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2003 J. Phys.: Condens. Matter 15 3641

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Photoluminescence from SiO₂/Si/SiO₂ structures

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Received 20 February 2003

Published 19 May 2003

Online at stacks.iop.org/JPhysCM/15/3641

Abstract

Si layers were developed on pre-oxidized Si wafers by decomposition of silane in a low pressure chemical vapour deposition reactor. By keeping the deposition time constant (2 min) three sets of samples were fabricated at deposition temperatures equal to 580, 610 and 625 °C. The deposited Si layers were thinned by high temperature dry oxidation thus forming SiO₂/Si/SiO₂ structures. Room temperature photoluminescence (PL) measurements showed that for those samples in which the thickness of the remaining Si layer was greater than ~6 nm, the spectra exhibited a peak at ~650 nm. Prolonged oxidations led to the formation of SiO₂/nanocrystalline-Si/SiO₂ structures in which the thickness of the remaining nanocrystalline Si (nc-Si) layer was smaller than 3 nm. The PL spectra obtained from these structures were at least ten times stronger compared to the previous ones. The PL peak wavelength exhibited a weak dependence on the nc-Si layer thickness shifting from 800 to 720 nm for nc-Si thickness decreasing from ~3 to ~0.5 nm. In this publication we present our experimental findings, which indicate that the intensity of the 720–800 nm PL band is influenced by the deposition temperature of the initial Si layer and by the thickness of the oxide layer between the nc-Si layer and the Si substrate.

1. Introduction

Thin nc-Si layers embedded in a dielectric host have attracted the attention of various research groups for their potential on silicon based optoelectronic devices and also for possible application in memory devices. Lu *et al* [1] in 1995 reported the fabrication of Si/SiO₂ superlattices (SLs) prepared by molecular beam epitaxy and ultraviolet ozone treatment. The Si layers were amorphous and the structures fabricated exhibited room temperature photoluminescence (PL) in the visible range when the amorphous-Si layer thickness was between 1 and 3 nm. One year later, Sullivan *et al* [2] reported that high temperature annealing

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of amorphous Si/SiO₂ (α -Si/SiO₂) SLs, prepared by radio frequency magnetron sputtering and ultraviolet ozone treatment, increased the observed PL intensity by two orders of magnitude. Following these publications a lot of effort has been directed towards the fabrication and understanding of the mechanism of the PL from Si/SiO₂ SLs, having a Si layer thickness smaller than 5 nm [3–8].

In the majority of the reports that have appeared up to now, the fabrication of nc-Si/SiO₂ SLs proceeds through two stages: the first stage aims at the fabrication of an α -Si/SiO₂. During the second stage various annealing processes are employed in order to turn the amorphous Si layers into nanocrystalline ones. Vinciguerra *et al* [6] reported the fabrication of α -Si/SiO₂ SLs prepared by successive cycles of SiO₂ and Si deposition in a plasma enhanced chemical vapour deposition (PECVD) reactor. After the fabrication, the SLs were annealed at 1200 °C in nitrogen ambient, resulting thus in the formation of Si nanocrystals arranged in ordered planar arrays. Other publications have reported the fabrication of α -Si/SiO₂ SLs by using molecular beam epitaxy (MBE) followed by *in situ* plasma oxidation [1, 3, 7, 9]. Magnetron sputtering Si deposition is another technique, which has been employed for the fabrication of α -Si/SiO₂ SLs [8, 10, 11].

According to Zacharias *et al* [12], the crystallization temperature of nanometre sized amorphous Si layers increases with decreasing layer thickness due to strain effects. Recent publications have investigated the effectiveness of different annealing techniques by comparing the results of PL and Raman scattering experiments [7, 11]. The published results show that in the case of ultra-thin amorphous Si layers ($d_{nc-Si} < 3$ nm), the amorphous phase still exists even after annealing of the samples at temperatures as high as 1200 °C [7].

