Mat. Res. Soc. Symp. Proc. Vol. 677 © 2001 Materials Research Society

Electronic and Optical Properties of Si/SiO_2 Superlattices from First Principles : Role of Interfaces.

Pierre Carrier[1], Gilles Abramovici[1,2], Laurent J. Lewis[1] and M. W. C. Dharma-wardana[3]
[1]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, Canada H3C 3J7
[2]Laboratoire de Physique des Solides, associé au C.N.R.S., Université Paris Sud, Centre d'Orsay, 91405 Orsay, France
[3]Institute for Microstructural Sciences, National Research Council, Ottawa, Canada K1A 0R6

ABSTRACT

The observation of intense luminescence in Si/SiO_2 superlattices (SLs) has lead to new theoretical research on silicon-based materials. We have performed first-principles calculations using three Si/SiO_2 SL models in order to examine the role of interfaces on the electronic structure and optical properties. The first two models are derived directly from crystalline structures and have simple interfaces. These models have been studied using the full-potential, linearized-augmented-plane-wave method, in the local-density-approximation (LDA). The optical absorption within the interband transition theory (excluding excitonic effects) have been deduced. The Si(001)-SiO_2 interface structure is shown to affect the optical behaviour. Following these observations, we have considered a more realistic, fully-relaxed model. The projector-augmented-wave method under the LDA is used to perform the structural relaxation as well as band structure and optical calculations. The role of confinement on the energy gap is studied by inserting additional silicon slabs into the supercell. Direct energy gaps are observed and the energy gap is found to decrease with increasing silicon slab thickness, as observed experimentally. The role of the interface has been considered in more details by studying the contribution to the energy gap of Si atoms having different oxidation patterns; partially oxidized Si atoms at the interface, as well as Si atoms inside the Si layer, are shown to contribute to the transitions at the energy gap.

INTRODUCTION

Lu *et al* [1], and many others [2] have reported enhanced luminescence in the visible part of the spectrum of Si/SiO_2 superlattices (SLs). A shift of the energy spectrum towards the blue is observed when the thickness of the Si layers is reduced from 6 to 2 nm. In contrast to porous silicon [3], Si/SiO_2 SLs present the advantage of being stable, with no significant decrease of the luminescence observed with time. From this experiment, it can be inferred that confinement plays a major role on the optical enhancement of SLs. However, confinement cannot explain the whole optical mechanism. It has been observed in experiments by Kanemitsu [4], and from first-principles calculations performed by Kageshima [5], that the Si(001)-SiO_2 interface plays as well, a non-negligible role on the optical properties of the SLs. It is worth noticing that Si and SiO_2 are both already standard components of MOSFETs and other devices where the Si(001)-SiO_2 interface is of great interest; optical properties of Si(001)/SiO_2 SLs and their Si(001)-SiO_2 interfaces can give insights on the (single) MOSFET interface structure [6].

Motivated by these promising experimental observations, and to provide insight into the microscopic physics associated with the luminescence efficiency of Si based devices, we have carried out detailed first-principles investigations of the electronic and optical properties of Si/SiO_2 SLs. The electronic-structure calculations were carried out within two approaches: the full-potential, linearized-augmented-plane-wave (LAPW) method implemented in the WIEN97 package [7] and the projector-augmented wave (PAW) approach [8] implemented in the VASP package [9]. Determination of the optical variables, such as the dielectric function (ε) and the absorption coefficient (α), are carried out within the interband theory (excluding excitonic effects which are important only at very small carrier densities) [10].

MODELS

Three models (and some modifications of these) are considered. The first two are constructed by superposing the diamond-Si structure onto the β–cristobalite SiO_2 (Fd3m group) structure. They differ in the way dangling bonds are satisfied at the interfaces: the *double-bond model* (DBM) proposed by Herman and Batra [11] and depicted in figure 1(a) has double Si=O bonds at the interfaces; the *bridged-oxygen model* (BOM) introduced by Tit and Dharma-wardana [12], and shown in figure 1(b), has one oxygen that bridges two Si atoms at the interfaces, with Si-O-Si angles of 144° (as measured in silica). The resulting unit cell dimensions are based on experimental lattice constants. The BOM has 21 atoms while the DBM has 23.

