studied the PL spectra and light emitting centre of porous silicon. Samples were prepared under long anodic etching of p-Si in electrolyte with an internal current source, and the PL spectra were monitored at room temperature both pre- and post-annealing in air and vacuum. It was shown that this annealing had a significant effect on the intensity and content of the spectra.

The PS includes silicon NCs (nanocrystallites) in the form of nanowires on the surface layer of monocrystalline silicon with different phases of crystalline c-Si and amorphous a-Si, covered with oxides (SiO$_y$) and hydrides (SiH$_x$). The nature of PL light-emitting centres is yet to be fully established, hence various models are offered for its explanation [8]. One of the earliest and most widely-used models is the PL quantum model in which luminescence is determined by the recombination of NCs’ excitons. Another model suggests that the luminescence is related to hydride (Si-H$_x$) bonds on the nanocrystalline PS surface. A PL model is also related to the presence of defect centres in oxides (SiO$_y$) at the interface of NCs PS/SiO$_y$. The most widely-accepted model that seeks to explain the maximum intensity of PL at $\lambda_{\text{max}} = 640$ nm is associated with the defective levels of complexes hydrides and oxides on the surface of NCs (nanocrystallites), such as SiH$_x$ or SiO$_y$ ($x$, $y = 1-4$). Maximum PL intensity at $\lambda_{\text{max}} = 440$ nm is related to the radiative recombination of excitons in NCs PS [9].

In this paper, we present the results of photoluminescence experiments on PS at various temperatures. For the evaluation of PL spectra, we used a decomposition procedure based on the fitting of measured spectra by the set of Gaussian peaks. The number of peaks in a spectrum was determined using the residuum of the fit.

2. Experimental Part

In the first step of porous silicon preparation, wafers of P-type (thickness: 600-650 nm, resistance: 8-12 $\Omega$ cm) were cleaned in HF vapor for 30 s, rinsed in distilled water and subsequently in methanol, and air-dried. In the second step, the sample was etched in a 1:2 mixture ratio of HF and methanol for 5 min. A 50 mA current was applied during the process. The prepared sample was rinsed in distilled water and inserted into ethanol, and finally dried in a vacuum at ambient temperature.

PL measurements were performed on a homemade, liquid He cooled apparatus described in detail in Ref. [10]. Ar ion laser was used as the excitation light
source with light wavelength of 488 nm. Measurements were performed at temperatures of 30, 40, 70, 150, 200, and 250 K.

We consider the presence of fine structure produced by the etching process to be the dominant factor controlling PL in porous silicon. Due to the low temperatures applied during sample preparation, we presume that the role of SiOₓ complexes will be less important in this case because of their etching by HF solution. In our opinion, the dominant PL control mechanism is the quantum confinement in nanocrystalline-like structures on the sample surface. The PL spectra evaluation was performed by fitting individual peaks with Gaussian functions published for example in Ref. [10]—an approach that was most applicable for structures composed of relatively homogeneous domains (usually layers). Photon emission is seen as an individual event independent of other emission acts, and characterized by the specific spectral distribution of energy. This independence allows us to apply a central limit theorem, which leads directly to the Gaussian peak profile. If multiple PL processes occur in the sample (it contains different types of light-emitting centres), the spectrum may be composed of a set of Gaussians.

The parameters of peaks were calculated via the fitting of measured spectra by a set of Gaussian functions of proper parameters (energy, intensity and FWHM) and constant bias representing the noise component, where the difference between approximation and experimentally-measured spectrum, expressed as RMS (root-mean-square) value, was used as a merit function in the minimization process. The PL signal was pre-processed using the loess transformation, where the tricube weight function and smoothing parameter \( \alpha = 0.02 \) were applied in order to eliminate the noise component (since noise could lessen the accuracy of computed results and thus reduce the stability of computation). The main advantage of loess is that it is a non-parametrical method based on the local regression model. Hence in comparison with standard approaches that use global parametric fitting functions (e.g. polynomial is a frequent case), loess substantially reduces the increase of data set correlation.