As we have already reported, nc-Si/SiO₂ SLs can be fabricated by successive cycles of Si deposition followed by a high temperature oxidation step [5]. According to our published results, a 12 nm thick amorphous Si layer, developed by LPCVD at 580 °C on a pre-oxidized Si substrate, is thinned down to ~ 2 nm after a 50 min oxidation step at 900 °C, thus forming a SiO₂/nc-Si/SiO₂ structure. This method has the advantage that it overcomes the problem of the crystallization of a nanometre sized α -Si layer by employing an alternative process during which the thinning and the crystallization of the deposited Si layer proceed simultaneously. A planar array of Si nanocrystals placed between two SiO₂ layers (SiO₂/nc-Si/SiO₂) is the structural unit for building up nc-Si/SiO₂ SLs. Consequently, the examination of the PL properties of this simple structure can provide useful information for understanding further the PL from nc-Si/SiO₂ SLs.

In the present publication we show that the 600–650 nm PL component recorded from SiO₂/Si/SiO₂ structures where the Si layer thickness is greater than 6 nm is not related to any quantum size effects but it rather originates from defects in the SiO₂. Additionally, we present our results concerning two factors, which appear to influence the intensity of the 750–800 nm PL band: the crystallinity of the initially deposited Si layer, which is influenced by the temperature during Si deposition, and the thickness of the oxide layer separating the Si nanocrystals from the Si substrate.

2. Experimental details

The samples were developed on p-type Si wafers. A typical procedure for the sample fabrication was the following: after RCA cleaning of the wafers, a thin pad oxide (~ 6 nm) was developed by thermal oxidation at 850 °C for 15 min. A thin silicon layer was then deposited by decomposition of pure silane (SiH₄) in a low pressure chemical vapour deposition (LPCVD) reactor. Three sets of samples were prepared by using isochronal (2 min) Si depositions at 580 (sample set A), 610 (samples set B) and 625 °C (sample set C). For all three sample sets

prepared the pressure during Si deposition was 300 mTorr. LPCVD silicon deposition was followed by an oxidation step at 900 °C in oxygen ambient. During this step a SiO₂ layer is formed on top of the deposited silicon layer. As the oxidation proceeds the thickness of the SiO₂ overlayer increases, while the thickness of the deposited Si layer decreases.

In the present study the oxidations were performed in steps of 15 min each. After each oxidation step the PL spectrum was acquired. During the PL measurements the samples were excited by the 457.9 nm Ar⁺ laser line. The PL signal was analysed by a single 0.25 m monochromator and detected by a photomultiplier tube. The spectral sensitivity of the system was between 500 and 800 nm and the spectral response function of the spectrometer is rather flat in this region.

3. Results and discussion

Ellipsometry measurements showed that a 2 min Si deposition at 580, 610 and 625 °C results in the formation of a continuous film having thickness equal to 12, 20 and 24.5 nm respectively. For Si deposition the reaction-rate coefficient is strongly dependent on temperature. Its value is proportional to $\exp(-E_a/kT)$, where E_a is an activation energy typically in the range 1.5–2 eV [19]. In the reaction-rate limited regime the deposition rate is proportional to the reaction rate coefficient with a typical value of $E_a = 1.6$ eV. Thus, for isochronal Si depositions it is expected that the thickness of the Si layer will depend upon the reaction temperature proportionally to $\exp(-1.6/kT)$. The temperature during Si LPCVD influences strongly the crystallinity of the deposited Si layer. Low temperature depositions favour the formation of amorphous Si films, while at high deposition temperatures the deposited Si is polycrystalline [13]. The variation of the crystallinity of the deposited Si layer with deposition temperature implies that the oxidation rate of LPCVD Si will vary across the three sets of samples fabricated.

3.1. PL from SiO₂/Si/SiO₂ structures with $d_{Si} > 6$ nm

The first sample examined was a 13 nm thick Si layer deposited by LPCVD at 580 °C, on a preoxidized Si substrate. Figure 1(a) shows the PL spectrum obtained immediately after Si deposition (solid square symbols) and also after 40 min of nitrogen annealing at 900 °C (continuous curve). The PL peak of the as-prepared sample is at 630 nm and it is shifted to 610 nm after annealing. The full width at half maximum (FWHM) is reduced from 178 nm (as deposited sample) to 154 nm (annealed sample). Figure 1(b) shows the PL spectrum after oxidizing the as-deposited Si layer for 30 min at 900 °C in oxygen ambient (hollow square symbols). According to transmission electron microscopy (TEM) measurements [5], after this oxidation step the deposited amorphous Si layer becomes nanocrystalline and its width is reduced to ~6 nm. The maximum of the PL spectrum appears at ~655 nm and the FWHM is equal to 170 nm. A post-oxidation, annealing step (900 °C, 30 min in N₂) does not significantly alter the PL spectrum (figure 1(b), dotted curve): the PL peak is slightly shifted to the red (664 nm) while the FWHM remains approximately the same (164 nm).