The third model is based on a Si(001)-SiO_2 interface study performed by Pasquarello et al [13]; the SL structure is obtained by applying a symmetry-rotation operation of the supercell; this gives rise to the so-called *partially relaxed structure* (PRM) used by Tran, Tit and Dharma-wardana [14]; a final relaxation leads to the *fully relaxed model* (FRM). In order to assess the effect of confinement on the energy spectrum, two additional layers of crystalline Si atoms have been introduced in the supercell, thus varying the thickness of the Si-slab from ~0.8nm,

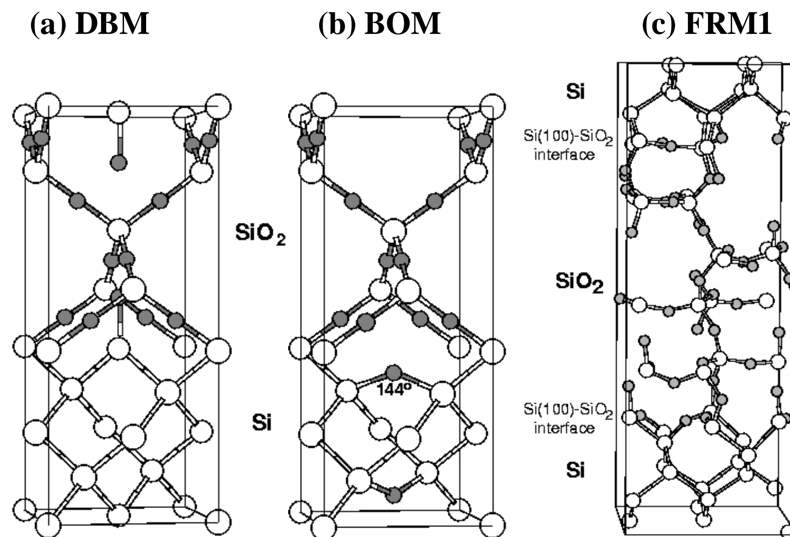

Figure 1. The three supercell models : (a) the double-bond; (b) the bridged-oxygen with a 144° Si-O-Si bridge angle at the interface; and (c) the fully relaxed (FRM1).

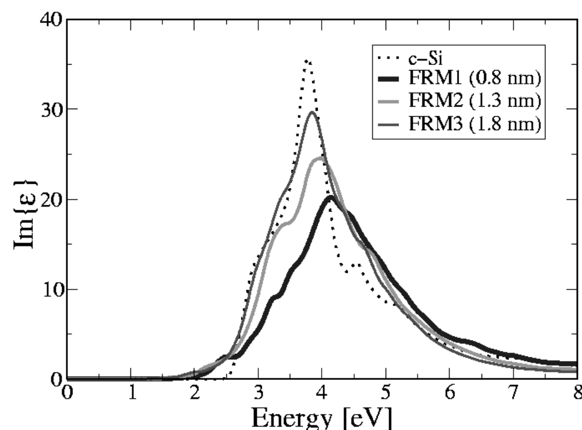

Figure 2. Dielectric function (*z* component, or the growth axis) of the *fully relaxed models*.

to ~1.3 nm, and to ~1.8 nm. The SiO_2 thickness is ~1.6 nm in all three models. All supercells are structurally relaxed; they are refered to, hereafter, as FRM1, FRM2 and FRM3. Figure 1(c) shows the FRM1 having 96 atoms (52 Si atoms and 44 O-atoms); 16 more Si atoms are added in the FRM2, and 16 more in the FRM3.

RESULTS and DISCUSSION

The nature of the energy gap is *direct* in both the FRM2 and FRM3, on the whole Γ−Z axis of the Brillouin zone, but *nearly direct* for the FRM1 (with only 0.12 eV between the direct and indirect energy gap at Γ). The values of the energy gaps are 0.99 eV, 0.81 eV and 0.68 eV for the FRM1, FRM2 and FRM3, respectively. The position of the *minimum* gap transition is thus blue shifted with increasing confinement. Energy bands are dispersionless in all growth axis of the BZ, which shows that the confinement is not due to impurity states; it is due to the *quantum* nature of the electronic states, in a periodic layer. Dispersionless energy bands are as well observed in both the DBM and the BOM. Their band gaps are nearly direct (0.86 eV for the DBM and 1.5 eV for the BOM). However, gap states are observed in the BOM, showing that complete relaxation of the structures are necessary to get realistic optical results, as further discussed below. In order to get a complete picture of *all* possible transition probabilities, calculation of the imaginary part of the dielectric function has been performed, using the Fermi Golden Rule and the interband approach [10]. The integration in the BZ is done by summing over all tetrahedra [15]. Figure 2 shows the overall picture of the *z* component of the dielectric function. The shift towards the blue with increasing confinement is indeed visible and for all the FRMs, the functions slowly increase, starting from their respective band gaps, and then remain *significantly* higher than that of c-Si, around 2 eV. The onset for c-Si happens only at 2.52 eV. It is well known that the LDA and interband approaches lower the first (of two) main peak of the dielectric function for c-Si; interacting electron-hole calculations (using e.g. the Bethe-Salpeter equations) would capture this peak (see for instance [16]). However, such calculations are prohibitive for the models considered here. As a result, electron-hole interactions would *enhance* the effects for c-Si as well as for the FRMs and this would lead to the same conclusion that the optical properties are higher for all the SL models as compared to c-Si.

