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VISIBLE LUMINESCENCE FROM POROUS SILICON*

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This paper presents results of investigation of the temperature dependence of visible luminescence in porous silicon layers prepared by anodization in hydrofluoric acid. Luminescence spectra were measured in the temperature range between 40 K and 350 K. Room temperature reflectivity spectra were also measured in vacuum ultraviolet radiation range from 4 eV to 12 eV.

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The visible photoluminescence (PL) at room temperature from electrochemically etched Si has attracted much attention as it opens up new possibilities for Si as a material for optoelectronic applications. The origin of this interesting and potentially important effect is not well understood [1-6].

We measured photoluminescence spectra of porous Si layers as a function of temperature between 30 K and 330 K [7]. The PL was excited with 366 nm light from high pressure mercury lamp (200 W). The PL signal was detected with Hamamatsu-375R photomultiplier. The porous silicon layers were prepared by electrochemical etching of the 15 μm thick *p*-type epitaxial layer ($\rho = 10 \Omega \text{ cm}$), deposited on low resistivity ($\rho = 0.01 \Omega \text{ cm}$) *p*⁺ boron doped (111) silicon substrate. The anodization was performed in the electrolyte containing hydrofluoric acid, water, and isopropyl alcohol. The HF concentration in the electrolyte was changed from 10% to 45% [7]. High reproducibility of the properties of the porous silicon layers was obtained due to good control of proper parameters of its technology. The thickness of the porous layer increases linearly with the time of anodization

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[7]. In general, PL spectra of measured samples consist of broad emission bands with maxima positioned in the energy range from 1.75 eV to 1.95 eV at room temperature (RT) and from 1.77 eV to 2.2 eV at $T = 40$ K. In some samples,

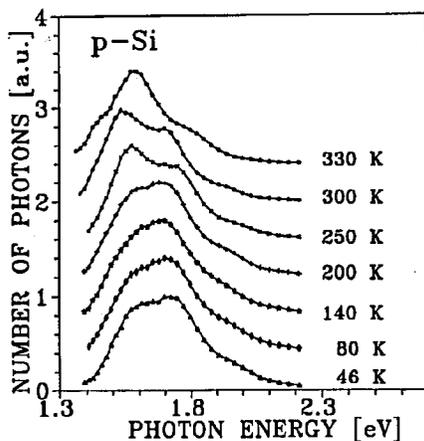


Fig. 1. Photoluminescence spectra of porous Si with porosity 66% measured at various temperatures. Excitation source — mercury lamp HBO-200, $\lambda_{\text{ex}} = 366$ nm.

however, the PL spectrum displays well resolved structure with three or four maxima (Fig. 1). Such spectra can be fitted as a sum of Gaussian components, whose positions and separations depend on the porosity of Si layer. One should mention here that the energetical positions of particular Gaussian components in PL spectra measured at different temperatures are almost independent of temperature. To explain these results we assumed model in which the multi-barrier structure is formed by Si crystal (quantum well) surrounded by Si crystallites (barrier region). The multicomponent structure of our PL spectra can be explained as originated from radiative recombination between discrete energy levels in quantum well [8]. When the size of crystallites is small (narrow quantum well), in high-energy part of luminescence spectrum only one broad band is observed. According to our model [8] in the case of narrow quantum well only one energy level, broadened due to the coupling is present. When the size of crystallites increases, the energy separation between levels in quantum well decreases and more than one narrower emission bands are observed, which can explain the multicomponent structure in the photoluminescence spectrum.

In many porous Si layers the intensity of luminescence (measured at the maximum of PL spectrum) of as prepared samples cooled in the dark under vacuum and then heated under illumination up to RT does not depend significantly on temperature. After annealing of the sample at 330 K in vacuum the intensity of PL continuously increases as the temperature decreases from 330 K to about 80 K and then starts to decrease when the sample is still cooled down up to 40 K (Fig. 2). After this process the sample becomes *stabilized* and the dependence of the intensity of PL on temperature is reproducible during cooling and heating

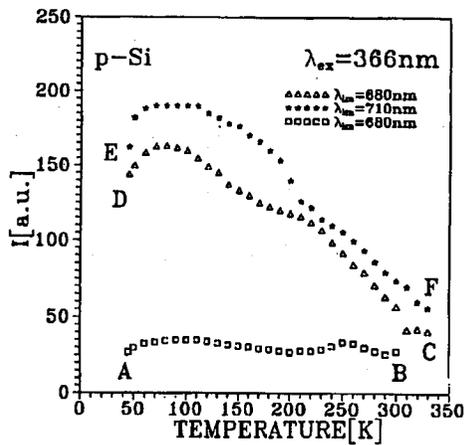


Fig. 2. The temperature dependence of photoluminescence intensity of porous silicon measured under different conditions: curve *AB* — during heating of the sample after cooling in the dark under vacuum, curve *CD* — while cooling after heating of the sample at 330 K under excitation light, and curve *EF* — during heating after measurements of curve *CD*.

cycles; PL is quenched when temperature increases with an activation energy of a few meV.

The temperature dependence of luminescence intensity was also measured as a function of the photon energy in the emission spectrum for samples which exhibit multicomponent structure in the photoluminescence spectrum. It was found that in the high-energy part of PL spectrum the intensity monotonically decreases as the temperature increases, but the low-energy part displays quite opposite behavior: the intensity of PL increases with the increase in temperature. The described dependence of the PL intensity on temperature can be understood considering presented above quantum confinement effects as the origin of the photoluminescence in the porous silicon. We would like to point out that the peak energy, peak intensity, as well as integrated intensity of the photoluminescence spectra for as prepared samples are likely to show different temperature dependence in different samples [9, 10].

The room temperature reflectivity spectra of porous Si were measured in the vacuum ultraviolet radiation range from 4 to 12 eV. The reflectivity spectra were measured for the set of wafers with gradually increasing thickness of the porous layer, starting from non-porous epitaxial layer. Because the thickness of the porous layer increases linearly with the time of anodization, the samples corresponding to the anodization time: shorter than 1 s, 1 s, 3 s, 6 s, 300 s, were measured. The spectra obtained for crystalline Si surface were markedly modified by the porous layer created on it. This effect was observed for thin porous layer (1 s) while for thick porous layer the structure of the crystalline Si disappears and it comes to be more complex. For thin porous layer the reflectivity spectra look like for crystalline

Si but with absorbed high-energy part of each reflectivity peak. We can assume that the electrons confinement effect in porous silicon skeleton leads to the increase in the distance between the bands [8]. It leads to the absorption of the incident and reflected photons corresponding to the crystalline silicon reflectivity peak. As the confinement leads to the increase in the distance between the bands, the absorption occurs on the high-energy side of the crystalline Si reflectivity peak. We can conclude that the appearance of the electrons confinement in the elements of the porous silicon skeleton leads to the increase in the distance between valence and conduction bands and it influences the visible luminescence of the porous silicon.

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