Photoluminescence within Crystalline-Si/SiO_2 Single Quantum Wells.

D. J. Lockwood[1], M. W. C. Dharma-wardana[1], Z. H. Lu[2], D. H. Grozea[2], P. Carrier[3] and Laurent J. Lewis[3]

[1]Institute for Microstructural Sciences, National Research Council, Ottawa, K1A 0R6 Canada
[2]Department of Materials Science and Engineering, University of Toronto, Toronto, M5S 3E4, Canada
[3]Département de Physique et Groupe de Recherche en Physique et Technologie des Couches Minces (GCM), Université de Montréal, Case Postale 6128, Succursale Centre-Ville, Montréal, Québec, H3C 3J7 Canada

ABSTRACT

Ultrathin single quantum wells of crystalline silicon (c-Si) confined by SiO_2 have been prepared by chemical and thermal processing of silicon-on-insulator wafers. The photoluminescence (PL) produced by these nanometer-thick single wells contains two bands: one exhibits a peak energy of ~1.8 eV, while the second increases rapidly in peak energy with decreasing c-Si layer thickness. Comparison with theories based on self-consistent first-principles calculations shows that the increase in PL peak energy of the second band is consistent with that predicted for the c-Si energy gap of such wells. It also agrees with the measured band gap variation. The ~1.8 eV PL band is attributed to the recombination of electron-hole pairs confined at the c-Si/SiO_2 interface.

INTRODUCTION

The discovery by Lu, Lockwood, and Baribeau [1] of intense luminescence in Si/SiO_2 superlattices (SL) has led to numerous experimental [2-6] and theoretical studies [7-11] of their structural, electronic and optical properties. A blue shift with increased confinement is reported in most experimental and in all theoretical works. In general, the atomic structure of Si in the quantum well (QW) is amorphous, as for the two SiO_2 barriers. This is due to the growth process in combination with the considerable lattice mismatch between silicon and silicon dioxide in their crystalline phases, being 5.43Å for diamond-like Si versus for instance 7.16Å for the beta-cristobalite SiO_2. Several attempts have been conducted in order to fabricate ***crystalline*** silicon quantum wells. Takahashi *et al* [5] followed by Kanemitsu and Okamoto [6] have first reported the fabrication of single quantum wells obtained after adjoining two semiconductor-on-insulator (SOI) wafers. The asymmetry in the lineshape of the photoluminescence (PL) suggested the presence of two main peaks: one major PL peak (centered around 1.65 eV) that remains unshifted in all the QW samples while a minor peak undergos a blue shift with increased confinement. Thus, two main mechanisms describe the PL intensities, one unshifted energy peak that is attributed to the interfaces owing to its observation in all QWs while the other shifted energy peaks are attributed to the varying well thickness, i.e., to the confinement. We report here new results that confirm the presence of these two peaks, one major peak centered about 1.8 eV and another that increases in energy with increased confinement. These results are compared to calculations performed within the density functional theory and the local density approximation based on structurally relaxed models.

The objective of this article is to give a clear demonstration of these two mechanisms. The experimental and theoretical approaches are jointly described as follows. We first describe the fabrication of the quantum wells as well as the construction of the model structures. Second, we recall some results relative to the enhancement and the blue shifting obtained from experiment [4] and theory [10]. Third, confinement effects are investigated with the use of X-ray near edge absorption spectra (XANES) described here for two QWs. These results are then correlated to calculations of the *2p*-core excitation absorption (A_{2p}) for corresponding well thickness in the Si/SiO_2 models. Strongly confined states are clearly established, which demonstrates the important role of confinement on the electronic properties. Finally, interface states are confirmed from the experiments, in rather good agreement with results reported earlier in Ref. [6]. This is examined with the theoretical models by comparing the density-of-states of bulk-like Si atoms located inside the Si-well with suboxide Si atoms located at the two Si/SiO_2 interfaces; their relative magnitudes give further knowledge on the likelihood of their optical transitions. However, incomplete agreement between the models and the QW experimental results is obtained. This could be ascribed to impurity states, or defects, such as dangling bonds, hydrogen, or P_b centers [12] that are by model construction not considered in our $SiO_2/Si/SiO_2$ SL models. We thus infer that the unshifted peak observed in the experiment, but not excerpted from the (impurity-free interfaces) models, should be attributed to interface states.