By comparing the spectra of figures 1(a) and (b), it is seen that thinning the Si layer down to ~6 nm by dry oxidation has no effect on the intensity of the observed PL, and it slightly shifts the PL peak wavelength. The insensitivity of the observed PL to the structural changes of the Si layer, during annealing, and the decrease of its thickness, during oxidation, show that the observed PL is not related to quantum size effects and it is more likely to originate from interfacial Si/SiO₂ energy states.

In order to clarify this point the PL spectra from oxidized Si substrates were also measured. The results obtained indicate that the PL from oxidized Si consists of two bands: one having a

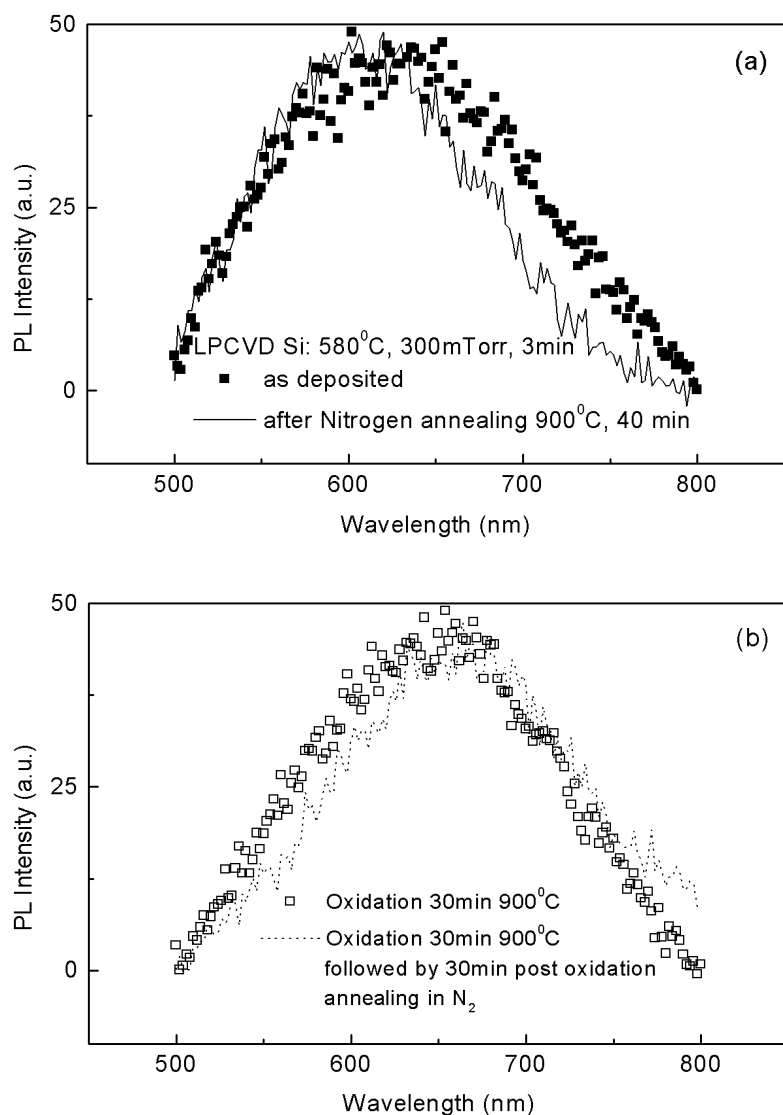


Figure 1. (a) PL spectra from ~ 13 nm LPCVD Si immediately after deposition (■), and after nitrogen annealing (continuous curve). (b) PL spectra immediately after thinning (~ 6 nm Si remaining) the deposited Si layer by dry oxidation (□), and after post-oxidation annealing (dotted curve).

peak between 500 and 550 nm, which tends to decrease under continuous excitation [4], and a second, which exhibits its peak intensity between 610 and 660 nm. The two bands usually coexist in the same spectrum while it appears that shorter oxidations favour the appearance of the 610–660 nm band. Figure 2 shows the PL spectra obtained from Si oxide films prepared by dry oxidation at 950 °C for 7, 15 and 90 min. For the shortest oxidation (open symbols) the PL spectrum obtained appears to be quite similar to the spectra of figure 1, both in terms of intensity and peak wavelength. For longer oxidations (figure 2, solid symbols) the spectrum is broadened towards shorter wavelengths due to the varying contribution of the ~ 550 nm band.

