Effect of material structure on photoluminescence spectra from silicon nanocrystals

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Effect of material structure on photoluminescence spectra from silicon nanocrystals

S. M. Orbons, M. G. Spooner, and R. G. Elliman

Electronic Materials Engineering Department, Research School of Physical Sciences and Engineering, Australian National University, Canberra, ACT 0200, Australia

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The thickness of a silicon dioxide layer is shown to have a significant effect on the measured photoluminescence spectrum from silicon nanocrystals embedded in the layer. This can range from significant but subtle spectral distortions that are difficult to detect, including changes in intensity, peak position and peak width, to gross distortions that are readily apparent as a modulation of the measured spectrum. These distortions are shown to be a simple consequence of the wavelength dependent reflectivity of the sample structure but to have important implications for determining nanocrystal properties from such data. © 2004 American Institute of Physics.

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Bulk silicon generally exhibits weak luminescence at room temperature due to its indirect band gap and the dominance of nonradiative recombination processes. However, it has been shown that silicon based nanostructures can exhibit efficient photoluminescence at room temperature. This discovery has sparked considerable debate regarding the mechanism for improved emission efficiency and an intrinsic element of this debate has been the comparison of experimentally measured photoluminescence (PL) spectra with theoretical predictions based on various models. Such analysis is predicated on the assumption that measured PL spectra reflect the properties of the silicon nanostructures. However, the broad spectral emission that is typically observed from Si nanocrystals can be distorted by the spectral response of the measurement system as well as by the optical properties of the sample.

A broad range of material structures have been employed by researchers studying Si nanocrystals, each with a characteristic, wavelength-dependent reflectivity. Indeed, the optical properties of such structures are often employed to modify the nanocrystal emission, as exemplified in microcavity structures employing distributed Bragg mirrors. However, in other cases, the impact of the sample structure on the measured nanocrystal emission is unintentional and often misleading. The spectral distortion due to simple material structures is a much more subtle and often misleading. The spectral distortion due to simple material structures is a much more subtle and often misleading. The spectral distortion due to simple material structures is a much more subtle and often misleading.

In this study, commercially prepared (100) oriented silicon wafers were oxidized to produce SiO2 layers of 5 μm, 970 nm, 650 nm, and 103 nm. These, together with a 1 mm thick fused silica plate were implanted at room temperature with 30 keV Si ions to a fluence of 2.5 × 1016 ions/cm². Figure 1 shows the Si depth distribution resulting from the implant. Each sample was subsequently annealed at 1050°C for 1 h in a forming gas (95% N₂, 5% H₂) ambient. By keeping both the implantation and annealing conditions constant for each sample, it is expected that they will have the same Si concentration-depth profile and the same nanocrystal size distribution. The only significant parameter that differs from sample to sample is the thickness of the oxide layer as illustrated schematically in Fig. 2. PL spectra were collected at room temperature using a 532 nm Rumzing diode pumped solid state laser as the pump source (incident angle 14°) and a TRIAX 320 spectrometer with a liquid nitrogen cooled SpectrumOne charge-coupled device as the detection system. The PL emission was collected with f4 optics consisting of two matched plano-convex lens of 50 mm diameter and 200 mm focal length, giving a collection angle of up to ±7°. Reflectivity measurements were performed at an incident angle of 5° using a Shimadzu UV-3101PC spectrophotometer with a specular reflectance attachment (P/N 206-14046). The bandwidth for the illumination system was set at 5 nm.

Figures 3(a)–3(d) show both the normalized PL intensity and the measured reflectance for each sample as a function of wavelength. It is immediately apparent that the measured PL spectra vary significantly as a function of oxide thickness, with variations in peak position, width and structure clearly evident. Inspection of panel 3(a) indicates that the fused silica sample yields an approximately constant reflectance over the entire wavelength range of interest. The PL spectrum is therefore not expected to be distorted significantly by...
the material structure, even though the PL intensity will still be affected. The strong correlation between the reflectivity of the material structure and the measured PL spectra is most readily apparent for the 5 μm thick SiO₂ layer, shown in Fig. 3(d). In this case the PL spectrum is clearly modulated by the reflectivity of the structure resulting in an obvious distortion of the emission spectrum.

