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1999 J. Phys.: Condens. Matter 11 1927

(http://iopscience.iop.org/0953-8984/11/8/006)

J. Phys.: Condens. Matter **11** (1999) 1927–1934. Printed in the UK PII: S0953-8984(99)98609-5

Interface-related restriction to potential depth estimates for single Si/SiO_2 quantum wells

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Received 21 October 1998, in final form 5 January 1999

Abstract. We compare the difference between the energy levels of electrons and holes in single Si/SiO_2 quantum wells calculated within an abrupt-interface picture and by considering the existence of few SiO_x interfacial monolayers at the well borders. Our results indicate a strong interface-related restriction to potential depth estimates for actual single Si/SiO_2 quantum wells based on explaining experimental data with a finite-square-quantum-well model. Overestimation of the potential depth by as much as 2.1 eV and 3.1 eV for electrons and holes, respectively, may result.

The discovery of room temperature photoluminescence (PL) in porous silicon by Canham [1] has stimulated many efforts to obtain an understanding of silicon-based confinement systems in view of their potential for technological applications [2–10]. Particularly interesting is the proposal made by Tsu [11] of Si/SiO_2-based two-dimensional quantum wells (QWs), in which very thin SiO_2 barriers (a few nanometres wide) can confine carriers in a crystalline (c-Si) or amorphous (a-Si) silicon region of width L. Several authors have demonstrated PL from these structures [9, 12–16]; it is generally explained by resorting to confinement effects in sharp quantum wells, despite controversial aspects related to surface chemistry and interface states [9, 16].

One of the key parameters in the description of the PL observed in single Si/SiO_2 QWs is the depth of the electron and hole confinement potentials, V_e and V_h respectively, whose precise values are far from being agreed upon. Early attempts have estimated V_e to lie in the large range 0.25 eV–3.2 eV [17, 18]. More recently, using high-resolution x-ray photoelectron spectroscopy, Alay and Hirose [19] have evaluated the Si/SiO_2 hole barrier height as 4.49 eV and 4.43 eV, respectively, for their dry and wet $Si(100)/SiO_2$ interfaces. On the other hand, Tsu *et al* [20] have estimated an effective electron barrier height of over 1 eV. They have used theoretical expressions based on a double-barrier square potential to fit current–voltage measurements for a Si/SiO_2 structure with 1.1 nm of epitaxially grown silicon. Ding and Tsu [21] have reported an even lower estimate, in the range 0.51–0.57 eV, for the effective electron barrier height. Their estimate was based on an Arrhenius plot of temperature-dependent current–voltage characteristics and on theoretical expressions obtained by considering an abrupt-interface model. When performing theoretical calculations, the values most commonly used nowadays for the confinement potential depth for electrons and for holes in Si/SiO_2 confinement systems are 3.2 eV and 4.6 eV, respectively [3, 6–9].

0953-8984/99/081927+08$19.50

A common feature of the great majority of present theoretical research on Si/SiO_2 QWs properties is the assumption that the interfaces are very sharp (abrupt). The existence of non-abrupt interfaces has been systematically neglected in studies of quantum confinement effects in Si/SiO_2 QW systems [15, 16, 22–24]. However, for over twenty years now, there has been strong evidence of the non-abrupt nature of Si/SiO_2 interfaces [25]. A revision of early work on Si/SiO_2 interface effects was published by Ando, Fowler, and Stern [26]. In particular, Stern [27] originally used a graded Si/SiO_2 interface model to study the effect of a thin transition layer at a Si/SiO_2 interface on electron mobility and energy levels. More recently, Ngueyen *et al* [28] have carefully characterized interface regions in Si/SiO_2 systems using spectroscopic ellipsometry, obtaining a mean interface thickness $\sigma = 2.2$ nm for their samples. Kim *et al* [29] listed several experiments where Si/SiO_2 transition layer widths were reported to be in the range 0.5 nm–25.0 nm for a variety of oxides, depending on the sample processing conditions, as well as on the growth direction. Lockwood *et al* [15] have also concluded that the x-ray reflectivity curves of their high-quality Si/SiO_2 samples indicated interfacial widths (σ) such that 1.4 nm $< \sigma$(a-Si) $<$ 11 nm, 0.4 nm $< \sigma(SiO_2) <$ 0.8 nm, scaling roughly with the thickness of the a-Si layers.

