THE TEMPERATURE DEPENDENCE OF PHOTOLUMINESCENCE PEAKS OF POROUS SILICON STRUCTURES

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Abstract

We present the photoluminescence spectra of porous silicon (PS) prepared using electrochemical etching. Subsequently, the samples were measured using photoluminescence (PL) at various temperatures. The corresponding parameters of peaks (energy, intensity and width) were calculated. PL spectrum was approximated by utilizing a set of Gaussian peaks. This model is approved if individual acts of photon emission in the PL process are independent. Peak parameters were calculated using the fitting procedure. We estimate the optimal number of peaks included in the model using residuum of the approximation. 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 reciprocal character of observed dependence – peak energies increase with temperature – requires additional explanation.

1. Introduction

In the quantum confinement model proposed by Canham [1], visible emission originates from the electron-hole recombination between the discrete energy levels inside the quantum wells formed by bulk silicon regions 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 Si_4 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 the doping level. Energy of the PL peak was affected by the emission from localized states, and was not suitable for the determination of the 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, the second band – that prevailed 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 regarding the electron-phonon interaction and different transfer processes in the quantum dot – wetting layer – barrier system. This model enables the separation of the effects of various mechanisms of excitation transfer in the PL spectra, 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, full width at half maximum). They found the direction of peak position shift with 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 composition 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 centers with shallow localization energy in high-In-content InGaN quantum wells, and also cause reduced integrated PL intensity. Tynishtykbaev et al. studied the PL spectra and light emitting centra 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 nanocrystallites (NCs) 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 centers is still not fully established, hence various models are offered for its explanation [7]. 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 ($Si\text{-}H_x$) bonds on the nanocrystalline PS surface. A PL model is also related to the presence of defect centers in oxides (SiO_y) at the interface of NCs PS/SiO_y. The most widely accepted model that seeks to explain maximum intensity of PL at λ_{max} = 640 nm is associated with the defective levels of complexes hydrides and oxides on the surface of nanocrystallites (NCs), such as SiH_x or SiO_y (x, y = 1-4). Maximum PL intensity at λ_{max} = 440 nm related to the radiative recombination of excitons in NCs PS [8].

In this paper, we present the results of photoluminescence experiments on PS. 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 Ω 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 [9]. Ar ion laser was used as excitation light source, the light wavelength was 488 nm. Measurements were performed at temperatures 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 SiO_x 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 [9] – an approach that is 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 centers), 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 width – FWHM) and constant bias representing the noise component, where root-mean-square (RMS) value was used as a merit function in the minimization process. PL signal was pre-processed using the loess transformation, where tricube weight function and smoothing parameter $\alpha = 0.02$ were applied in order to eliminate the noise component. Noise could lessen the accuracy of computed results and thus reduce the stability of computation. The main advantage of loess is its 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 increased 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 on the number of peaks involved in the computational model. The residuum of approximation function was used to estimate this error.

3. Results and discussion

Figure 1 demonstrates the PL spectra decomposed into two Gaussian peaks. All measurements were performed for temperatures of 30, 40, 70, 150, 200 and 250 K. The corresponding tables show the parameters of peaks. Figure 2 shows the dependence of residuum of the approximation process for a different number of peaks at various temperatures: it clearly illustrates that a signal composed from two peaks is the optimal model.

The spectra 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. No passivation steps were applied in this case. In our opinion, the formation of silicon-oxygen bounds was suppressed in this way, and the PL is mainly controlled by quantum confinement effects. The presence of two Gaussian components (with corresponding two energies) only in the PL spectra is partly contrary to some of our previously unpublished results, in which a third energy was observed at 1.8 eV (a fact interpreted as a consequence of the applied technology and which will be subsequently studied in further detail). The positions of both peaks' maxima in the model are shown in Fig.3, whereby straight lines show linear approximation fits of peak position dependence on temperature. Tab.1. shows the coefficients of linear fit of the thermal dependence of peak positions.