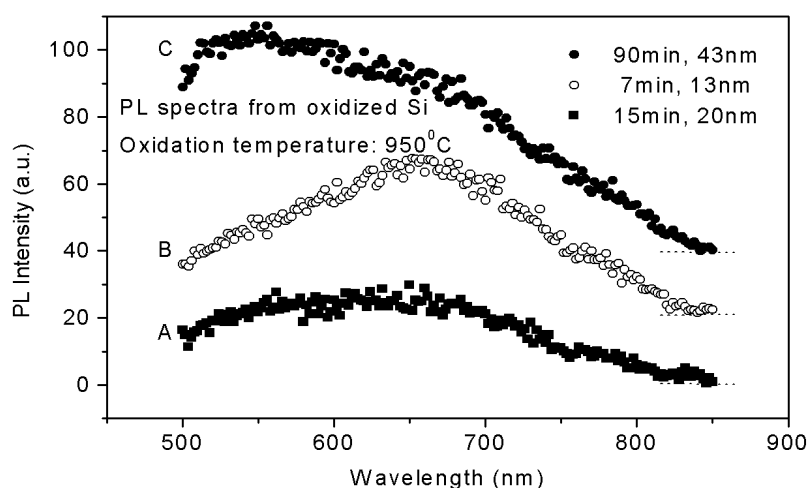


Figure 2. PL spectra from oxidized Si. The spectra are vertically displaced. The horizontal dotted lines correspond to the zero level.

The similarity of spectrum B shown in figure 2 (open symbols) to those of figure 1 indicates that the PL from SiO₂/Si/SiO₂ structures with $d_{\text{Si}} > 6$ nm is most probably related to energy states at the Si/SiO₂ interface and not to the confinement of excited carriers in the Si layer. The PL spectra peaking between 610 and 660 nm are most probably due to localized defects such as non-bridging oxygen hole centres (NBOHCs) [14]. Such defects have been reported in silica optical fibres [15, 16] and their typical PL emission ranges between 590 and 650 nm, while interface strains can cause some changes in the emission energy [17]. Other research groups have also attributed the PL around 2 eV to defects. Shimizu-Iwayama *et al* [18] have reported a luminescence band around 620 nm from Si implanted SiO₂, which they attributed to the formation of excess silicon defects. Averboukh *et al* [8] in studying the luminescence from Si/SiO₂ SLs found that the PL maximum intensity appeared at 600 nm. They interpreted the observed luminescence as a case where the carriers generated by optical excitation inside the Si layers (1.8 nm) diffused through the thin oxides (1.5 nm in their samples) towards higher energy levels of interface states.

3.2. PL from SiO₂/nc-Si/SiO₂ structures with $d_{\text{nc-Si}} < 3$ nm

This section presents the results of the PL measurements from the three sets of SiO₂/nc-Si/SiO₂ structures prepared by thinning the initial Si layers down to a few nanometres. The line curves in figure 3 correspond to the PL spectra obtained after oxidizing the Si layer deposited at 580 °C for 45 and 75 min; the square symbols correspond to 90 and 120 min oxidation of the Si layer deposited at 610 °C and the round symbols represent oxidation of the Si layer deposited at 625 °C for 105 and 135 min. For each pair of spectra the longer oxidation, i.e. thinner nc-Si layer remaining, corresponds to the spectrum shifted to the blue. The spectra can be approximated by a single Gaussian having an FWHM approximately equal to 120 nm.

