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L Khomenkova[1]**, N Korsunska**[1]**, T Torchynska**[2]**, V Yukhimchuk**[1]**,
B Jumayev**[1]**, A Many**[3]**, Y Goldstein**[3]**, E Savir**[3] **and J Jedrzejewski**[3]

[1] Institute of Semiconductor Physics, National Academy of Science of Ukraine,
45 Prospect Nauky, 03028 Kyiv, Ukraine
[2] ESFM—Instituto Politecnico Nacional, Ed. 9, UPALM, 07738, Mexico DF, Mexico
[3] Racah Institute of Physics, Hebrew University, Givat Ram, 91904 Jerusalem, Israel

E-mail: khomen@lumin.semicond.kiev.ua

Abstract

Photoluminescence (PL), photoluminescence excitation (PLE), and Raman spectra of Si–SiO$_x$ layers were measured as a function of Si content. Samples were prepared by co-sputtering of Si and SiO$_2$ and post-annealing. The average size of Si nanoparticles was estimated from Raman measurements. It was shown that, in general, the PL spectra consist of two bands with maxima in the 'red' and 'green' spectral ranges. The 'red' PL band is complex and contains two (IR and red (R)) components. The shift of the peak position of the IR component from 1.38 to 1.54 eV correlates with the decrease of the Si nanoparticle size from 5 to 2.7 nm. It was shown that this PL component could be ascribed to carrier recombination in silicon nanoparticles. The R component of the 'red' band as well as the 'green' band have similar dependences of the peak positions and intensities on the Si content and can be ascribed to defect-related luminescence. It was concluded that the light absorption in silicon nanocrystallites plays the main role in PLE process. Hot-carrier participation in the excitation of defect-related bands was deduced.

1. Introduction

The discovery of visible light emission from porous silicon at room temperature [1] stimulated great interest in investigations of various silicon nanostructures because of the need to create Si luminescent objects fully compatible with Si processing. Applying various techniques such as sputtering [2–5], ion implantation [6–8], plasma-enhanced chemical vapour deposition [9, 10], and molecule beam epitaxy [11] allowed this task to be carried out and light-emitting Si–SiO$_x$ systems (such as Si nanoparticles or wires in a silicon oxide matrix [2–10] and Si–SiO$_2$ superlattices [3, 11]) to be produced. It was shown that variation of the parameters of the formation regimes and following treatments allows control of Si–SiO$_x$ layer properties.
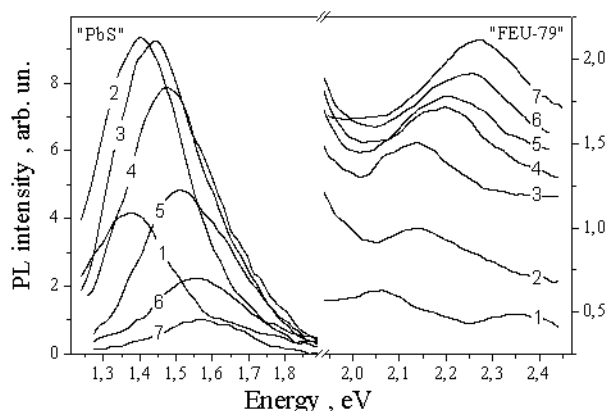
Figure 1. PL spectra of a Si–SiO$_x$ layer measured for values of C_{Si} (%) of (1) 57, (2) 54, (3) 48, (4) 43, (5) 40, (6) 36, (7) 33.

On the other hand, there was a need to elucidate the mechanism of bright visible photoluminescence (PL). On the basis of numerical theoretical and experimental investigations, models were proposed ascribing the visible PL to quantum confinement effects in Si nanocrystals [1] or to defects (oxygen vacancy or non-bridging oxygen hole centres) in the silicon oxide matrix [12, 13] or at the Si–SiO$_x$ interface [14]. In addition, it is apparent that different mechanisms can make contributions to the emission process. In fact, the interface between Si nanoparticles and the amorphous SiO$_2$ matrix can contain many defects due to the large lattice mismatch (about 7% or more), surface roughness, and variation in surface stoichiometry (SiO$_x$) [14]. So, in this case the PL intensity must depend on the types and quantities of the interface defects. Also, the defects in the SiO$_2$ matrix can participate in light emission. In this work, PL, PLE, and Raman spectra of Si–SiO$_x$ layers were studied as a function of Si content.