Spectrum decomposition can be an ambiguous process due to the perturbation of measured experimental data and limited measurement precision. Another source of computational error is the instability of numeric procedure, which mathematically results from approximation (Gaussian) functions forming a non-orthogonal set. Approximation precision could be improved regardless of physical background if more peaks are included in the model. But for physical reasons, only a restricted “reasonable” number of peaks—corresponding to the processes taking place in the sample—should be used in such a way. To ascertain this optimal number, we utilized the dependence of approximation error expressed as residuum on the number of peaks involved in the computational model. This dependence contains a “knee”, which indicates that an increased number of peaks in the model does not approximate any further relevant peak in the PL spectrum [10].

3. Results and Discussion

Fig. 1 shows the normalized PL spectra measured at temperatures 30, 40, 70, 150, 200 and 250 K. The corresponding Table 1 shows calculated parameters of the peaks.

The spectra, as well as their deconvoluted Gaussian components, show only a small shift of both overall maximum and individual Gaussian peaks in relation to temperature—a fact explained as the effect of the high defect concentration caused by low-temperature chemical procedures used during sample preparation.

Energy corresponding to Gaussian components increases as temperature decreases. Mitra et al. [11] investigated the PL spectra of mechanically-pulverized electrochemically-etched silicon. This material, surface-treated using a RF (radio-frequency) microplasma system, showed a similar “controversial”
Fig. 1 PL spectra decomposition calculated for sample measured at different temperatures.
Temperature Dependence of Photoluminescence of Porous Silicon

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>No.</th>
<th>Energy (eV)</th>
<th>Intensity (A.U.)</th>
<th>FWHM (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>1</td>
<td>1.536</td>
<td>1.425e-6</td>
<td>0.273</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.646</td>
<td>8.022e-7</td>
<td>0.444</td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>1.534</td>
<td>1.607e-6</td>
<td>0.265</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.666</td>
<td>1.354e-6</td>
<td>0.366</td>
</tr>
<tr>
<td>70</td>
<td>1</td>
<td>1.509</td>
<td>1.519e-6</td>
<td>0.238</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.652</td>
<td>1.838e-6</td>
<td>0.348</td>
</tr>
<tr>
<td>150</td>
<td>1</td>
<td>1.549</td>
<td>2.855e-6</td>
<td>0.275</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.710</td>
<td>2.090e-6</td>
<td>0.398</td>
</tr>
<tr>
<td>200</td>
<td>1</td>
<td>1.580</td>
<td>5.867e-6</td>
<td>0.298</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.743</td>
<td>4.264e-6</td>
<td>0.402</td>
</tr>
<tr>
<td>250</td>
<td>1</td>
<td>1.546</td>
<td>1.782e-6</td>
<td>0.293</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>1.706</td>
<td>1.613e-6</td>
<td>0.390</td>
</tr>
</tbody>
</table>

Fig. 2 Positions of maxima of both peaks in the model. Straight lines show fits of linear approximation of peak position dependence on temperature.

The positions of both peaks’ maxima in our experiment are shown in Fig. 2. The straight lines show linear fits that demonstrate the dependence of peak position on temperature.

The presence of two Gaussian components (with corresponding two energies) is demonstrated in the presented PL spectra. There is a difference from our previous results [12], obtained by measurement at 300 K, where beside the energies 1.57 eV and 1.70 eV a third component 1.89 eV was observed. The main difference is that contrary to recent samples, samples in Ref. [12] were passivized by annealing after etching. Missing energy 1.89 eV corresponds to the surface states involved Si = O bonds on the small size (0.55 nm) Si quantum dot [13].

4. Conclusion

A porous silicon sample was investigated at temperatures of 30, 40, 70, 150, 200, and 250 K. Each PL spectrum was approximated by a set of Gaussian peaks. Two Gaussians were used as the optimal model.

A third peak at 1.8 eV that had been observed in our previous works [12] was not found in this case. This can be attributed to the absence of SiO₂ groups’ passivated defects, and their creation during the
thermal annealing passivation process. Observed peaks showed only a low dependence of energy on temperature, whereas energy increased along with temperature (blue shift). The low thermal dependence was explained as the consequence of high defect concentration in the porous Si structure.

Acknowledgments

This work was partly financially supported by the following agencies: APVV—project No. APVV-15-0152, and VEGA—projects No. 2/0076/15 and No. 1/0676/17.

The authors wish to thank Mrs. Silvia Bačová, Dr. Ján Greguš, and Mr. Peter Zitto for their valuable help preparing the samples.

References