Figures 4(a) and (b) show the variation of the PL peak wavelength and PL peak intensity versus oxidation time for the three sets of samples examined. For oxidations a bit shorter than 45 min for sample set A, 75 min for sample set B and 105 min for sample set C, the spectra peaked at longer wavelengths compared to the spectral limit of the spectrometer (800 nm) and consequently only the high energy side of the spectra were recorded. From figure 4(a) it is seen

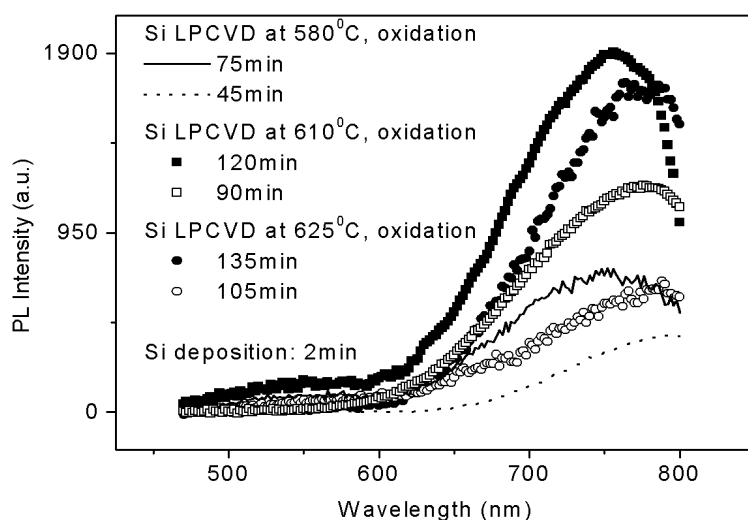


Figure 3. PL from $\text{SiO}_2/\text{nc-Si}/\text{SiO}_2$ structures, $d_{\text{nc-Si}} < 3$ nm. Oxidation temperature 900°C .

Table 1. Comparison of the three samples exhibiting the strongest PL from sample sets A, B and C.

Sample set	LPCVD ^a temp ($^\circ\text{C}$)	Si initial thickness (nm) ^b	Oxidation time (min) ^c	PL peak wavelength (nm)	Relative PL intensity
A	580	12	60	772	0.61
B	610	20	120	755	0.86
C	625	24.5	150	755	1

^a 300 mTorr, 2 min.

^b Deposited on a 6 nm pad oxide.

^c At 900°C .

that for each one of the three sets of samples fabricated, longer oxidations shift the PL spectrum to shorter wavelengths. For sample set C by increasing the oxidation time from 105 to 165 min the PL peak wavelength shifts from ~ 785 to 734 nm. For sample set B a similar spectral shift is observed when the oxidation time increases from 75 to 135 min. Finally, for sample set A the PL peak wavelength shifts from 790 to 730 nm when the oxidation time increases from 45 to 90 min. According to published results [4], it is expected that the dimensions of the Si nanocrystals in the resulting $\text{SiO}_2/\text{nc-Si}/\text{SiO}_2$ structures decrease respectively from ~ 3 to ~ 0.5 nm.

The weak dependence of the PL peak wavelength on the thickness of the nc-Si layer favours those explanations that invoke the existence of energy states inside the bandgap of the Si nanocrystals. Wolkin *et al* [20] have suggested that the high stresses at the Si/SiO₂ interface may break some of the Si-Si or Si-O-Si bonds. The formation of Si=O bonds is then, a possible way to stabilize the interface. The presence of a Si=O bond on the nanocrystals introduces size dependent energy levels inside the bandgap.

From figure 4(b) it is seen that, for the samples of the same sample set, by increasing the oxidation time the PL intensity increases up to a certain point (corresponding to oxidations of: 60 min for sample set A, 120 min for sample set B and 150 min for sample set C). For longer oxidations the PL peak intensity starts decreasing again presumably because very long oxidations create discontinuities in the nc-Si film. Figures 3 and 4(b) show that the PL spectra

