

Accurate prediction of the Si/SiO₂ interface band offset using the self-consistent *ab initio* DFT/LDA-1/2 method

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(Received 31 March 2009; published 23 June 2009)

We use the density functional theory/local-density approximation (DFT/LDA)-1/2 method [L. G. Ferreira *et al.*, Phys. Rev. B **78**, 125116 (2008)], which attempts to fix the electron self-energy deficiency of DFT/LDA by half-ionizing the whole Bloch band of the crystal, to calculate the band offsets of two Si/SiO₂ interface models. Our results are similar to those obtained with a “state-of-the-art” *GW* approach [R. Shaltaf *et al.*, Phys. Rev. Lett. **100**, 186401 (2008)], with the advantage of being as computationally inexpensive as the usual DFT/LDA. Our band gap and band offset predictions are in excellent agreement with experiments.

DOI: 10.1103/PhysRevB.79.241312

PACS number(s): 73.20.At, 71.15.Mb, 71.15.Qe, 71.20.Nr

The quality of the Si/SiO₂ interface is key for the proper operation of field effect transistors, the workhorse of the microelectronics industry. Because this interface has been investigated and perfected for decades, it is also a good test bed for new theoretical techniques aiming to calculate its electronic properties. In particular, density functional theory (DFT) (Ref. 1) with approximated exchange and correlation functionals [e.g., the local-density approximation (LDA)] has been the main theoretical tool in solid-state materials simulations, accurately predicting their ground-state properties at a modest computational cost. However, the calculation of excited states is still a subject of intense research. Of special interest is the calculation of energy band gaps of semiconductors and insulators, which are seriously underestimated under LDA.² Predicting computationally the band alignment across interfaces is even more challenging as it often requires a large number of atoms for the proper description of the interface, thus demanding numerical schemes that scale favorably with this number. Moreover, difficulties in handling interface properties such as stress, defects, electrical dipoles caused by long-range Coulomb interactions, and quantum confinement further limit or even impair our ability to achieve predictive calculations of band offsets. The *GW* approach³ does not suffer from the same fundamental shortcomings as DFT/LDA, and has been successfully applied to model Si/SiO₂ interfaces.⁴ However its considerable computational cost imposes stringent limitations on system size, and therefore poor outcomes from *GW* calculations can be expected for those interface properties that require large systems for their proper description. Recent research in the application of hybrid density functionals to the calculation of band offsets,⁵ despite showing excellent agreement with experimental data for some interface models, indicates that the method is limited by the absence of a systematic approach for determining the optimal parameter for mixing the Hartree-Fock exchange and the LDA exchange correlation in the case of composite systems.⁵

On the other hand, a newly developed technique named LDA-1/2 has been proposed and shown to yield excellent band gaps for a wide range of semiconductors and insulators

at a computational cost comparable to that of regular LDA.⁶ The LDA-1/2 method follows the footsteps of the half-ionization technique (transition state) of individual atoms, which gives excellent values for ionization potentials.⁶ In summary, the LDA-1/2 method consists of subtracting the electron orbital-dependent self-energy $S_\alpha = \int d^3r n_\alpha(\mathbf{r}) V_S(\mathbf{r})$, where both V_S , the atomic self-energy potential, and $n_\alpha(\mathbf{r})$, the electronic density, belong to the one-particle Kohn-Sham state α . The potential V_S can be interpreted as the work to join the charge of a Bloch function into a localized state. It can be shown⁶ that $V_S \approx V(0, r) - V(-1/2, r)$, the difference between the all-electron potentials of the atom and of the half-ion. This potential has a long-range Coulomb tail that is cut by means of a function whose range is such that the resulting fundamental band gap of the crystal is at an extremum. The corrected eigenvalues e_α are then obtained from the solution of the usual Kohn-Sham equation with the pseudopotentials to which we add the cut self-energy potential at each atomic site. It is worth mentioning that the extremization of the fundamental band gap is justified in Ref. 6 by means of a Harris-like functional^{7,8} so that LDA-1/2 does not use arbitrary or adjustable parameters. The cutoff value is not directly related to the atomic radius since its role is to screen the otherwise long-range self-energy potential. Nevertheless, as Fig. 1 illustrates, the optimized cutoff value is close to the extension of the transition state. Figure 1 also shows that the short-range part of the self-energy is not affected by the cutoff function proposed in Ref. 6.