In this work, we investigate the consequences of using an abrupt-interface picture to explain the experimental data with the aim of estimating the potential depth of single Si/SiO_2 QWs. We show that single Si/SiO_2 QW energy levels can be strongly overestimated when calculated within an abrupt-interface picture, since the actual interfaces of single Si/SiO_2 QW samples are not sharp, and their control may strongly depend on the experimental growth or deposition technique used. This imposes a striking interface-related restriction on potential well depth estimates for these systems when theoretical calculations performed within the abrupt-interface picture are used to fit experimental data.

Since carrier confinement is the main characteristic of semiconductor QWs, their borders have to be defined in such a way that their localization determines precisely the region where the carrier can be confined. Accordingly, the external non-abrupt quantum well borders in our Si/SiO_2 QW model coincide with those of the abrupt quantum well, as shown in figure 1. The

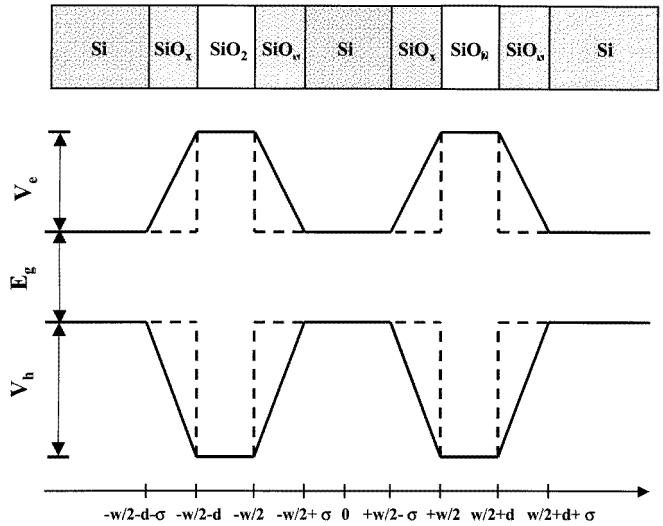

Figure 1. The picture of a single non-abrupt Si/SiO_2 quantum well, indicating the distinct regions of pure Si, SiO_x, and pure SiO_2.

interfacial regions of width σ are constituted of intermediate-composition SiO_x layers, where $x \to 0$ ($x \to 2$) at the border of the pure Si (SiO_2) region. It is important to mention here that in this work we do not aim or attempt to model and describe the microscopic and/or atomistic nature of the Si/SiO_2 interfacial region.

Grunthaner and Grunthaner [25] have extensively discussed and elucidated many experimental and theoretical aspects of the nature of these SiO_x layers. A few years later, several papers by Pasquarello *et al* [4], Chelikowsky and co-workers [5], and Tit and Dharmawardana [10] described first-principle investigations of structural and electronic properties of the Si/SiO_2 interface, the SiO_x layer, Si clusters, and nanocrystals. Although a number of new and interesting results arose from these theoretical works, not much information on quantum confinement has been presented as a result of these atomistic models, and in particular related explicitly to Si/SiO_2 QWs. Also, Delerue, Allan, and Lannoo [6] have assumed recently the existence of intermediate-composition SiO_x layers in their study of the electronic and optical properties of porous silicon crystallites and wires. Due to the absence of experiments on the energy gap and carrier effective mass in thin SiO_x films, we argue for the existence of SiO_x layers in our interface description by assuming a linear variation of both the carrier confinement potential and effective mass through the Si/SiO_2 interfaces. Figure 1 shows the non-abrupt confinement wells for electrons and holes, where the Si, SiO_x ($0 < x < 2$), and SiO_2 regions are also indicated.