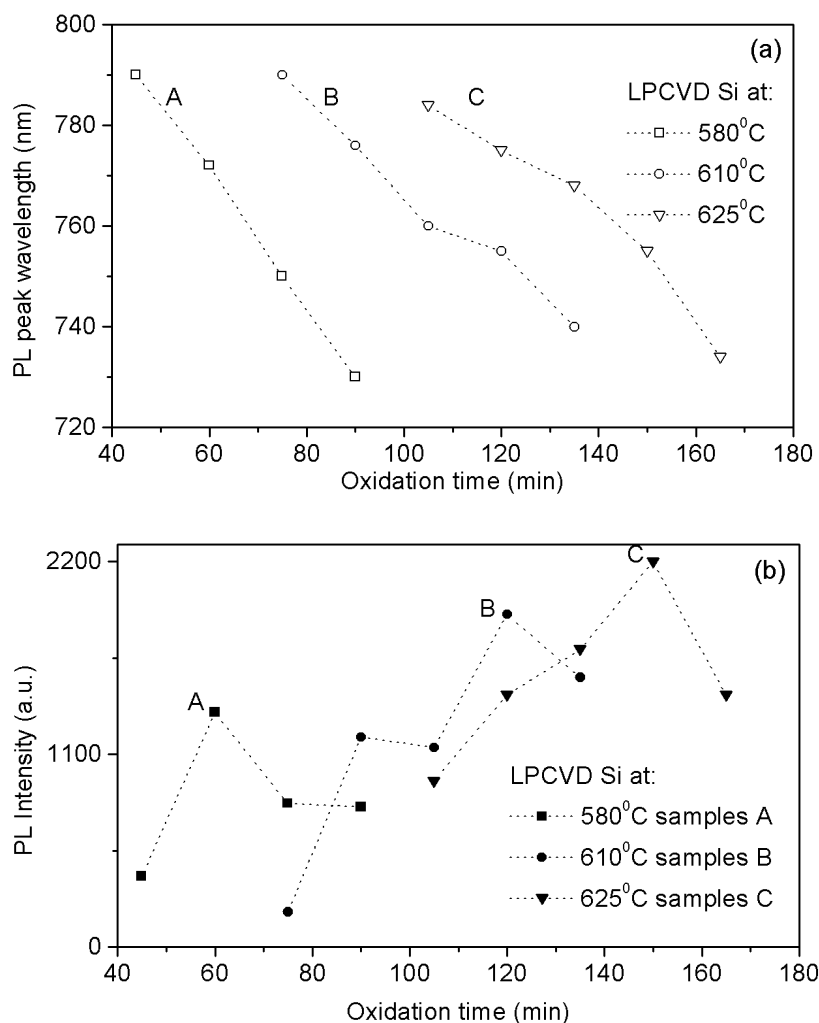


Figure 4. (a) Shift of the PL peak wavelength versus oxidation time. (b) Variation of the PL peak intensity versus oxidation time. The curves are only guides to the eye.

recorded from sample set C exhibit systematically stronger PL compared to the spectra recorded from sample sets A and B. Table 1 resumes the characteristics of the samples exhibiting the most intense PL from each one of the three sets of samples fabricated.

The strongest PL intensity is observed for the sample prepared after oxidizing the Si layer deposited at 625 °C for 150 min. This can be related to the following possible factors: the longer thermal treatment during the oxidation step or the increased crystallinity of the as-deposited Si layer. In order to clarify the case, the samples from sample set A were annealed in nitrogen at 900 °C for 1 h. After nitrogen annealing the PL intensity decreased by ~50%, while the peak wavelength slightly shifted to the red (figure 5). This result excludes the first of the two possibilities addressed above. Although the results presented here do not provide conclusive evidence, it appears that the crystallinity of the initial Si layer is a factor affecting the PL intensity recorded after thinning the deposited Si layer down to a few nanometres.