In this work we apply LDA-1/2 to the calculation of the band offsets of two Si/SiO₂ interface models. All calculations were performed with the SIESTA code.⁹ Exchange and correlation were treated at the LDA level using the Ceperley and Alder form.¹⁰ The double *zeta* plus polarization (DZP) basis set was employed in all calculations. Atomic positions were relaxed until the maximum residual force was less than 0.05 eV/Å. Total energy and atomic relaxation were well converged with 18 *k* points in the *xy* plane using the Monkhorst and Pack¹¹ *k*-point sampling technique. To converge the band gaps better than 10 meV we employed 338 *k* points in the *xy* plane. Without further atomic relaxation, the

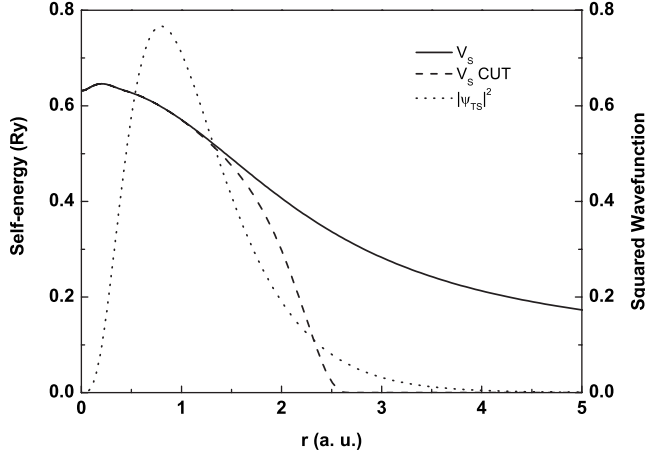


FIG. 1. The radial extension of the atomic O $2p$ transition state (dotted) is comparable to the cutoff applied to the self-energy potential (dashed). The full atomic O $2p$ self-energy potential (solid) is shown for comparison.

eigenenergies were corrected with the LDA-1/2 method which was applied only to the p orbitals of Si and O. LDA-1/2 correction to the s orbitals in the present case changes the eigenenergies negligibly. This is expected since the valence-band edges of the two materials are p type. Being more localized than the conduction band states, the valence-band states have higher self-energies and therefore should be more affected by the reduction in the electron self-interaction brought in by the method.

Our first interface (model I) consists of a β -cristobalite SiO_2 slab ($\beta\text{-SiO}_2$: space group $Fd\bar{3}m$ and calculated bulk lattice parameter $a_{\text{SiO}_2}=7.49$ Å) rotated by $\pi/4$ and strained to fit to the Si (001) lattice vectors (calculated bulk lattice parameter $a_{\text{Si}}=5.43$ Å) along the interface plane xy [Fig. 2(a)]. The resulting SiO_2 lattice vectors along xy are $a_{\text{SiO}_2}=\sqrt{2}\times a_{\text{Si}}=7.68$ Å (2.5% tensile lattice mismatch). We terminated the Si and SiO_2 exposed stack surfaces with hydro-

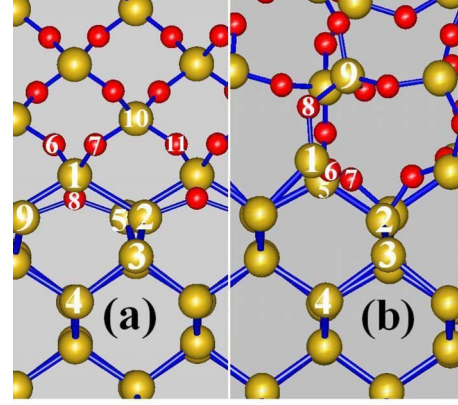


FIG. 2. (Color online) Ball-and-stick DFT-LDA relaxed interface models: (a) β cristobalite (model I) and (b) β tridymite (model II) SiO_2 on the Si (001) surface. Light gray (yellow online): Si; dark gray (red online): O.

gen and separated the periodic images along the normal (z) to the interface by a vacuum slab 20 Å thick. The presence of vacuum allows for some of the tensile (compressive) xy strain to be relieved by shortening (elongating) the oxide along the z direction. The model structural parameters are detailed in Table I. Notice that the bond angles at the interface are smaller than their values in the middle of the SiO_2 slab (inner region), which in turn are larger than their bulk value due to the tensile strain. Bond lengths are elongated at the interface with respect to their inner values. The tensile strain has little impact on the bond lengths away from the interface with respect to their bulk values. Interface I does not display dangling bonds and is the same used in Ref. 4 so that GW and LDA-1/2 results on band gaps and band offsets can be compared.