In order to understand the role played by the interfaces on the optical properties of the SLs,

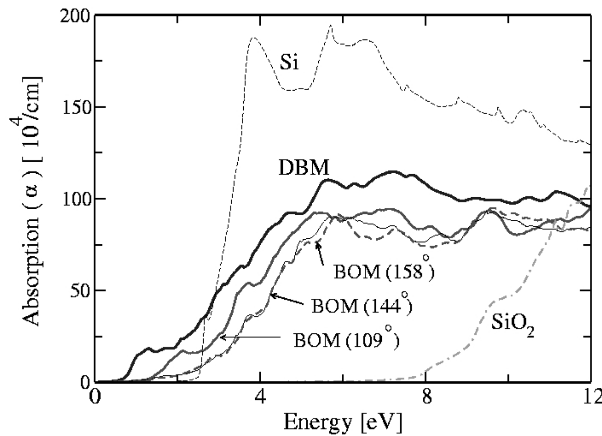

Figure 3. Absorption of the DBM and BOM as compared to bulk Si and bulk SiO_2. The role of the interface can be appreciated from the differences at the onset.

we have compared the absorption coefficient of the DBM with the BOM and have considered Si-O-Si bridging angles other that 144° at the interfaces of the BOM [see figure 1(b)], namely: 109° and 158°. The results are summarized in figure 3. We see, first, that the onset of absorption for the DBM and the BOM (with 144°) are quite different; we thus conclude that absorption is sensitive to the interface chemical bonds. Second, a comparison of the BOMs having different interfacial Si-O-Si bridging angles shows that the distorsion of the partially oxidized Si atoms at the interface modify, as well, the optical properties [compare for instance the absorption of the BOM (144°) with the BOM (109°) in figure 3].

Given these observations, we undertook a detailed analysis of the interface structure of the FRM. Si atoms can have five possible oxidation states – if nearest-neighbours only are taken into account. Figure 4 shows the five tetrahedra and the corresponding bondlengths, as they appear in the FRM1. We define the interface to be formed by *all* Si atoms having suboxide bonds (Si^{+1}, Si^{+2}, Si^{+3}). Experiments have shown [17] that suboxide Si atoms at the Si/SiO_2 interface are almost equally distributed – with a slightly higher distribution for the (Si^{+3}) atoms. The interface of the FRMs have been constructed assuming, for simplicity, an equal distribution of the suboxide Si atoms.

The Si-O bondlengths and Si-O-Si angles at the interface of the BOM have been shown to affect the optical properties. This is confirmed by noticing that the Si-Si and Si-O bondlengths

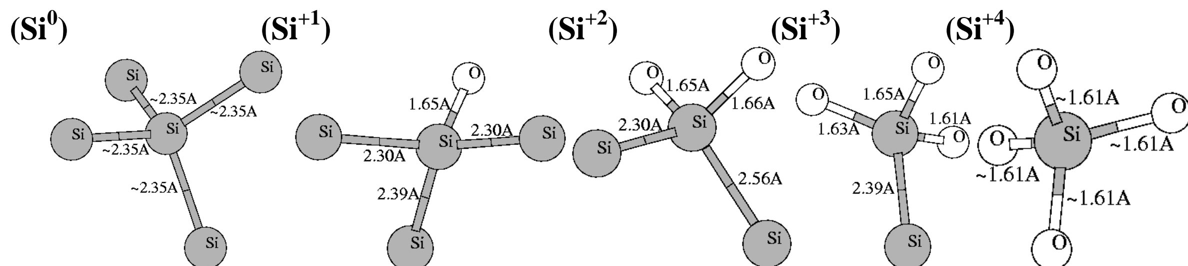

Figure 4 : Five oxidation states of Si atoms in the FRM1, calculated from the PAW method. The bondlengths do not differ greatly in the FRM2 and FRM3. The suboxide Si atoms (Si^{+1}, Si^{+2} and Si^{+3}) define the interface.