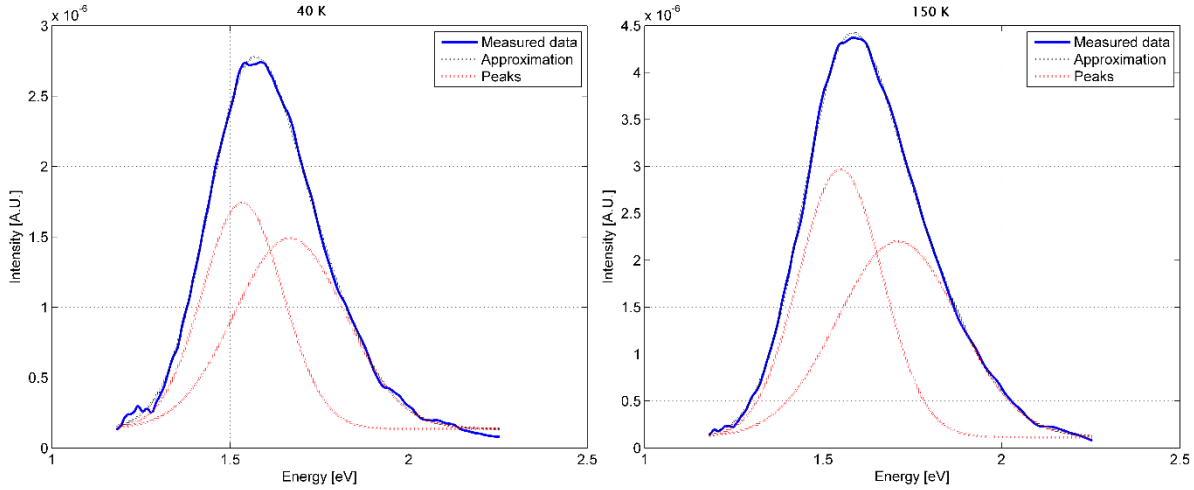

Fig. 1: *PL spectra decomposition calculated for sample measured at temperatures 40 K and 150 K, respectively.*

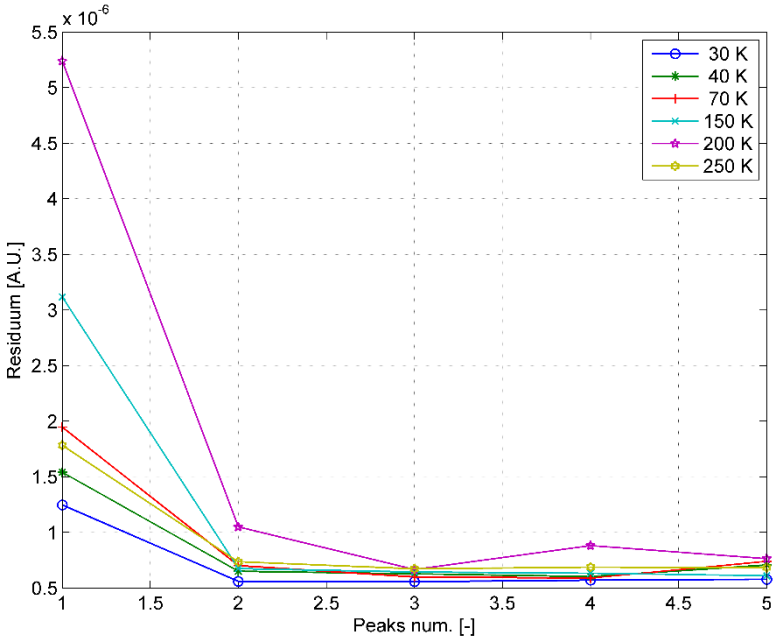

Fig. 2: *Residua of fits at various temperatures. The clearly-visible knee-point indicates that two peaks is the optimal number of peaks in the model.*

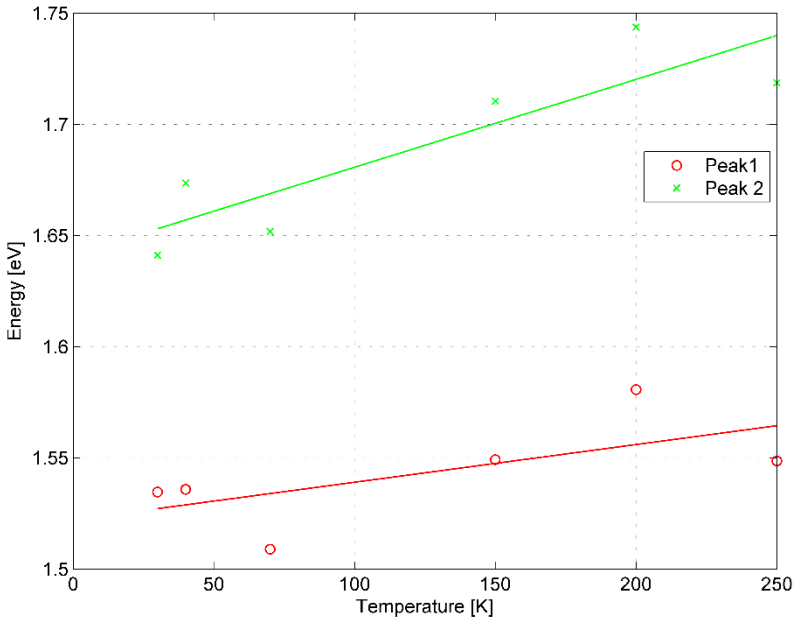

Fig. 3: *Positions of maxima of both peaks in the model. Straight lines show fits of linear approximation of peak position dependence on temperature.*

Tab. 1: *Coefficients of the linear fit of thermal dependence of peak positions.*

Peak # i	$k_{0,i}$ [eV]	$k_{1,i}$ [eV/K]
1	1.522	$1.69 \cdot 10^{-4}$
2	1.641	$3.95 \cdot 10^{-4}$

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 [10] was not found in this case. This can be attributed to the absence of SiO_x 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 porous Si structure.

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