Our second interface (model II) was proposed previously by Dharma-wardana and co-workers¹² [Fig. 2(b)] and consists of β -tridymite SiO_2 ($\beta\text{-SiO}_2$: space group $P6_3/mmc$ and calculated bulk lattice parameters $a_{\text{SiO}_2}=9.17$ Å,

TABLE I. Bond angles and bond lengths in models I and II calculated at the interfaces, away from them (inn) and from bulk (blk).^a

| Model | Bond angles (deg) | | | Bond lengths (Å) | |
|-------|-----------------------------|------------------------------|-----------------------------------|------------------|------------------------|
| | Si-O-Si | O-Si-O | Si-Si-Si | Si-O | Si-Si |
| I | $\alpha_{9\hat{8}5}=140.5$ | $\alpha_{6\hat{1}7}=109.9$ | $\alpha_{1\hat{2}3}=97.6$ | $d_{58}=1.74$ | $d_{12}=2.56$ |
| | $\alpha_{1\hat{7}10}=150.4$ | $\alpha_{7\hat{1}011}=121.7$ | | $d_{16}=1.70$ | $d_{53}=2.33$ |
| | $\alpha_{inn}=173.0$ | $\alpha_{inn}=114.0$ | | $d_{17}=1.69$ | $d_{23}=2.36$ |
| | $\alpha_{blk}=180.0$ | $\alpha_{blk}=109.5$ | $\alpha_{inn}=\alpha_{blk}=109.5$ | $d_{inn}=1.63$ | $d_{34}=2.35$ |
| | | | | $d_{blk}=1.62$ | $d_{inn}=d_{blk}=2.35$ |
| II | $\alpha_{1\hat{6}5}=153.4$ | $\alpha_{6\hat{5}7}=106.5$ | $\alpha_{5\hat{2}3}=98.3$ | $d_{16}=1.67$ | $d_{23}=2.37$ |
| | $\alpha_{1\hat{8}9}=118.6$ | | | $d_{18}=1.67$ | $d_{34}=2.38$ |
| | $\alpha_{inn}=172.1$ | $\alpha_{inn}=104.2$ | | $d_{89}=1.67$ | $d_{52}=2.29$ |
| | $\alpha_{blk}=179.8$ | $\alpha_{inn}=109.5$ | $\alpha_{inn}=\alpha_{blk}=109.5$ | $d_{inn}=1.64$ | $d_{inn}=d_{blk}=2.35$ |
| | | | | $d_{blk}=1.62$ | |

^aThe corresponding atom numbers are indicated in Fig. 2.

TABLE II. Bulk and stack Si and SiO₂ band gaps.

| Gap gap (eV) | LDA | LDA-1/2 | GW | Exp. ^a |
|-----------------------------------|-----|---------|-----|-------------------|
| Bulk Si | 0.5 | 1.2 | 1.3 | 1.2 |
| Bulk βc -SiO ₂ | 6.6 | 8.6 | 8.8 | 8.9 |
| Bulk βt -SiO ₂ | 6.6 | 8.6 | | |
| Stack Si | 0.6 | 1.2 | | |
| Stack βc -SiO ₂ | 6.1 | 8.1 | | |
| Stack βt -SiO ₂ | 6.1 | 8.1 | | |

^aFrom crystalline Si (Ref. 13) and amorphous SiO₂ (Ref. 14).

$b_{\text{SiO}_2} = 8.64 \text{ \AA}$, and $c_{\text{SiO}_2} = 5.30 \text{ \AA}$ fit to the Si (001) lattice vectors along the interface plane xy (maximum compressive lattice mismatch of 16.3%). Between the βt -SiO₂ slab and the Si surface a transition region is used to properly adjust the Si oxidation states as described in Ref. 12. Both surfaces are terminated with hydrogen atoms as in the previous case. The model structural parameters are detailed in Table I. As in model I the bond angles at the interface are smaller than their values in the middle of the SiO₂ slab (inner region). However, due to compressive strain, in this case the bond angles in the inner region are smaller than their bulk values. Bond lengths are elongated at the interface with respect to their inner values. The compressive strain is relieved in the inner region by adjusting bond angles only, with minor changes in bond length away from the interface compared to their bulk values. Model II also does not display dangling bonds. Models I and II differ at the interface not only by the level of stress but also by the number of Si oxidation states: three for the former, Si⁺¹, Si⁺², and Si⁺⁴, and four for the latter. To minimize the impact of geometrical quantum confinement on the band gaps and band offsets the thicknesses of our slabs were 20.2 Å (15 planes) for Si and 27.5 Å for SiO₂ in model I, and 35.3 Å (26 planes) for Si and 23.6 Å for SiO₂ in model II.