QUANTUM WELLS AND Si/SiO_2 MODEL STRUCTURES

Figure 1(a) shows a TEM photograph of the cross section of one $SiO_2/Si/SiO_2$ single quantum well. The quantum wells were all fabricated with ELTRAN (100) SOI wafers as starting materials, taking advantage of their flat interface (while Takahashi *et al* [5] and Kanemitsu *et al* [6] used *separation-by-implanted-oxygen* SIMOX-SOI wafers). A furnace dry oxidation was then used to reduce the silicon layer thickness from 50 nm to a few nanometers, as shown in Fig. 1. The advantage of this procedure is that it is highly reproducible and well understood. The Si film layers were then thinned down, Si layer by Si layer, by combining room-temperature UV-ozone oxidation and wet-chemical etching. Full details are given in Ref. [4].

Figure 1(b) now shows the cross section of one of the fully-relaxed models (FRM1) of $SiO_2/Si/SiO_2$ multiple quantum wells, or superlattices (the supercell depicted in the figure being repeated periodically). The model contains an equal distribution of the three types of interface suboxide Si atoms, i.e., the Si^{1+}, Si^{2+}, and Si^{3+} atoms [10,13]. It comprises five bulk-like Si monolayers (the so-called Si^0 atoms) while each interface suboxide layer is made of one monolayer (~0.16 nm). The letters ABCD refer to the four types of diamond-like Si monolayers while the O's refer to oxygen layers. The primes stand for structural reconstructions of the bulk-like Si layers. The total thickness of the SL model (that includes the two interfacial suboxide layers and the bulk-like Si layers, 0.8 nm thick) is 1.1 nm. Two additional models having respectively 9 and 13 Si-monolayers – i.e., respectively 1.7 nm (FRM2) and 2.2 nm (FRM3) thick – have been constructed and structurally relaxed. The nature of the energy gap is generally direct (nearly direct only in the case of FRM1 model). Full details are given in Ref. [10] where structural properties, band structure as well as absorption calculations are described. We recall that this particular model has been constructed starting from a Si/SiO_2 interface

model due to Pasquarello *et al* [14]. Additional models have also been considered in order to span wider thickness for the silicon wells, as described in Ref. [11]. The latter are referred to as double-bonded (DBM) and bridge-oxygen (BOM) models and contain respectively one and three bulk-like Si layers, corresponding to ~0.41 nm and ~0.70 nm thick Si-wells (after inclusion of the two interface suboxide layers).