To investigate effects on the carrier energy levels due to the conduction band discontinuity at Si/SiO_2 QW interfaces, we assume that the confinement potential depths for electrons and holes may vary in the ranges $0.5\ \text{eV} < V_\text{e} < 3.2\ \text{eV}$ and $0.5\ \text{eV} < V_\text{h} < 4.6\ \text{eV}$, respectively. We have used the effective-mass theory to calculate the electron and hole energy levels due to the quantum confinement [30]. Since the electron (hole) effective mass $m_{\text{e (h)}}$ is position dependent, $m_{\text{e (h)}} = m_{\text{e (h)}}(z)$, we have resorted to the position-dependent kinetic energy operator of BenDaniel and Duke [31], $\hat{p}\,[m(z)]^{-1}\,\hat{p}$, to obtain Schrödinger-like equations which describe our single Si/SiO_2 QWs. They are solved numerically by means of the multistep formulation of Ando and Itoh [32]. Continuity conditions are imposed on $\Psi_{\text{e (h)}}(z)$ and $[m_{\text{e (h)}}(z)]^{-1}\,\mathrm{d}\Psi_{\text{e (h)}}(z)/\mathrm{d}z$ at the interface borders $\pm(w/2) \pm d \pm \sigma$, $\pm(w/2) \pm d$, $\pm(w/2)$, and $\pm(w/2) \mp \sigma$, where w, d, and σ are the widths of the Si well, SiO_2 barriers, and SiO_x interfaces, respectively (see figure 1). We consider the electron and hole effective masses in silicon as, respectively, $m_{\text{e,Si}} = [m^{\text{L}}_{\text{e,Si}} m^{\text{T}}_{\text{e,Si}}]^{1/2}\, m^* = 0.4315\, m^*$ and $m_{\text{h,Si}} = 0.3\, m^*$, where $m^{\text{L}}_{\text{e,Si}}$ ($m^{\text{T}}_{\text{e,Si}}$) is the longitudinal (transverse) electron effective mass in silicon, and m^* is the electron effective mass in the free space [33]. In the case of silicon dioxide, there is considerable uncertainty in estimations of the conduction band effective mass [34–36]. In this work, we have assumed $m_{\text{h,SiO}_2} = 0.24\, m^*$.

Several combinations of interface width and depth of the carrier confinement potential can be linked to the same carrier ground-state energy level. Figure 2 presents isoenergetic lines in the σ–$V_{\text{e (h)}}$ space for allowed ground states of electrons (left) and holes (right) in a Si/SiO_2 QW 1.1 nm wide. By disregarding the existence of SiO_x interfaces, we see that the ground-state electron (hole) energy level is ~446 meV (~412 meV) if $V_\text{e} = 3.0$ eV ($V_\text{h} = 4.0$ meV). Supposing that an actual Si/SiO_2 QW sample, 1.1 nm wide, has interface widths of 0.3 nm, the same figures (as in the sharp-interface case) for the electron and hole ground-state energy levels are obtained if $V_\text{e} \sim 1.0$ eV ($V_\text{h} \sim 1.0$ eV). The strong overestimation of the carrier energy levels due to the abrupt-interface picture may be reflected in different experimental evaluations of the effective barrier height, since actual Si/SiO_2 QW interfaces are not sharp. This is particularly true when referring to theoretical calculations based on square-barrier and square-well models to explain the experimental data. In addition, the fact that different growth techniques may yield Si/SiO_2 systems with quite different interface widths and profiles [29]