Table II summarizes the calculated bulk and stack band-gap values. For models I and II the Si and SiO₂ band gaps were obtained from the projected density of states (PDOS) onto Si atoms as far as possible from the interface. The calculated LDA-1/2 bulk band gaps for Si and SiO₂, 1.17 and 8.60 eV, respectively, are in excellent agreement with their experimental values. For SiO₂ the agreement between bulk and stack band gaps for both models is not as good as for Si, a consequence of the strain imposed along the oxide xy plane in order to lattice match the Si slab. Surprisingly the band gaps of the SiO₂ slabs are the same despite the difference in stresses, which we attribute to the considerable level of atomic reorganization in model II. The stressed SiO₂ band gaps are still within 0.5 eV of their bulk values, pointing to one of the sources of uncertainty in our band offset calculations.

Table III shows the band offsets calculated with LDA, LDA-1/2, GW, and experimental data. The valence-band offsets (VBOs) are 4.0 eV for model I, in excellent agreement with the GW value of 4.1 eV obtained for the same model,⁴ and 3.6 eV for model II. For the conduction-band offsets (CBOs) we obtained 3.0 eV for model I, also in excellent

TABLE III. Valence and conduction band offsets for models I and II calculated with LDA, LDA-1/2, GW, and from experimental data.

| | LDA | LDA-1/2 | GW ^a | Exp. ^b |
|----------|-----|---------|-----------------|-------------------|
| VBO (I) | 2.2 | 4.0 | 4.1 | 4.5 |
| VBO (II) | 2.4 | 3.6 | | |
| CBO (I) | 3.3 | 3.0 | 2.9 | 3.3 |
| CBO (II) | 3.0 | 3.2 | | |

^aReference 4.

^bReference 14 measured for amorphous SiO₂ on Si.