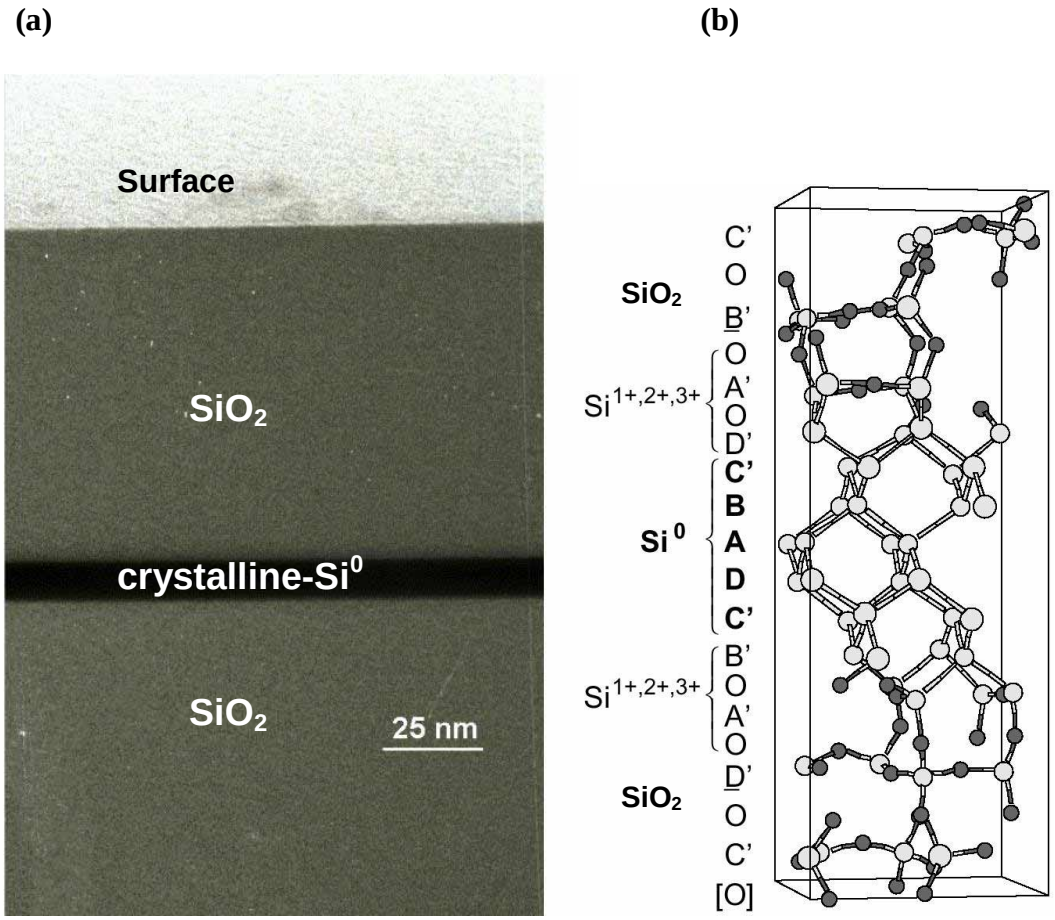

Figure 1. (a) Cross section of one SiO_2/Si/SiO_2 quantum well. (a) Side view of Si/SiO_2 SLs model (with 5 bulk-like Si monolayers). The growth axis is the Si-(001) direction in both cases.

The experimental energy gaps of the QWs having various thickness are given in Figure 2 and are compared with the theoretical gaps obtained from the different models discussed above. The electronic properties are calculated within the density functional theory and the local density approximation [15] (after adding a correction of 0.6 eV to all gaps, which corresponds to the underestimation of the LDA gap for diamond-like silicon). The FRMs give, as expected, better agreement than the BOM and DBM models [10,11] due to their much simpler and non-relaxed interface structures. Good agreement between the various models and the experimental energy gaps is obtained, demonstrating the blue shifting of the absorption (and thus emission) properties with increased confinement.

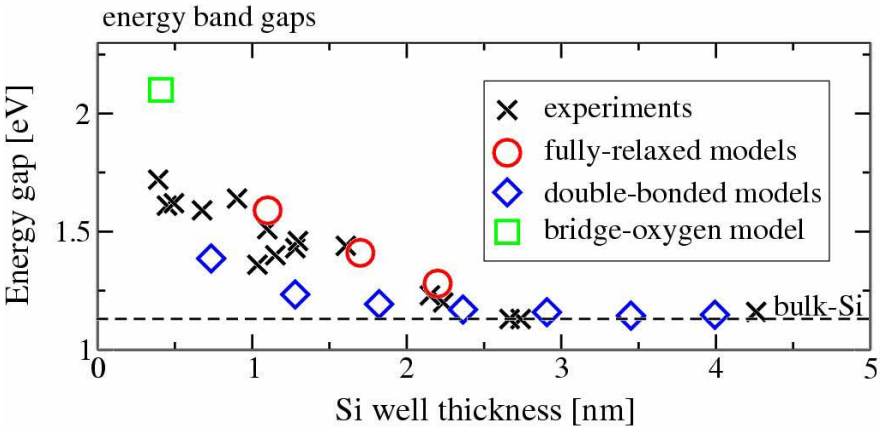

Figure 2. Experimental energy gap variation compared to three models structures, the fully-relaxed, the double-bonded, and the bridge-oxygen models.

