Role of defects in the electronic properties of amorphous/crystalline Si interface

Maria Peressi\textsuperscript{a,b,*}, Luciano Colombo\textsuperscript{a,c} and Stefano de Gironcoli\textsuperscript{a,d}

\textit{(a) Istituto Nazionale per la Fisica della Materia}
\textit{(b) Dipartimento di Fisica Teorica, Università di Trieste, Strada Costiera 11, I-3414 Trieste, Italy}
\textit{(c) Dipartimento di Fisica, Università di Cagliari, Cittadella Universitaria, I-09042 Monserrato (CA), Italy}
\textit{(d) Scuola Internazionale Superiore di Studi Avanzati, via Beirut 2-4, I-3414 Trieste, Italy}
\textit{(March 22, 2022)}

The mechanism determining the band alignment of the amorphous/crystalline Si heterostructures is addressed with direct atomistic simulations of the interface performed using a hierarchical combination of various computational schemes ranging from classical model-potential molecular dynamics to ab-initio methods. We found that in coordination defect-free samples the band alignment is almost vanishing and independent on interface details. In defect-rich samples, instead, the band alignment is sizeably different with respect to the defect-free case, but, remarkably, almost independent on the concentration of defects. We rationalize these findings within the theory of semiconductor interfaces.

Amorphous-crystalline silicon interfaces (a-Si/c-Si and a-Si:H/c-Si) are of unquestionable technological importance for their use in solar cells and in other optoelectronic devices. Their electronic and optical properties are governed by the band discontinuities $\Delta E_g$, whose value and origin however have not been clearly established so far. To our knowledge, few and conflicting experimental results exist for a-Si:H/c-Si, ranging from 0 to 0.7 eV for the valence band offset (VBO) (see Refs. \textsuperscript{[1]} \textsuperscript{[2]} and references therein), and even less informations are available for a-Si/c-Si \textsuperscript{[3]}. On the theoretical side, the problem of band alignment is addressed in two papers \textsuperscript{[4]} \textsuperscript{[5]}, but only from a comparison of the two phases separately and not from a direct simulation of the interface. The atomic-scale modelization of the interface and its structural properties are the subject of few other works \textsuperscript{[6]} \textsuperscript{[7]}, which, however, do not examine the electronic structure. The combined study of the structural and electronic properties is necessary to understand the mechanism determining the band alignment and in particular the role of bulk-related and interface-specific details.

With this aim we address here our attention to the a-Si/c-Si junction, described using periodically repeated supercells. To generate the structures we adopted a hierarchical combination of models and simulation schemes, including the well known Wooten-Winer-Weaire (WWW) model \textsuperscript{[4]}, model-potential \textsuperscript{[3]} and semi-empirical tight-binding (TB) molecular dynamics (MD) \textsuperscript{[5]}. We used then ab initio state-of-the-art pseudopotential calculations \textsuperscript{[4]} \textsuperscript{[5]} to refine the equilibrium geometries and to compute the electronic structure.

We will consider a-Si/c-Si structures with different a-Si atomic-scale morphologies. In order to investigate the bulk-related effects, we will also study for comparison the band lineup at crystalline strained/unstrained Si homojunctions and at heterocrystalline cubic diamond/hexagonal diamond interfaces.

Atomic-scale model for a-Si/c-Si interface. – For the description of the (001)-oriented a-Si/c-Si interface we consider periodically repeated tetragonal (001) supercells containing 320 Si atoms, with cell dimensions $a = 2a_0$ and $c \approx 10a_0$, where $a_0$ is the lattice parameter of the crystalline phase. The analysis of the electronic structure, in particular of the spatial decay in the crystalline region of the gap states induced by coordination defects of the a-Si region, shows that this cell size is large enough to recover crystalline bulk features in the middle of the c-Si slab.