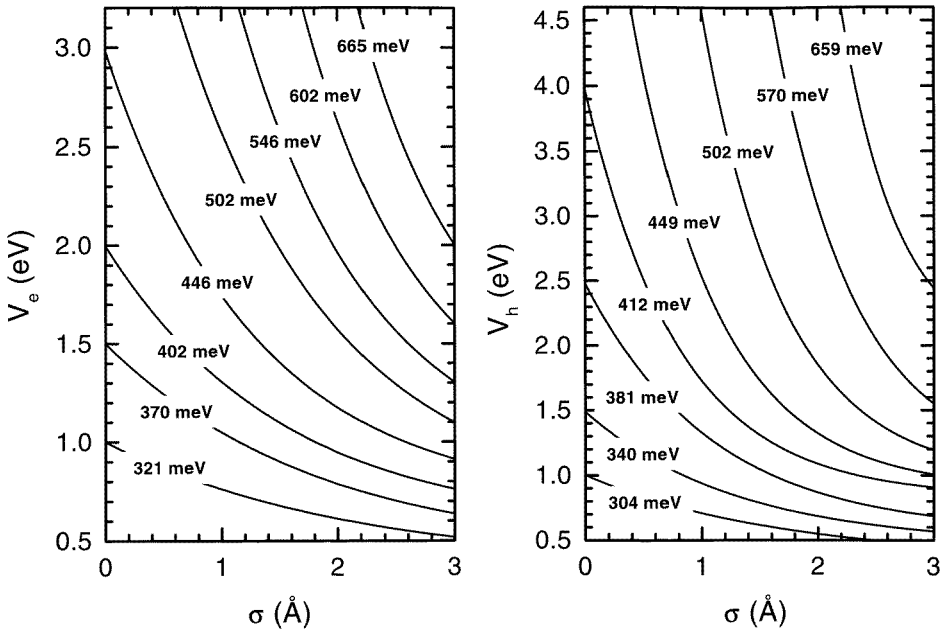

Figure 2. The electron (left) and hole (right) ground-state energy dependence on the interface width σ and on the depth of the confinement potential in single non-abrupt Si/SiO_2 QWs. The single abrupt Si/SiO_2 quantum well is 1.1 nm wide.

strongly suggests that care should be taken when analysing photoluminescence data from Si/SiO_2 confinement systems, in particular when comparing samples containing epitaxial and amorphous silicon layers [9].

We have also investigated the effects of the interface width and well potential depth on the lowest recombination energy ($E_{e,0} - E_{h,0}$) of electrons and holes in single Si/SiO_2 QWs that are 1.1 nm and 3.0 nm wide. Depending on the sample fabrication process, discrepancies as regards the energies of the photoluminescence peaks may be observed. In our ($E_{e,0} - E_{h,0}$) recombination energy calculations, we have incorporated the band-gap dependence of thin (<5 nm) Si/SiO_2 systems on the width of the confinement structure. According to Delley and Steigmeier [23], the gap energy in two-dimensional single Si/SiO_2 slabs varies as

$$E_g = 1.142 + 0.356(1/L) + 0.363(1/L^2)$$

where L is the confinement width in nanometres [30]. Figure 3 shows the dependence of the recombination energy ($E_{e,0} - E_{h,0}$) on the depth of the confinement potential for interface extensions of 0 nm (solid), 0.1 nm (dashed), and 0.2 nm (dotted). It can be clearly seen from figure 3 that ($E_{e,0} - E_{h,0}$) increases when the interfaces become thicker, but decreases when the Si/SiO_2 QW becomes wider. For the same value $V_e = 3.2$ eV of the electron confinement potential, the recombination energy is underestimated by 400 meV and 120 meV when the existence of 0.3 nm interfaces is disregarded for Si/SiO_2 QWs 1.1 nm and 3.0 nm wide, respectively.

The abrupt-interface definition that we have used in this paper seems to be appropriate, since actual Si/SiO_2 QWs must be considered to begin with the existence of the first intermediate SiO_x interfacial layer, and their external borders must coincide with those of a hypothetical abrupt well. This abrupt-interface localization was used previously by Proctor *et al* [37] to