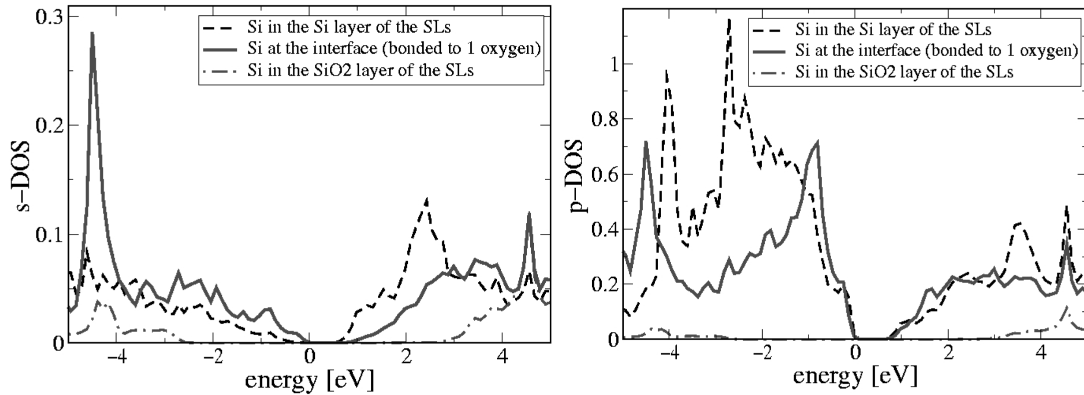

Figure 5 : s-DOS and p-DOS (in the FRM3) of one Si^{+1} at the interface compared to Si^{0} and Si^{+4} atoms in the center of their respective layers (see the text).

of the suboxide Si atoms of the *fully relaxed* structures are greatly modified (see figure 4): the Si-Si and Si-O bondlengths of the (Si^{+1}), (Si^{+2}) and (Si^{+3}) atoms in figure 4 depart from the Si-Si bondlengths of (Si^{0}) being normally ~2.35Å, as well as the Si-O bondlengths of (Si^{+4}), being normally ~1.61Å. Simple counting of the different oxidation states in the three FRMs can account for the influence of the interface on the energy gap. (Recall that the FRM2 and FRM3 were constructed by introducing additional *bulk* Si layers in the FRM1 supercell). The proportion of Si^{0} atoms, from the FRM1 to the FRM2 and finally to the FRM3, increases from 38.5% to 53%, and finally to 62%, respectively. This is, of course, related to the confinement. On the other hand, the proportion of suboxide Si atoms at the interface decreases from 23% to 18% and finally to 14%, respectively. Thus, the interfaces of the FRM1 represent about a 1/4 of the whole system, while for the FRM3, they represent about 1/7 of the whole system. In order to quantify furthermore the importance of interfaces, we have determined the density of s-states and p-states (s-DOS; p-DOS) of a Si^{+1} atom (at the interface) and compared it to the DOS of Si^{0} and Si^{+4} atoms in the center of their respective layers (see figure 4 for the definition of index Si^{m}). We conclude from figure 5 that Si atoms at the interface (Si^{+1}) contribute to the optical transitions at the energy gap, as well as Si^{0} atoms inside the silicon layer do – since their s- and p-DOS are both non-zero at the gap with similar variation of their respective DOS. Furthermore, Si^{+4} in the silica layer do not contribute to the energy gap, but still, contribute to the confinement of the silicon layer. Thus, in addition to Si^{0} atoms in the Si layer, the interface contributes to the optical transitions in the SLs. A quantitative evaluation of the role of suboxide Si atoms on the energy gap is under investigation.

