OPTICAL PHENOMENA IN Si LOW-DIMENSIONAL STRUCTURES DEPENDENT ON MORPHOLOGY AND SILICON OXIDE COMPOSITION ON Si SURFACE

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Abstract.

It has been shown that intensive and broad “red” photoluminescence band in porous silicon is non-elementary one and could be decomposed on at least three elementary bands. Photoluminescence, ultra-soft X-ray emission spectroscopy, infrared absorption and Atomic Force Microscopy methods were used to study the reasons of both luminescence band appearance in porous silicon photoluminescence spectra, prepared at different electrochemical etching conditions. The mechanisms of radiative transition for both elementary bands have been discussed as well.

Keywords: Porous Silicon: PSi; Photoluminescence: PL; Atomic Force Microscopy: AFM; Ultra-soft X-ray emission spectroscopy: USXES; Infrared absorption: IR absorption.

1. Introduction

The intensive and broad “Red” (~600-800 nm) photoluminescence (PL) band in porous silicon (PSi) was discovered in 1990 [1]. Since this discovery numerous characterisation techniques have been used to elucidate the PL mechanism and more than 1000 articles were published concerning this effect during last 10 years. This band was explained either as related to the size distribution of quantum confined nanocrystals or as a result of emission of different types of radiative centres on Si wire surface, like: silicon clusters [2], polysilicon complexes [3], siloxene molecules [4] and defects in silicon oxide [5-8]. The mechanisms connected with the emission of excitons at the Si/SiO₂ interface [9] or some oxide related species on the Si wire surface have been suggested as well [10]. However the detailed physical mechanism of the red PSi luminescence still remains unknown.

Recent investigations have shown that red PL band is complex and can be decomposed on two or three elementary PL bands peaked at hv=1.50-1.70 eV, 1.70-1.90 eV and 1.90-2.10 eV [8]. The variation of maximum positions depends on PSi samples used. The relative intensities of elementary PL bands change with the variation of PSi preparation conditions [10,11], temperature of PL measurement [12], PL excitation light wavelength [8,13], as well as during aging processes in ambient air or in vacuum [10,13]. The shape of elementary bands is as a rule symmetric Gaussian type [8,14,15]. The last fact indicates that these PL bands connect with the radiative transitions between localised states. The vacuum storage research gave the evidence to assign the PL band hv=1.50-1.70 eV to emission of Si-Hₓ or hydroxyl-related species on Si crystallite surface, which can be disorbed in vacuum [8,13]. The nature of last two bands still under the discussion.

Furthermore, it has been proposed early [1] that only in PSi with a high level of porosity (70-80%) the strong PL could be expected. But there are many examples of high PL intensity in PSi with very low porosity, like 10% [16] or 22% [17]. Moreover it was discovered that in PSi only the upper surface layer is highly luminescent [18-20]. This suggests that combined investigations of the PSi surface morphology by AFM and PL peculiarities should be promising.
In this paper photoluminescence, infrared (IR) absorption, ultra-soft X-ray emission spectroscopy (USXES) and atomic force microscopy (AFM) researches were used to study the reasons of different luminescence bands appearance in red spectral range for PSi samples, prepared at different anodization conditions.

2. Experimental results

The PSi samples were prepared from p-type, B-doped, (100) oriented silicon wafers with 1.0-10.0 Ωcm resistivity. The porous layers were obtained by electrochemical etching in a solution: HF: H₂O: C₂H₅OH (1:1:2). Several groups of samples prepared at etching current density Iₐ= 25 mA/cm² and different etching times tₑ (from 1 up to 60 minutes) were investigated. As we have shown early [8], the thickness of PSi layers prepared at mentioned technological conditions is in the ranges 6-60 µm.

A Xenon-150 lamp with a grating monochromator MDR-23 or an Ar laser tuned at a wavelength 514.5 Å excites PL. PL was dispersed by an infrared spectrometer IKS-12 with photomultiplier FEU-62. Nano Scope III-a was used for AFM investigation in tapping and covered modes, respectively. Silicon and silicon nitride tips with a radius of curvature of 5 nm were used for this aim. Infrared absorption spectra were measured with IKS-29 spectrometer. Ultra-soft X-ray emission Si L₂,₃ spectra were obtained with X-ray spectrometer-monochromator RSM-500 under excitation by electron beam. The energies of electrons in the beam were of 1.5 and 3.0 keV. These values corresponding to the depths of the analysis equal 20 and 50 nm. The pressure in the X-ray tube while registering spectra was 3 x 10⁻⁶ Torr. Apparatus broadening was not more than 0.3 eV.

PL spectra measured at different excitation light wavelengths are shown in Fig.1.