CONFINEMENT EFFECTS

The confinement effect has first been demonstrated in the theory from the aspect of the energy bands that are shown to have absolutely no-dispersion in the growth direction axis of the Brillouin zone, corresponding to an *infinite* effective mass and thus to strong confinement. Additional confined models, starting from the FRM2 have also been constructed in order to evaluate the role of the suboxides and their oxygen as barriers. All suboxides were shown to form acute barriers, meaning that the wave functions in the Si-well die out exactly right after the interface suboxides Si atoms [10].

On the experimental side, confinement has been confirmed from XANES measurements. Figure 3(a) shows the measured XANES derivatives of the *2p* core-level transition for two quantum wells and is compared to that of bulk-Si. The lowest energy edges at the Si conduction-band minimum shifts to the blue in the transition from c-Si to the 1.6 nm and then to the 1.1 nm thick QWs. These relative shifts then fade away when XANES energies above ~102.7 eV are reached. The confinement thus takes place within an energy window of ~2.7 eV above the conduction band minimum (CBM). This clearly demonstrates the confinement of the electronic states in the QWs.

In order to determine the electronic properties of the confined states, we calculated the *2p* core absorption using the following (two-step) procedure. First, due to the strong localization of the *2p* core level, the *joint* density of states involved in the application of the Fermi Golden Rule is now determined solely by the density of states (D_s and D_d) of the *s* and *d* conduction bands (after application of the appropriate selection rules), multiplied by their corresponding matrix elements ($M_{2p,s}$ and $M_{2p,d}$). The optical transition is thus governed by:

$$T(\omega) = \left|M_{2p,s}\right|^2 D_s(\varepsilon_{2p} + \omega) + \left|M_{2p,d}\right|^2 D_d(\varepsilon_{2p} + \omega)\,. \qquad (1)$$