CONCLUSIONS

Using first-principles calculations, we have studied three models for the Si/SiO_2 superlattices; two simple crystalline structures and one fully relaxed structure. Direct energy gaps in the fully relaxed models are obtained and a blue shift of the optical response (the dielectric function) with confinement is observed. The bondlengths of the three partially oxidized Si atoms at the interface (bonded to 1,2 and 3 oxygen atoms) are shown to be modified when compared to their bulk counterparts. Interface atoms, as well as atoms inside the silicon confined layer are shown to contribute to the transitions at the bandgap, and thus, to the optical response (and its blue shift).

ACKNOWLEDGMENTS

It is a pleasure to thank Cristiano Luis Dias, Ralf Meyer and Michel Côté for useful discussions. This work is supported by grants from the Natural Sciences and Engineering Research Council (NSERC) of Canada and the *Fonds pour la formation de chercheurs et l'aide à la recherche* (FCAR) of the Province of Québec. We are indebted to the *Réseau québécois de calcul de haute performance* (RQCHP) for generous allocations of computer resources.

REFERENCES

1. Z. H. Lu, D. J. Lockwood, J.- M. Baribeau, *Nature* **378**, 258 (1995)
2. Y. Kanemitsu, S. Okamoto, *Phys. Rev. B*, **56**, R15561 (1997) ; S.V. Novikov, J. Sinkkonen, O. Kilpelä, S.V. Gastev, *J. Vac. Sci. Technol. B* **15**(4), 1471 (1997); L. Khriachtchev, M. Räsänen, S. Novikov, O. Kilpelä, J. Sinkkonen, *J. Appl. Phys.* **86**, 5601 (1999) ; V. Mulloni, R. Chierchia, C. Mazzeleni, G. Pucker, L. Pavesi, P. Bellutti, *Philos. Mag. B* **80**, 705 (2000) ; Y. Kanemitsu, M. Liboshi, T. Kushida, *Appl. Phys. Lett.* **76**, 2200 (2000).
3. L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990); V. Lehman, U. Gösele, *Appl. Phys. Lett.* **58**, 856 (1991).
4. Y. Kanemitsu, S. Okamoto, *Phys. Rev B* **56**, R15561 (1997).
5. H. Kageshima, K. Shiraishi, *Mat. Res. Soc. Symp. Proc.* **486**, 337 (1998).
6. J. B. Neaton, D. A. Muller, N.W. Ashcroft, Phys. Rev. Lett. **85,** 1298 (2000).
7. P. Blaha, K. Schwarz, J. Luitz, **WIEN97**, Vienna University of Technology 1997. [Improved and updated Unix version of the original copyrighted WIEN code, which was published by P. Blaha, K. Schwarz, P. Sorantin, S.B. Trickey, *Comput. Phys. Commun.* **59**, 399 (1990).]
8. P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994); G. Kresse, D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
9. G. Kresse, J. Furthmüller, **VASP 4.4**, Vienna University of Technology 1997. [Improved and updated Unix version of the original copyrighted VASP/VAMP code, which was published by G. Kresse, J. Furthmüller, *Comput. Mat. Sci.* **6**, 15-50 (1996).]
10. P. Y. Yu, M. Cardona, *Fundamentals of Semiconductors*, page 251, (Springer, Berlin, 1996).
11. F. Herman, I. P. Batra, *The Physics of SiO_2 and its Interfaces,* page 1, ed. by S.T. Pantelides, (Pergamon, Oxford, 1978).
12. N. Tit, M. W. C. Dharma-wardana, *J. Appl. Phys.* **86**, 1 (1999).
13. The initial Si/SiO_2 structure used here to generate the FRMs is the 'Model III' described in A. Pasquarello, M. S. Hybertsen, and R. Car, *Appl. Surf. Sci.* **104/105**, 317 (1996).
14. M. Tran, N. Tit, M. W. C. Dharma-wardana, *Appl. Phys. Lett.***75**, 4136 (1999).
15. P. E. Blöchl, *Phys. Rev. B* **49**, 16223 (1994); G. Gilat, N. R. Bharatiya, *Phys. Rev B* **12**, 3479 (1975); J. Rath, A. J. Freeman, *Phys. Rev. B* **11**, 2109 (1975).
16. S. Albrecht, L. Reining, R. Del Sole, G. Onida, *Phys. Rev. Lett.* **80**, 4510 (1998).
17. Z. H. Lu, M.J. Graham, D. T. Jiang, K.H. Tan, *Appl. Phys. Lett.* **63**, 2941 (1993); F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J.A. Yarmoff, *Phys. Rev. B* **38**, 6084 (1988).