The peak positions of the red band, excited by ultraviolet light, as a rule, are shifted to higher energies side 1.9-2.1 eV in comparison with the peak position of 1.70-1.85 eV of the PL band, excited by visible light. With the shortest ultraviolet light excitation (300 nm) the full width at half maximum (FWHM) of red band was not more than 320 meV (Fig.1, curve 1). When the excitation light wavelength is increased from 300 to 400 nm the red band spectrum changes mainly as a result of an increase of low energy part of luminescent band. At the same time the peak position shifts to 1.90 eV and a FWHM value increases to 440 meV (Fig.1, curves 2, 3). With a further increase of the excitation light wavelength (up to 450 nm) the PL peak position effectively does not change (Fig.1, curve 4), but it's FWHM decreases. Thus we can conclude that a new luminescence band appears with an increase of excitation light wavelengths. The late one is the reason of PL spectrum change mainly in the low-energy side. The peak position of new PL band is different for different PSi samples and lies in the 1.70-1.8-5 eV ranges. The FWHM of new low energy PL band lies in the ranges 290-300 meV (Fig.1, curve 5).

The PL spectra depend on electrochemical etching conditions at the creation of PSi. The intensity of red luminescence band increases and its peak position shifts to lower energy side (from 1.91 to 1.83 eV) for PSi samples created at the current density of Iₐ=25 mA/cm² and the different duration's from 1 to 10 min (Fig.2).

In last case the luminescence band mainly coincides with low-energy elementary PL band. For PSi samples, prepared at duration tₑ from 10 to 60 min the intensity of the red PL band decreases and the maximum shifts to high-energy side up to 2.0 eV. For last regime the PL band coincide with high-energy elementary PL band.
The AFM investigation has shown the nanometer scale low-dimensional substructure on PSi surface—w ith the wire diameter nearly 20-80 nm and the height equal 10-30 nm (Fig.4a) for PSi samples prepared at low etching duration (8 min). The low-energy PL elementary band 1.70-1.85 eV characterizes these samples.

With increase of etching duration at PSi creation from 10 to 60 min the surface morphology changes very much. As can be seen in the figure 4b, the low-dimensional nanoscale substructure (20-80 nm) practically does not exist. The size of residual Si between the pores approaches 100-200 nm or more. The low intensive high-energy PL band h\text{nm}= 1.90-2.10 eV characterizes this PSi.

In USXES experiment we have obtained Si L2,3 spectra, which represent the density of the occupied s(d) states of silicon in the valence band, according to the dipole approximation rules. Fig.5 represents Si L2,3 experimental spectra (point curves) of PSi prepared at low current density and different etching times.

Infrared absorption spectra of PSi layers are shown in the figure 3. As one can see mainly the bands connected with bending and deformation Si-H modes 600 - 680 cm\(^{-1}\) and 850 - 920 cm\(^{-1}\) were detected in spectrum of PSi layer, prepared at low duration (Fig.3, curve 1). At high duration the band connected with Si-O vibrations 1000 - 1200 cm\(^{-1}\) appeared additionally (Fig.3, curves 2).

In PSi only upper surface layer is high luminescent [18-20]. For understanding this phenomenon the comparative analysis of the PL spectra and PSi surface morphology has been done. AFM images of PSi layers fabricated at low current density and different duration's are shown in Fig.4.
In order to determine the phase composition of PSi layer we have obtained Si L\textsubscript{2,3} spectra of single crystal c-Si and some of its compounds (suboxide, dioxide and amorphous Si) presented in the figure 6. These materials prove to be the most probably phases under the etching of silicon.

3. Discussion of the experimental results

Thus the broad “Red” PL band (1.7-2.1 eV) in investigated PSi is non-elementary one and can be decomposed into at least two elementary bands. These bands are characterised by the peak positions at 1.70-1.85 eV and 1.9-2.1 eV, as well as a FWHM equal to 290-300 and 320 meV, respectively (in different samples).

The low-energy elementary band peaked at 1.70-1.85 eV was obtained in PSi with low-dimensional Si wire structure on the surface, characterized by the diameter 20-80nm. Thus, quantum confinement effect, which manifests themselves in nanoparticles below 5nm [1], is not expected in these samples. This elementary band intensity growth correlates with the increase of the roughness and the Si/SiO\textsubscript{x} interface area. Really, the surface of PSi layer is covered by silicon oxide [13,20,21]. In this case the adjustment of the luminescence band intensity can be connected with the increase of the Si/SiO\textsubscript{x} interface area and the interface-related radiative defect quantity. These centres could be, like no bridging oxygen hole centres (NBOHC), which are very well known in silicon suboxide, SiO\textsubscript{1.3} and amorphous Si (d).