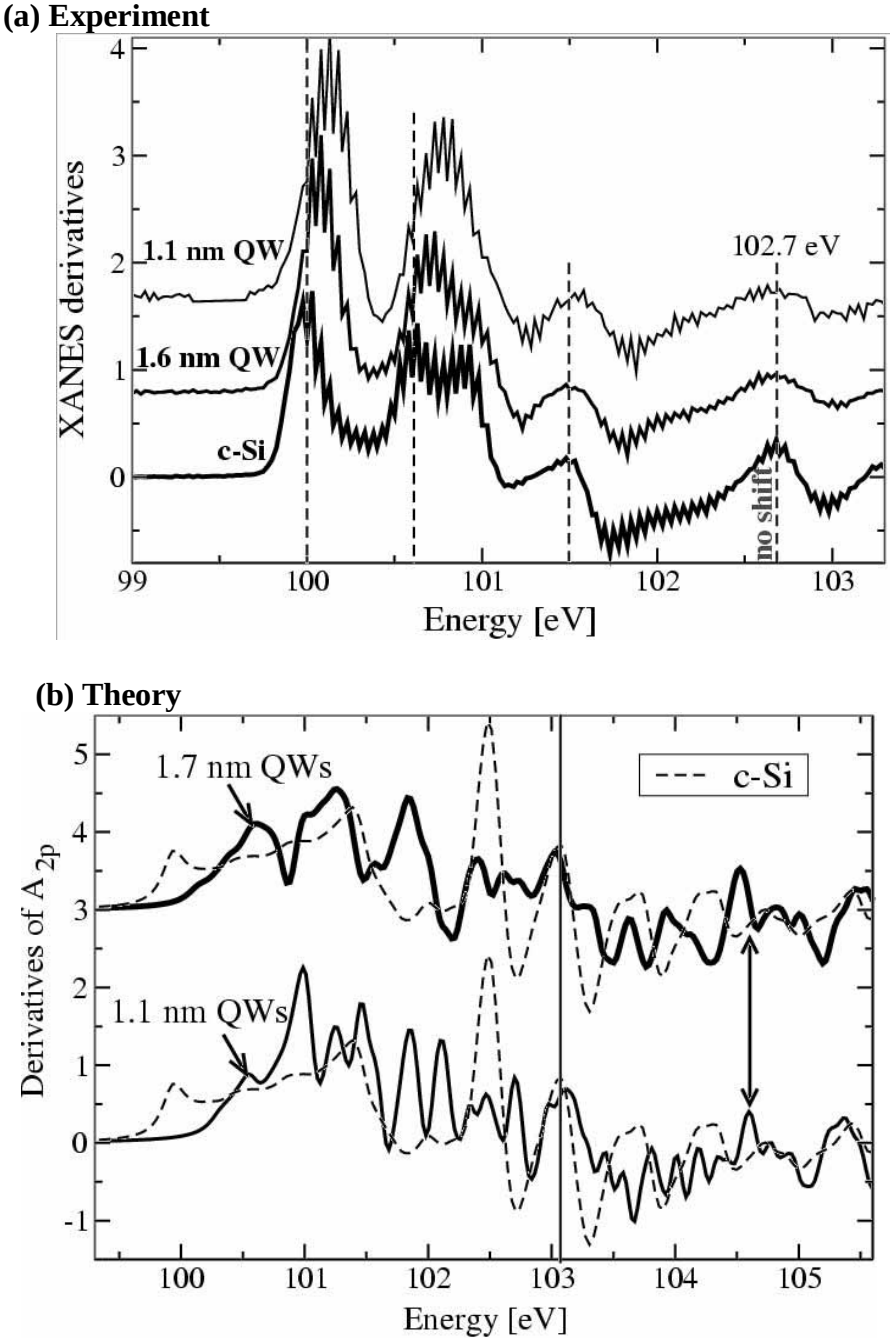

Figure 3. (a) derivative of the *2p* core excitation XANES and **(b)** theoretical absorption derivatives of A_{2p} (see the text).

Second, the spin-orbit coupling (that separates the $2p_{1/2}$ and $2p_{3/2}$ by 0.6 eV; see for instance Ref. [16]) is included in the calculation by summing the two shifted transitions *T*, with proper weights. The final expression for the absorption A_{2p} is thus given by:

$$A_{2p} = \frac{2}{6} T(\varepsilon_{2p} + \omega) + \frac{4}{6} T(\varepsilon_{2p} + \omega + 0.6 \text{ eV}) . \qquad (2)$$

This calculation has been performed for two superlattices models, 1.1 nm and 1.7 nm thick, as well as for crystalline silicon, within the DFT-LDA. Figure 3(b) shows the resulting derivatives of A_{2p} to be directly comparable with the experimental QWs of Fig. 3(a). The theory gives features similar to those found experimentally, i.e., one observes strongly confined states below ~103 eV, while band states (i.e., bulk-like Si "unconfined" states) are formed of a transition domain, from ~103 eV up to ~105 eV, where the two quantum wells have similar transition edges with slight differences with c-Si (compare for instance the curves at 104.6 eV where a double vertical arrow is depicted), and finally pure band states, above ~105 eV, where both quantum wells and bulk-Si have similar properties [17]. These two approaches, experimental and theoretical, further demonstrate the overwhelming role of confinement on the optical transitions in these SL structures.

INTERFACE STATES

We describe in this section additional results related to interface states observed in the PL. A constant energy peak in the PL located at 1.8 eV is observed in all quantum wells. Figure 4 shows the PL peak energies as a function of the well thickness, which clearly exhibits peaks at an energy peaks located at 1.8 eV. The following analysis concentrates on three QWs, 1.3 nm, 0.68 nm, and 0.39 nm thick.