2. Experimental procedure

The Si–SiO$_x$ layers were prepared by co-sputtering from two electrodes, one with a silicon target and the other with a quartz target on a silicon substrate. A change of the Si content (C_{Si}) along the layer from 71 down to 9% was obtained, which allows variation of the number and sizes of silicon particles over a wide range. C_{Si} was obtained by the method described in [5]. The films were subsequently annealed at 1150 °C in an inert atmosphere. To measure Raman spectra, Si–SiO$_x$ layers were prepared not only on a silicon substrate but also on a quartz one, which allows avoidance of superposition of the Raman signal from bulk silicon.

PL spectra were excited by light from a Xe lamp passed through a grating monochromator, MDR-23, dispersed with a prism spectrometer, and registered by a PbS photodiode (for detection in the 1.2–2.0 eV range) or photomultiplier, FEU-79 (for recording in the 1.7–2.5 eV domain), and were divided by their spectral responses. Photoluminescence excitation (PLE) spectra were measured at different detection energies. Raman spectra were measured under Ar$^+$ laser light illumination (2.54 eV). All measurements were performed at room temperature.

3. Experimental results

The emission was observed in the interval of Si content (C_{Si}) from 67 to 22% and the highest total intensity corresponded to $C_{Si} = 43$–47%. In general, the PL spectra consisted of two
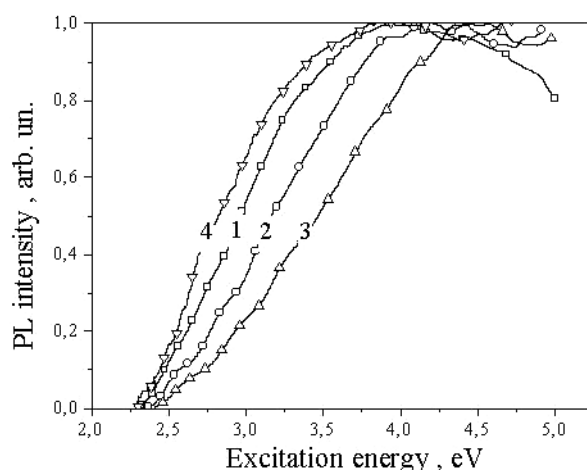
Figure 2. The dependence of the PLE spectra of 'red' (1–3) and 'green' (4) bands detected at their maximal energies on C_{Si} (%): (1) 48, (2) 43, (3) 36.

wide bands: 'red' and 'green' (figure 1). The peak positions of these bands, their full widths at half-maximum (FWHM), and their intensities changed along the layer.

With C_{Si} decreasing from 63 to 57%, the maximum position of the 'red' band was practically unchanged and was at 1.38 eV. Then it shifted towards high energy, up to 1.58 eV ($C_{Si} = 37$%), and the FWHM at first increased and then decreased (figure 1). The intensity of this band increased up to $C_{Si} = 43$–47%, then decreased, and at $C_{Si} = 30$% dropped sharply.

In the green spectral range for C_{Si} (the interval 63–57%), two bands peaked at 2.05 and at 2.35 eV were registered, while for other values of C_{Si} just one broad PL band was observed (figure 1). The peak position of the latter band shifted from 2.15 to 2.25 eV with C_{Si} decreasing from 55 to 33%. The intensity of the total 'green' band increased down to $C_{Si} = 30$% and then dropped sharply, like the intensity of the 'red' band (figure 1).

The light from the 2.2–5.0 eV spectral region excited both PL bands (figure 2). The 'red' edge of the PLE spectra of the 'green' band was observed at lower energy than that of the 'red' band. At the same time, the 'red' edges of both PLE spectra shifted to the high-energy side with decrease of the Si content (figure 2).

Raman spectra demonstrate the presence of Si nanoparticles. The peak position of the Raman signal in the interval $C_{Si} = 67$–50% changed slightly, then it shifted from 517 to 505 cm^{-1} for $C_{Si} \sim 35$%, and its FWHM increased corresponding to change of the Si nanoparticle size from 5 down to 2.7 nm (figure 3). It should be noted that the intensity of the Raman signal drops sharply when C_{Si} becomes less than 30%, which is evidence of a sharp decrease in the number of silicon nanocrystallites. The Raman signal from silicon crystallites for a layer sputtered on a silicon substrate shows similar behaviour.