In this case the corresponding PL band could be attributed to the radiative centres in the bulk of silicon oxide layers on the PSi surface.

For understanding the different spectral positions of these two bands it is necessary to analyse the USXES results. As can be seen in Fig.5 the spectrum of PSi has a smeared structure with slightly distinguished three peaks in the ranges of 89-92eV and 96eV. The intensity ration between these peak changes with PSi preparation conditions (Fig.5). The comparison has shown that pure Si characterised by clearly distinct peaks (Fig.6). This mean that there are a lot of amorphous and silicon compound phases in porous layer. The peak with a weak relative intensity in the range of 94-95 eV compared with the spectrum of pure Si corresponds to the formation of Si-O bonds (Fig.6). Meantime, a slightly distinct peak at 96eV is characteristic of low co-ordinated Si (with coordination number less than 4 [22,23]) in agreement with the model of formation of low-dimensional structures in this layer. Thus, one can conclude that the main phase components in the porous layer are crystalline silicon with an admixture of amorphous silicon and the silicon oxide phases. The lines on the Fig.5 and the data in table 1 demonstrate the numerical calculation results.

The Table 1 has shown that both samples have practically the same quantity of amorphous Si phase. But the quantity of silicon oxide compounds is different. The low-energy elementary PL band 1.70-1.85 eV characterises of PSi with silicon suboxide composition on PSi surface mainly and low quantity of silicon dioxide (Table 1, sample 4). The high-energy elementary PL band 1.9-2.1 eV characterises of PSi with silicon dioxide compound on the surface (Table 1, sample 5). Thus, presented results indicate that difference in spectral position of the elementary PL bands may be connected with the difference of Si oxide compositions on the PSi surface. The obtained results confirm the early conclusion, which was made at X-ray photoelectron emission (XPS) investigation of PSi with different PL spectra [7,24,25].

Finally it is necessary to discuss, why the silicon oxide composition on PSi surface is different for investigated PSi samples. The last fact, as one can be seen from IR absorption results, could be due to the difference in electrochemical etching conditions.

Table 1. Quantity of different phases in PSi, estimated by USXES method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Quantity c-Si</th>
<th>Quantity SiO\textsubscript{2}</th>
<th>Quantity SiO\textsubscript{1.3}</th>
<th>Quantity Amorph Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-a</td>
<td>35.8</td>
<td>2.0</td>
<td>2.8</td>
<td>45.4</td>
</tr>
<tr>
<td>4-b</td>
<td>38.7</td>
<td>1.0</td>
<td>6.8</td>
<td>32.5</td>
</tr>
<tr>
<td>5-c</td>
<td>35.8</td>
<td>26.0</td>
<td>0.0</td>
<td>38.3</td>
</tr>
<tr>
<td>5-d</td>
<td>43.8</td>
<td>13.4</td>
<td>0.0</td>
<td>45.2</td>
</tr>
</tbody>
</table>

Fig.6. USXES Si L\textsubscript{2,3} spectra of single crystal Si (a), SiO\textsubscript{2} (b), Si suboxide, SiO\textsubscript{1.3} and amorphous Si (d).
Another explanation, connected with the modification of the boundary conditions on nanocrystallite edge for the bulk wave functions, has also been suggested [26]. As result the electronic energy levels on PSi surface and, consequently, the oxidation conditions could change for samples with different size of nanocrystalline structure.

4. Conclusions

The explanation of the bright “red” PL of PSi by the radiative recombination via defect-related centers in silicon oxide on Si wire surface or at the Si/SiO$_2$ interface was proposed early in [5,6,20]. In the frame of this PL mechanism we supposed latter, that the spectral position of PL bands depends on silicon oxide composition on Si wire surface [21]. The first experimental confirmation of this assumption has been received at the XPS investigation of PSi samples with different PL bands [7,24,25]. In presented article this assumption is confirmed independently by IR-absorption and ultra-soft X-ray emission studies of the PSi with different spectral position of PL bands.

Moreover, presented AFM and USXES results have shown the composition of the silicon oxide on wire surfaces depends on Si wire size and technological conditions. Sub-oxide layer mainly is created at the Si/SiO$_x$ interface of small nano crystallites (20-80nm). The last fact could be interesting for future Si nano crystallite electronics applications and require special investigation.

Acknowledgments

This work was supported by CONACYT (Project 33427-U) and CGPI – IPN Mexico, as well as Ministry of Sciences and Education of Ukraine. All AFM results were obtained in UAM-Azacapotzalco, Mexico, in area of the Atomic and Molecular Applied Physics. M.M.R. thanks to CONACYT for the scholarship.

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