Figures 3(b) and 3(c) show much more subtle distortions. For example, when compared to the spectrum from the silica sample, the PL spectrum from the 103 nm SiO₂ layer, Fig. 3(b), shows higher peak intensity but a similar full width at half maximum (FWHM) (143 nm, compared to 147 nm observed for silica). On the other hand the spectrum from the 970 nm SiO₂ layer, Fig. 3(c), exhibits two obvious peaks as a direct consequence of the spectral distortion caused by the surrounding material structure, with the main peak being centered at a wavelength of 780 nm compared to 740 nm recorded for the silica sample. Such a peak shift can readily lead to misinterpretation of the mean nanocrystal size.8,14,15 For example, using a simple expression for the relationship between the PL emission energy and nanocrystal diameter16 suggests that PL peaks at 780 nm and 740 nm correspond to nanocrystals with mean diameters of ≈4.8 or 4.1 nm, respectively.

The often subtle distortion of spectra is further highlighted in Fig. 4 which compares PL spectra from the 103 nm and 650 nm thick SiO₂ layers. The PL spectrum from the latter shows an increase in peak intensity as well as a considerable reduction in FWHM from 143 nm to 103 nm for the thicker layer. Assuming inhomogeneous broadening of the emission this corresponds to a change in the standard deviation of the nanocrystal size distribution from 0.3 nm for the narrower peak to 0.6 nm for the wider peak.5 It is interesting to note that this difference occurs despite the fact that the nanocrystal preparation conditions are identical, the only difference between the two samples being an additional 547 nm of oxide. Clearly, the assumption that the width of PL spectra from Si nanocrystals results primarily from inhomogeneous broadening due to the size distribution of nanocrystals assumes that due care has been taken to account for effects such as those illustrated in Figs. 3 and 4.

The data in Fig. 3 and 4 highlight the relationship between the observed PL and sample reflectance, demonstrating that this is the dominant effect leading to spectral distortion. Assuming that the structure is nonabsorbing, the transmission and reflection characteristics of a given structure are inversely related (i.e., $R + T = 1$, where $R$ is the reflectivity and $T$ the transmissivity of the structure). Hence, a local maximum in reflectivity corresponds to a local minimum in transmissivity and therefore to a minimum in the measured PL emission. A first-order estimate of the position of reflectivity maxima can be made from a simple constructive interference model, with $\lambda_{\text{max}} = 2nt/(m+1/2)$, where $\lambda_{\text{max}}$ is the wavelength for maximum reflectivity, $n$ is the refractive index of the SiO₂ layer ($n \sim 1.46$), $t$ is the film thickness, and $m$ is an integer.
thickness, and \( m \) is the interference order. (Comparison of the PL and reflectivity spectra reveals a small phase shift between the reflectance and PL spectra, most obvious in Fig. 3(d), an effect that is attributed to the different illumination conditions employed for each measurement.)

It should be noted that it is not always trivial to predict the reflectivity of the material structure as this depends not only on the initial material structure but also on the distribution and concentration of implanted silicon. By using the calculated implant profile, together with Maxwell-Garnet effective medium theory and the Fresnel equations, a reasonable estimate of the reflectivity can be achieved. However, such analysis confirms the significant role of the implanted silicon distribution in determining interference effects and highlights its influence on measured reflection and absorption characteristics.

(In previous measurements we have shown that this can lead to misinterpretation of optical absorption data.) Also implicit in the above discussion is the fact that the PL intensity and distribution will depend on the angle of detection, and on the wavelength and angle of incidence of the probe beam.

In conclusion, it has been shown that the PL emission from Si nanocrystals can be distorted by the optical properties of the sample structure, even in cases where that structure is relatively simple. These distortions affect the intensity, peak position, and width of the PL spectra and it is vital that such distortion be taken into account both when comparing PL spectra from different structures and when extracting nanocrystal parameters from observed PL spectra.

17. C. Bohren and D. Huffman, Absorption and Scattering of Light by Small Particles (Wiley, New York, 1983).