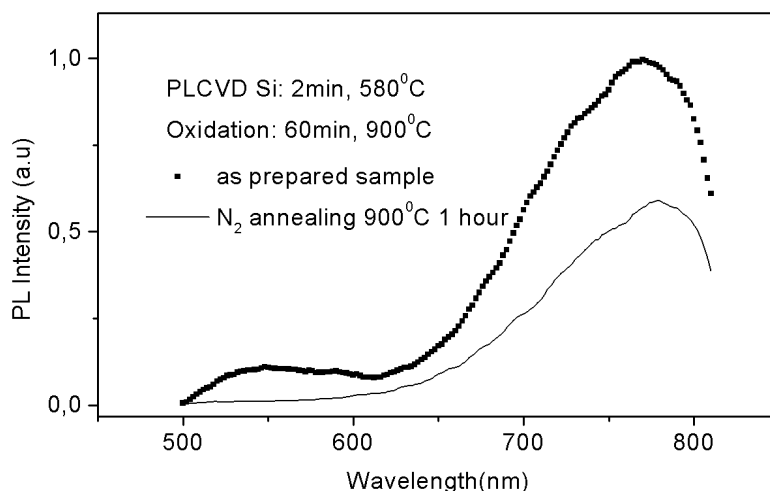


Figure 5. After nitrogen annealing at 900 °C, the PL intensity from a SiO₂/nc-Si/SiO₂ structure is reduced by ~50%.

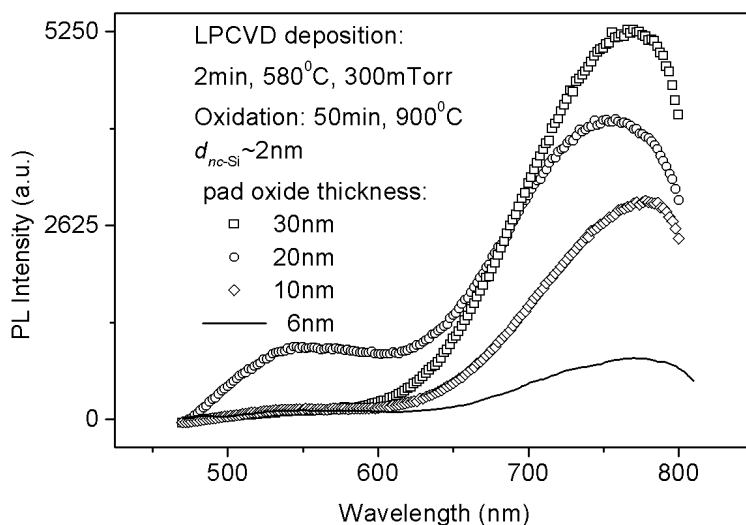


Figure 6. PL spectra from ~2 nm nc-Si layers fabricated on oxidized Si substrates. Each spectrum corresponds to a different thickness of the pad oxide.

3.3. The role of the thickness of the pad oxide

Figure 6 shows the PL spectra from SiO₂/~2 nm nc-Si/SiO₂ structures where the thickness of the pad oxide is varying from 6 to 30 nm. For the samples measured the initial Si layer was deposited at 580 °C and then it was oxidized at 900 °C for 50 min. The results obtained show that by increasing the thickness of the pad oxide a fivefold increase of the PL intensity is also observed, without affecting significantly the PL peak wavelength. We attribute the observed increase of the intensity of the PL band around ~750 nm to increased stresses and disorder present in the samples developed on thicker pad oxides.

The existence of strong stresses at the Si/SiO₂ interface plays a crucial role in the formation of the Si=O double bond which is supposed to be responsible for introducing the luminescent

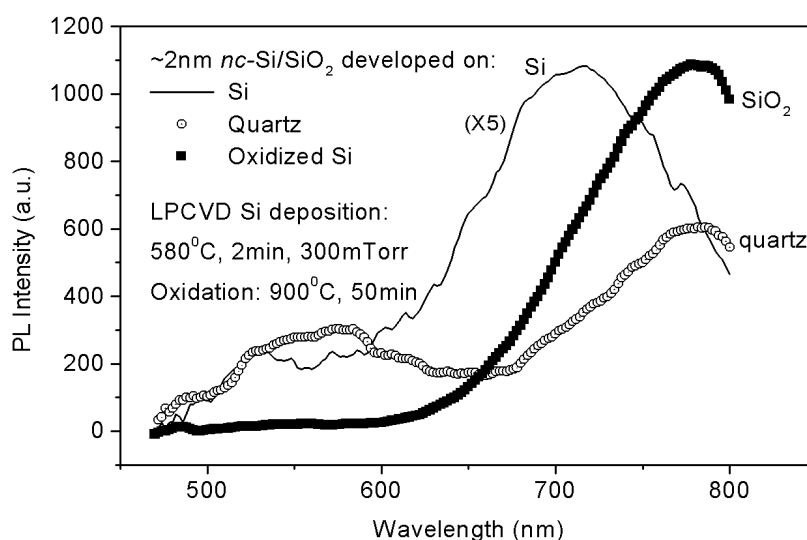


Figure 7. PL spectra from ~ 2 nm nc-Si layers developed on Si, quartz and oxidized Si substrates.