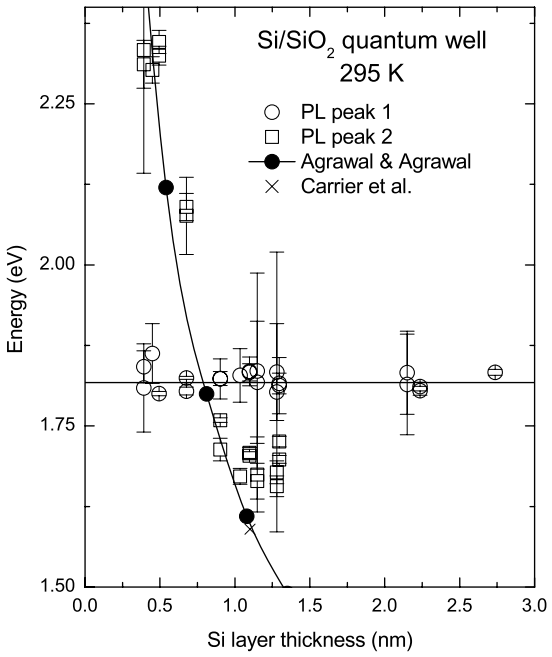

Figure 4. Variation of the PL energy peaks as a function of the Si well thickness that clearly exhibits a peak located at 1.8 eV whose position is independent of the well thickness.

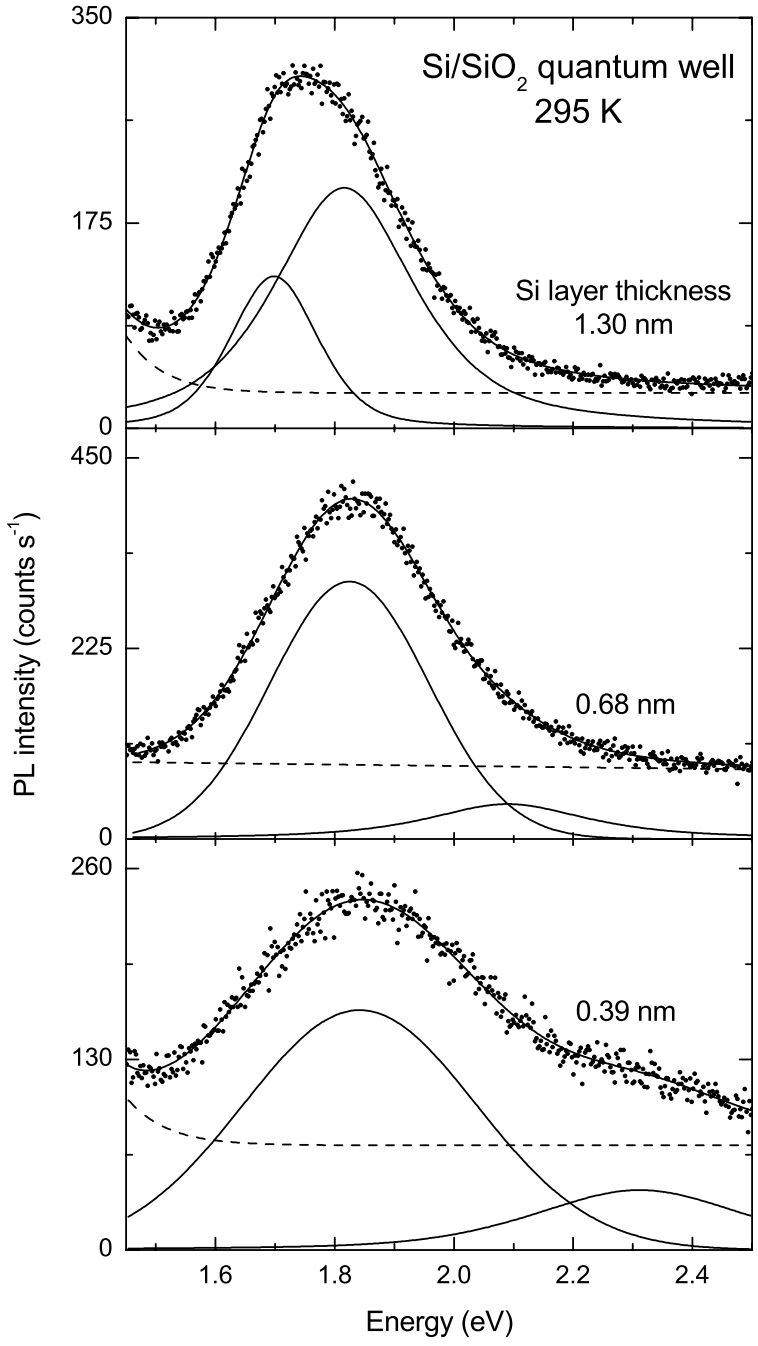

Figure 5. PL shifted (confined) energy peaks and unshifted (interface) energy peaks in three quantum wells. A common peak at 1.8 eV is observed in the three samples and is related to the interfaces. The secondary peak undergoes a blue shift with increased confinement. These particular cases are to be related to the ensemble of QW PL peaks given in Figure 4, above.