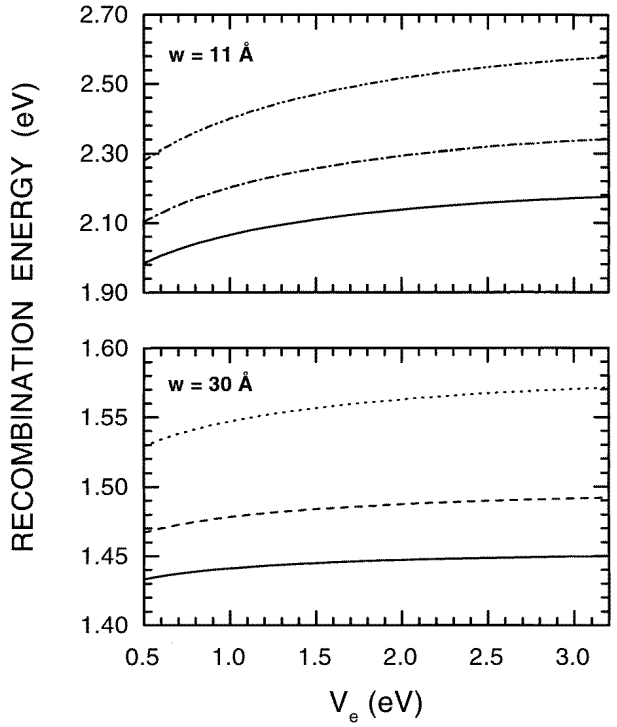

Figure 3. The $(E_{e,0} - E_{h,0})$ recombination energy dependence on the depth of the confinement potential for interface extensions of 0 nm (solid), 0.1 nm (dashed), and 0.2 nm (dotted). The single abrupt Si/SiO_2 quantum well is 1.1 nm wide (top), and 3.0 nm wide (bottom).

explain electron energy level measurements for a $GaAs/Al_xGa_{1-x}As$ quantum well. However, it is important to comment that most of the previous work on interface effects in semiconductor quantum wells took into account the fact that it is the middle of the interfacial regions in non-abrupt quantum wells that determines the abrupt-quantum-well interface positioning used in the comparison [38]. We argue that this usual abrupt-interface positioning should be considered in fact as a definition of an *abrupt equivalent quantum well* (AEQW), i.e. an abrupt well with an effective width $L_{\rm eff} = w - \sigma$ whose energy levels are as close as possible to those of its associated non-abrupt quantum well. Figure 4 depicts the difference $\Delta E = E_{\rm NA} - E_{\rm AEQW}$ between electron energy levels in a Si/SiO_2 QW that is 30 Å wide with $V_e = 3.2$ meV. $E_{\rm NA}$ is calculated by considering the non-abrupt-interface model of this work, while $E_{\rm AEQW}$ is obtained within the AEQW picture. We show that the description of actual graded Si/SiO_2 QWs that are 30 Å wide (with interface widths of 10 Å) within the AEQW picture ($L_{\rm eff} = 20$ Å) leads to underestimation of the ground and first excited electron energy levels by more than 295 meV and 96 meV, respectively.

Figure 5 presents the isoenergetic lines in the σ–$V_{e\,(h)}$ space for allowed ground states of electrons (left) and holes (right) in a Si/SiO_2 QW that is 1.1 nm wide calculated within the AEQW picture. Comparing figures 2 and 5, we see that a considerably smaller uncertainty of the well depth is obtained under the hypothesis that the experimentally determined Si/SiO_2 QW width (its mean value) is close to the AEQW width. This means that potential depth estimates of actual single Si/SiO_2 QWs depend on data concerning their interfaces, at least those related to their width and the localization of their borders.

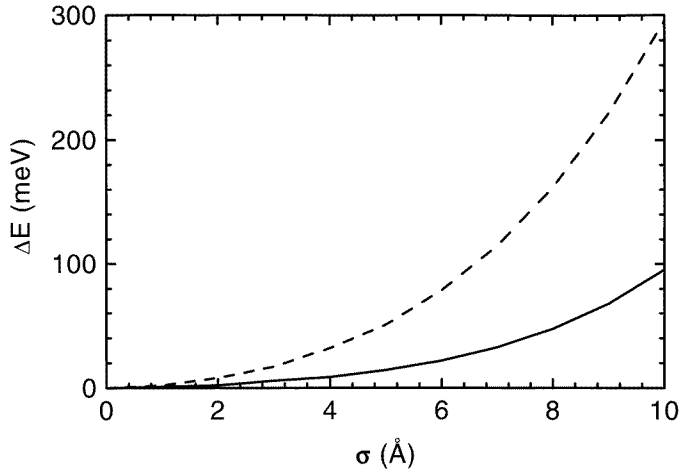

Figure 4. The difference $\Delta E = E_{\mathrm{NA}} - E_{\mathrm{AEQW}}$ between the ground (solid) and first excited (dashed) electron energy levels calculated considering the non-abrupt-interface model of this work (E_{NA}) and within the AEQW picture (E_{AEQW}). The Si/SiO_2 QW width is 30 Å, and the potential depth is $V_e = 3.2$ meV.