4. Discussion

As follows from Raman scattering data, the sizes of Si nanoparticles decrease monotonically with decrease of the Si content along the layer. At the same time, the peak position of the 'red' band is at first practically unchanged but then shifts towards high energy. The FWHM of the 'red' band at first increases and then decreases. Such behaviour can be explained by a superposition of two overlapping bands whose intensities have different dependences on C_{Si}. In fact, as curve 1 in figure 1 shows, in addition to the band in the spectral region of 1.2–1.6 eV,
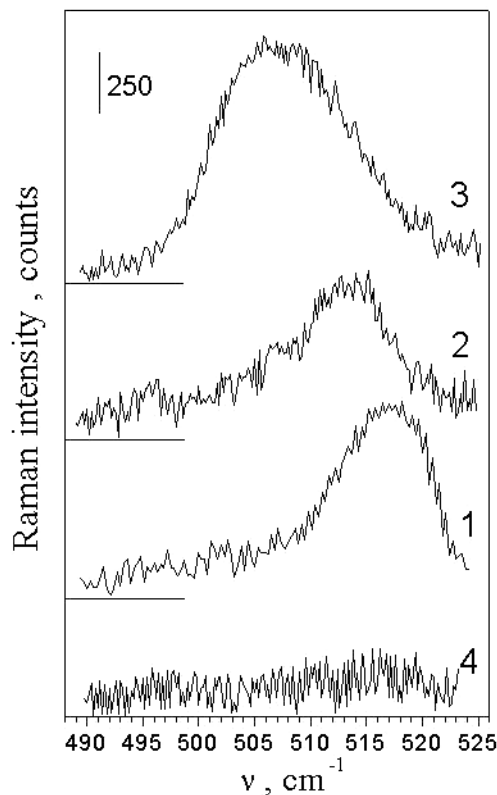
Figure 3. Raman spectra of a Si–SiO$_x$ layer sputtered on a quartz substrate measured for various values of C_{Si} (%): (1) 57, (2) 41, (3) 33, (4) less than 28.

a shoulder in the region of 1.6–1.9 eV is present. All other PL spectra can be decomposed into two bands in these regions (figure 1). The maximum of the low-energy (IR) component shifts towards high energy from 1.38 to 1.54 eV with decrease of C_{Si}, while the maximum of the high-energy (R) component shifts slightly (from 1.70 to 1.72 eV). The intensity of the IR component at first rises more sharply than that of the R component. Then the intensity of the IR component decreases, while that of the R component continues to increase. When the intensities of both components decrease, that of the IR component drops more sharply than that of the R component. Thus, the shift to high energy of the total 'red' band maximum could be caused not only by the shift to high energy of the peak position of the IR component but also by the increase in intensity of the R component.

As follows from investigations of the PL of Si–SiO$_2$/SiO$_2$ superlattices [2], the shift of the PL peak position from 1.42 to 1.54 eV corresponds to a decrease of the Si nanoparticle size from 3.8 to 2.7 nm. Our results are in a good agreement with these data. In fact, the peak position shift of the IR component from 1.38 to 1.54 eV corresponds to variation of the Si nanoparticle size from 5 to 2.7 nm. So, this PL component can be ascribed to carrier recombination in silicon nanoparticles.

Since the peak position of the R component is practically unchanged, this component can be attributed to defect-related recombination. The increase of the intensity of this component with increase of silicon oxide content leads us to think that this defect is a radiative defect at the Si–SiO$_x$ interface or in silicon oxide—such as a non-bridging oxygen hole centre (NBOHC) [12, 13].

The similar behaviour of the intensity of the 'green' band with increase of the silicon oxide content gives us reason to attribute this band to a defect in silicon oxide also, which is in agreement with the conclusions of other investigators [7].

Let us consider the PLE mechanism. The PLE spectra of all bands are similar (figure 2). The shift of the 'red' edges of PLE spectra towards high energy with decrease of the silicon content as well as the simultaneous sharp decrease in intensity of the total PL and the Raman signal allow us to connect PLE with light absorption in Si nanoparticles. The difference of 'red' edge of PLE spectrum of IR band from that of other PL bands can be ascribed to different depth distributions of emission centres.

Since the emission energies of defect-related PL bands exceed the energy of emission from Si nanoparticles, we are led to assume that hot carriers take part in the excitation of defect-related bands. Such a mechanism, which includes the ballistic transport of carriers, was discussed in our previous work [15].

5. Conclusions

In summary, our investigations of PL properties of co-sputtered Si–SiO$_x$ show that the PL spectrum consists of several bands. It is shown that a lower-energy band with its maximum at 1.38–1.54 eV can be connected with carrier recombination in silicon nanoparticles. The intensities of other bands, peaked at 1.7–1.72 eV and at 2.1–2.35 eV, increase with the rise of silicon oxide content and can be ascribed to defect-related luminescence. It is shown that the excitation of PL is mainly due to light absorption in silicon nanocrystallites. The participation of hot carriers in the excitation of defect-related bands is assumed.

Acknowledgments

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