QW thickness	Kanemitsu *et al*	Lockwood *et al*
1.70 nm	1.50 eV	-
1.30 nm	1.55 eV	1.7 eV
0.68 nm	-	2.1 eV
0.60 nm	1.80 eV	-
0.39 nm	-	2.3 eV
Interface state energy peak	**1.65 eV**	**1.8 eV**

Table 1. Energy peaks of several quantum wells. The "Interface state energy peak" is the peak that undergoes no shift, while the other values are the shifted energy peaks. Comparison between the former study of Kanemitsu *et al* [6], and this study, are in good agreement.

Table 1 lists the PL energy peaks for these three quantum wells, which are compared with the ones reported previously by Kanemitsu *et al* [6], while Figure 5(a) shows the corresponding photoluminescence spectra for the three particular quantum wells. Two main peaks are clearly visible; one weaker peak that undergo a blue shift from 1.7 eV (for the 1.3 nm QW), to 2.1 eV (the 0.68 nm QW), and finally to 2.3 eV (the 0.39 nm QW). The stronger PL peak located at 1.8 eV remains unshifted in all QWs and is omnipresent; it is thus attributed to interface states. This is consistent with the observation of Kanemitsu *et al* [6] who obtained similar features but at a different strong PL peak energy, i.e., located at 1.65 eV while the weak peaks related to the confinement are blue shifted from 1.50 eV (for the 1.7 nm QW), to 1.55 eV (the 1.3 nm QW), and finally to 1.80 eV (the 0.6 nm QW), corresponding to a slight underestimation of ~0.15 eV compared to this work. See Table 1 for the direct comparison.

Figure 6 shows the calculated partial densities of states of the four types of Si atoms present in the SLs, for two Si well thickness that contains 5 and 9 Si monolayers (i.e., QWs respectively 1.1 nm and 1.7 nm thick). The Si^0 are bulk-like Si atoms located inside the Si well while the Si^{1+}, Si^{2+}, and Si^{3+} are Si atoms located at both interfaces (respectively bonded to one, two and three oxygen atoms). This calculation of the partial DOS gives several insights on the *joint* density of states involved when a calculation of the absorption coefficient based on the application of the Fermi Golden rule is performed. One observes in Fig. 6 that for both SLs, the DOS in the valence bands are dominated by the interface suboxides Si atoms Si^{1+} and Si^{2+}. These two interface Si atoms should thus dispense higher transition rates than the bulk-like Si atoms located inside the well. We also observe that the first maximum just below the Fermi level in the 1.1 nm QW is downshifted by ~0.1 eV, compared to the first one in the 1.7 nm QW, while the energy gap difference between these two Si wells is approximatively increased by the same amount; the *joint* DOS should thus lead to a constant energy peak. However, to be complete, the *joint* DOS of each atom should directly be examined in the future, as well as their corresponding matrix elements, in order to get precise knowledge of these atomic transitions. Further types of Si/SiO_2 interface defects, such as dangling bonds, hydrogen incorporation or P_b centers should be considered in future superlattice models, in order to evaluate their consequences on the optical properties of the QW structures.