states inside the nanocrystal bandgap. Khriachtchev *et al* [7], in examining the PL from Si/SiO₂ SLs after high temperature annealing, found that the PL peak position depended on the substrate on which the SLs were developed. According to their results, the PL spectra recorded from SLs developed on quartz or oxidized Si substrates exhibited a peak around 800 nm while for SLs developed on Si the PL peak was around 600 nm. The SLs on quartz after annealing showed tensile stress and higher disorder compared to those developed on Si. They attributed this to the different coefficients for thermal expansion of quartz and Si. A similar tendency concerning the PL peak wavelength was observed during our experiments from a single nc-Si layer fabricated on different substrates. Figure 7 shows the PL spectra recorded from ~ 2 nm nc-Si layers developed on Si, quartz and a pre-oxidized Si wafer (~ 6 nm oxide thickness). The PL spectra from the samples developed on the quartz substrate or the oxidized Si substrate exhibit the main peak at 780 nm. For the sample developed on Si substrate the peak is blue shifted by ~ 70 nm and the intensity is ~ 5 times smaller. Assuming that the ~ 780 nm peak is associated with the presence of high tensile stresses and disorder, then thick pad oxides would enhance this peak because of excess stresses. The role of the interfacial stresses has been considered as an important parameter in a number of theoretical works concerning the luminescence from nc-Si. Allan *et al* [21] pointed out that in the case of Si nanocrystals embedded in an oxide matrix the dimers formed at the Si/SiO₂ interface cannot relax as easily as in the case of the hydrogenated nanocrystals because of the stronger elastic forces exerted by the insulating medium. Martin *et al* [22] in studying the PL from porous Si have pointed out that anisotropic elastic strains can play the same role as the anisotropy of the confinement, while Kamenev *et al* [23] have shown the existence of two decay times, one attributed to electron-hole recombination between states originating from the presence of Si=O bonds and the other due to self trapped excitons on Si dimers.

According to a previous publication [5], the PL from nc-Si/SiO₂ SLs prepared by successive cycles of Si deposition and dry oxidation increases superlinearly with the number of periods in the SL. Each period of the SL consisted of a ~ 2 nm nc-Si and a ~ 20 nm SiO₂ layer. Every period acts as a buffer layer between the Si substrate and the next period. For

example, while the first period is fabricated on a ~ 6 nm pad oxide developed on the wafer, the third one is developed on a ~ 30 nm oxide layer which contains two ~ 2 nm Si layers. The difference in the thickness of the insulator underlying the first and the third Si layers affects the stresses induced on them, during the thinning–oxidation step, which in turn affect the respective PL intensities. According to the experimental findings presented here, the PL intensity from the third period alone will be ~ 5 times stronger compared to the PL intensity from the nc-Si layer fabricated first. These results clarify the superlinear increase of the PL intensity with the number of the periods in the SL.

4. Conclusions

In conclusion, we studied the PL from $\text{SiO}_2/\text{Si}/\text{SiO}_2$ structures prepared by LPCVD Si deposition and subsequent high temperature dry oxidation at three deposition temperatures. The results obtained show that for Si layers of thickness greater than ~ 6 nm the PL spectra exhibit a peak around ~ 650 nm which is attributed to defects at the nanocrystal/ SiO_2 interface. For nc-Si layers thinner than ~ 3 nm a PL peak appears around 800 nm. This peak is slightly shifted to shorter wavelengths as the nc-Si layer is further decreased. These results were verified for all three temperatures of Si deposition. It appeared that the intensity of the PL band around 800 nm increases when the crystallinity of the initial Si layer is improved. The PL around 800 nm is highly influenced by strain effects, which are considered to be responsible for the superlinear increase of the PL intensity when the number of periods in the SL is increased. Our results indicate that the intensity of this PL band is influenced by the type of the substrate on which the nc-Si layer is developed as well as the thickness of the oxide between the nc-Si layer and the Si wafer. We interpreted these results by appealing to the role played by the stresses, induced during the thinning–oxidation step.

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