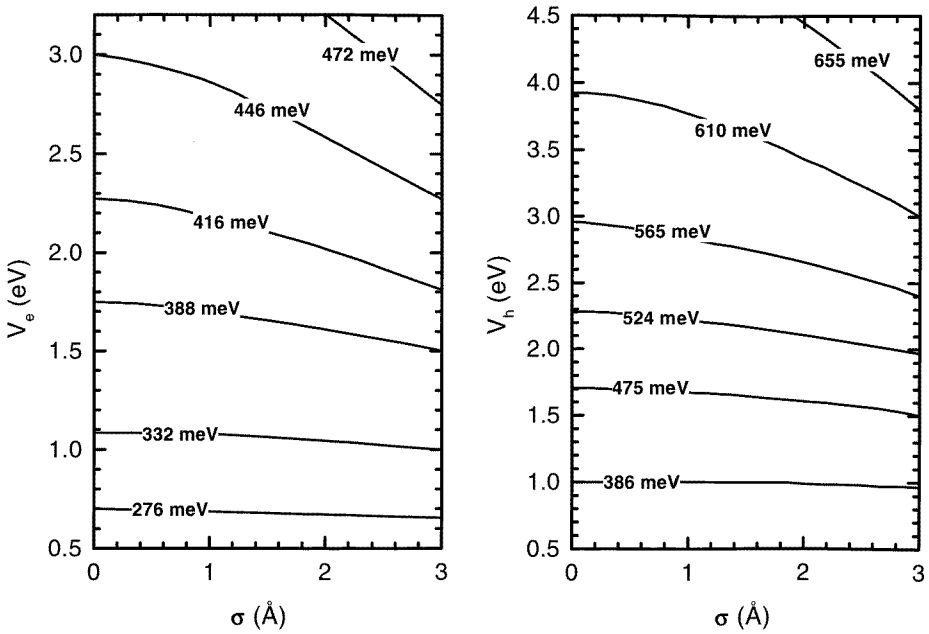

Figure 5. The ground-state energy dependence of electrons (left) and holes (right) on the interface width σ and on the depth of their confinement potential in single non-abrupt Si/SiO_2 QWs. The calculations were made considering the abrupt-well position at the middle of the interface region. The single abrupt Si/SiO_2 quantum well is 11 Å wide.

Since Si/SiO_2 QWs fabricated through different processing techniques have different interface characteristics (width, SiO_x interfacial profile, strain), our results allow us to reason that the interface characteristics are an important factor for the understanding of why PL

experiments performed on samples fabricated by different techniques may produce distinct blue-shifts of the PL peak, as recently reported for crystallized hydrogenated amorphous silicon (a-Si:H), separation by implanted oxygen (SIMOX), and porous silicon samples [9]. Our results are in good agreement as compared with the room temperature PL spectra of Si/SiO_2 superlattices obtained by Lockwood *et al* [15], who found a blue-shift of about 600 meV as the silicon layer thickness was reduced from 3.0 nm to 1.0 nm.

In conclusion, we have performed a study on interface-related restrictions to potential depth estimates for single Si/SiO_2 QWs. Our results indicate a strong overestimation of the confinement potential depth for electrons and holes, for samples fabricated with present technology, when an abrupt picture is used to explain the experimental data. For the case of $(E_{e,0}-E_{h,0})$ recombination energy, an underestimation of several hundred meV may result if an abrupt-interface picture is considered. The results suggest the need for a better characterization of Si/SiO_2 interfaces in thin QWs, and important limitations of the abrupt-interface model commonly used currently to describe the properties of single-Si/SiO_2-QW samples.

Acknowledgments

The authors would like to thank G D Wilk, from Texas Instruments, for providing information about the uncertainty in the current estimation of the SiO_2 hole effective mass. J S de Sousa is sponsored by a graduate fellowship from the Brazilian Ministry of Education at the Physics Department of the Universidade Federal do Ceará. GAF, VNF, and EFS Jr would like to acknowledge the financial support received during the development of this work from the Science Funding Agencies of the Ceará and Pernambuco states in Brazil (FUNCAP and FACEPE, respectively), the Brazilian National Research Council (CNPq), and the Ministry of Planning (FINEP) under PADCT/SDRI contract No 77.97.1120.00 3235/97.

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