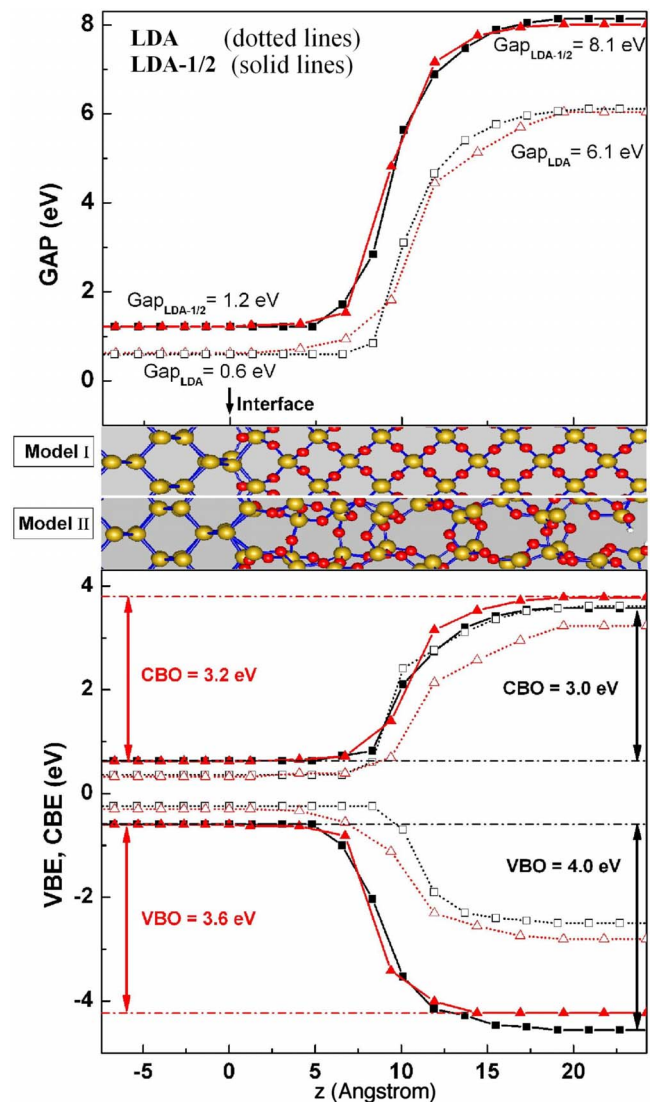


FIG. 3. (Color online) Spatial variation in the valence and conduction band edges of interface models I (squares/black) and II (triangles/red). Center: Si/SiO₂ ball-and-stick interface models with the Si planes aligned; top: spatial variation in the band gaps; and bottom: spatial variation in the Si/SiO₂ band offsets. Top and bottom diagrams are in scale with the interface models at the center (the origin of the z coordinate is indicated by the arrow). Lines between data points are guides to the eyes.

agreement with the *GW* value of 2.9 eV,⁴ and 3.2 eV for model II. Our results also compare well with experimental VBO and CBO values of 4.5 and 3.3 eV, respectively.¹⁴ Strain is likely to be the origin of the difference between the offsets calculated for the two models, even though some contribution from the different interface dipoles cannot be discarded. In this regard, notice that for LDA the larger CBO is obtained for model I and the larger VBO is obtained for model II, while for LDA-1/2 the ordering is opposite. Moreover, for model I the LDA-1/2 CBO is actually smaller than the LDA CBO. These effects may be due to the larger VBOs favoring hole spill over to the SiO₂ side, lowering the LDA CBO. It may also be caused by the way LDA-1/2 impacts the magnitude of the LDA interface dipole. A detailed analysis of this issue will be presented in a separate publication.

Figure 3 shows the variation in the Si and SiO₂ band gaps and of the valence and conduction-band edges (VBE and CBE, respectively) along the normal to the interface. Notice that convergence of the band gaps to their bulk values is fast on the Si side but is slow on the SiO₂ side. Moreover, the Si bands penetrate deep into the SiO₂ side of the interface by ≈ 4 Å for both LDA and LDA-1/2, without a noticeable increase in the local band gap. Transition from the Si to the SiO₂ band structure, once it starts in the oxide, spans ≈ 15 Å. Combined with the penetration of Si bands in SiO₂ we obtain converged SiO₂ bands ≈ 19 Å from the physical interface. The Si band penetration can be qualitatively explained by the weaker screening of SiO₂ due to its lower dielectric constant but disagrees quantitatively with previous work.¹⁵ The penetration length of the Si electronic states can be affected by the structural characteristics of the interfaces. Indeed, for model II, which includes more oxidation states than model I, the penetration of the Si states is shorter. The CBO and VBO asymptotic values for both structures are in

good agreement with experiment. A remarkable feature of Fig. 3 is that for these materials LDA-1/2 has very little impact on the conduction-band edges, with most of the corrections to the band gaps translating in large corrections to the VBOs. This was expected since the self-energy is larger for the more localized valence-band states than for conduction-band states, as already pointed.

To summarize, we employed the LDA-1/2 method to correct the band gaps and band offsets of two SiO₂/Si interface models—one of them chosen such that a direct comparison can be made with previous *GW* results.⁴ We have found that the corrected Si and SiO₂ bulk band gaps are in excellent agreement with *GW* calculations⁴ and with experimental data.¹⁴ The LDA-1/2 band offsets are in excellent agreement with *GW* and in good agreement with experimental data.¹⁴ Notice that the comparison with experimental values could have been more favorable if it were not for the strain in the oxide introduced artificially by the short-range periodicity of the model, which is extrinsic to the LDA-1/2 method. Because the calculation of the LDA-1/2 correction to the eigenenergies is no more demanding on computer resources than the usual LDA calculation, our method opens the opportunity for accurate band offset calculations using larger and more realistic interface models, where the effect of strain, for example, can be minimized. Finally it is worth mentioning that the LDA-1/2 technique has been devised for the calculation of excited states; not to perform structural relaxation. So far we have not identified situations involving semiconductors and insulators in which the technique breaks down. Further investigations employing different materials and interfaces are ongoing.

We thank Semp-Toshiba and FAPESP for financial support. We also thank D. Thober, M. Marques, and L. Teles for stimulating discussions.

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