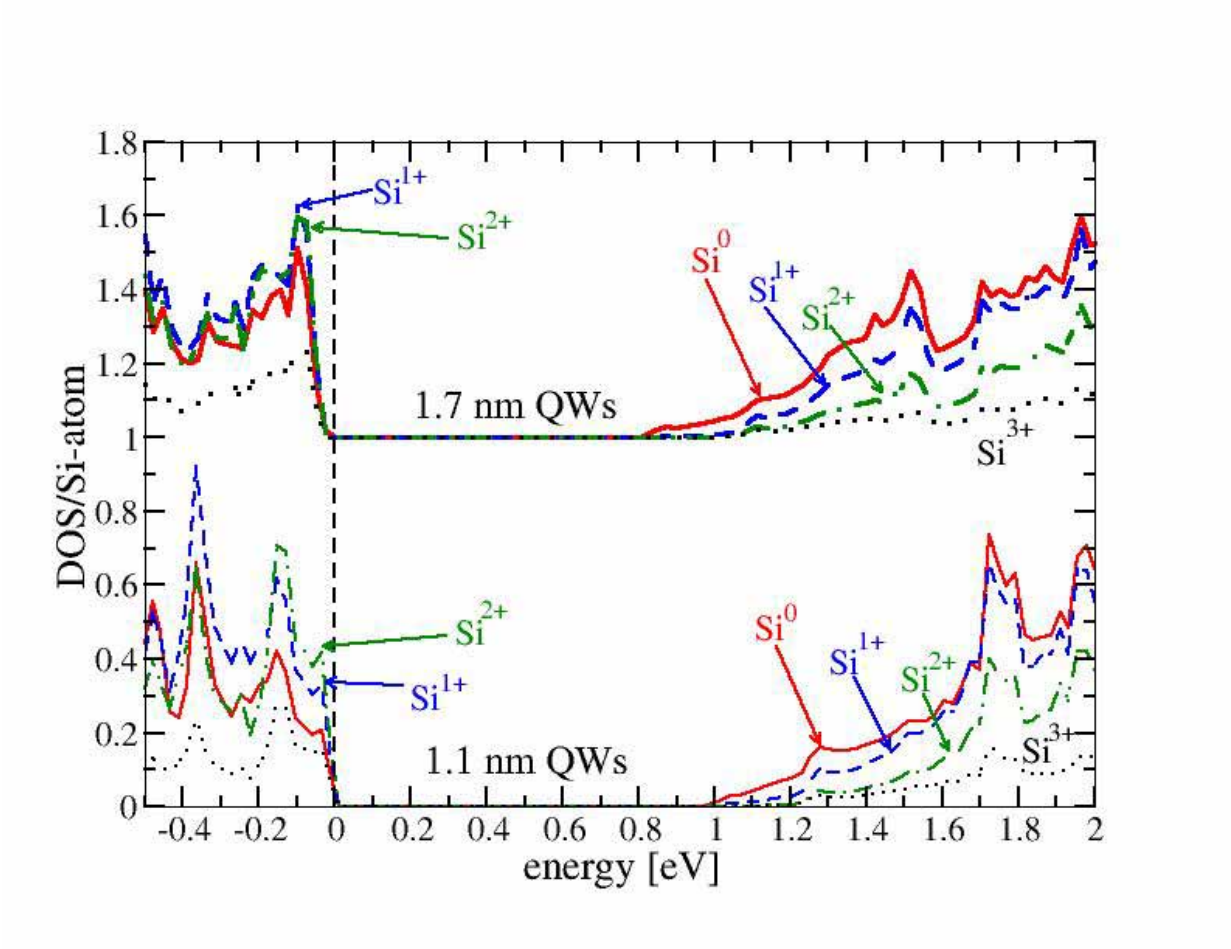

Figure 6. Densities of states of bulk-like Si atoms and suboxide Si atoms located at both interfaces in two quantum wells, 1.1 nm and 1.7 nm thick, within the LDA (one should thus add 0.6 eV in order to get realistic energy values).

CONCLUSIONS

The enhancement of the luminescence as well as the blue shift with increased confinement in Si/SiO_2 QWs have been confirmed from both the theoretical and the experimental sides. XANES measurements of several QWs and 2p core absorption calculations of several models have demonstrated the presence of strongly confined states. Interface states have been observed in the experiments and some insights are obtained from the valence bands DOS that lead to stronger optical transitions due to interface suboxide Si atoms. Clear evidence of interface states should be considered with the help of new models having various types of Si/SiO_2 interface defects.

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