The atomistic models of the interface structure are obtained according to a procedure that, basically, consists in the following four steps: \textit{(i)} a tetragonal cell of a-Si with dimensions $a = 2a_0$, $c = 5a_0$ and 160-atoms is created by quenching from the melt during a constant-pressure MD simulation based on the “environment dependent interatomic potential” (EDIP) \textsuperscript{[3]}; the quenching procedure was operated by velocity rescaling at a rate as slow as 0.1 K/ps (i.e. about 100 times slower than typical TB–MD simulations \textsuperscript{[4]}), so that density fluctuations during the liquid–amorphous transition were properly damped and a fully stress-free a-Si sample was indeed obtained; a sample interface is then created by joining through the smallest face the above a-Si sample to a c-Si one with the same cell; \textit{(ii)} the structure is further annealed up to 800 K (heating rate $\sim 1$ K/ps), aged at that temperature for about 100 ps, and finally relaxed down to 0 K (cooling rate $\sim 1$ K/ps) by means of constant-pressure, constant-temperature EDIP–MD simulations; \textit{(iii)} at this point we switch from EDIP–MD to TB–MD, adopting the parametrization described in Ref. \textsuperscript{[8]}; since the two models give different equilibrium lattice parameter for c-Si ($a_0^{E,DL}=5.43$ Å to be compared with $a_0^{DL}=5.45$ Å ), we first perform an homogeneous rescaling of the supercell dimensions and atomic positions, thus

\section*{Acknowledgments}

* E-mail: peressi@ts.infn.it
keeping the optimal c/a ratio provided by the previous two steps; (iv) the internal degrees of freedom are then further relaxed by means of a new constant-volume TB–MD annealing procedure (annealing temperature is 1000 K, the heating/cooling rates are, respectively, 500 K/ps and 160 K/ps). Overall the computational workload is heavy - especially for the TB–MD steps - and has to be mastered by means of O(N) formulation of TB–MD and/or extensive use of distributed computing [13].

The resulting structure is then used as input of ab initio calculations, performed within the framework of density-functional theory in the local density approximation, using norm-conserving pseudopotential [14], a plane-wave cutoff of 16 Ry, and 4 k points generated by a symmetrized Monkhorst-Pack grid [20]. We first perform a further homogeneous rescaling of the supercell dimensions and atomic positions according to the new theoretical equilibrium lattice parameter \(a_0^{SCF}=5.47\ \text{Å}\) of c-Si. We also perform an additional optimization of the internal degrees of freedom through minimization of the total-energy and atomic forces, and finally we use the resulting configuration for the calculation of the electronic structure. Because of the non-periodicity in the amorphous slab (see Fig. 1), it is not possible to define an average electrostatic potential in that region and therefore to extract the band alignment according to the usual procedure explained in Ref. [21] for the crystalline junctions. Instead, from the supercell calculations we can extract the Fermi energy \(E_F\) and the average electrostatic potential in the crystalline region, \(V_{c}\), both measured with respect to the average electrostatic potential of the entire supercell which is set to zero (see Fig. 2). From the electronic structure calculations of bulk c-Si we obtain the position of its valence band top edge \(E_{v,c}\) with respect to its own average electrostatic potential, and therefore we can calculate the band alignment in terms of the Schottky barrier: \(\phi_p = E_F - E_{v,c} - \langle V_{c}\rangle\). The numerical uncertainty associated to \(\phi_p\) coming mainly from the determination of \(E_F\), is of the order of 0.1 eV. Calculating the band alignment in terms of \(\phi_p\) is consistent also with the fact that we treat the a-Si/c-Si interface as a metallic system, due to the presence—in general—of defect-induced gap states.

We discuss the results for 6 different a-Si/c-Si configurations, obtained by means of different details in the above preparation procedure. Variations on such a protocol were aimed at producing a-Si samples with varying concentration of coordination defects. In Tab. I we report the relative occurrence in the amorphous part of under-coordinated and over-coordinated Si atoms, calculated simply using a bond-cutoff distance 15% larger than the crystalline bond length. This choice is consistent with the actual position of the first minimum of the pair correlation function computed in the amorphous slab. The six samples are representative of at least three quite different atomic–scale arrangements, with very low (sample A), intermediate (B, C) and high (D, E, F) concentration of defects. Such a diversity of relative occurrence of coordination defects also reflects in the absolute average atomic coordination that varies from 3.99 for sample A (small under–coordination) to 4.3 for sample F (sizeable over–coordination). These values are consistent with experimental findings on real a-Si samples [4]. Within the last two categories (samples B, C and D, E, F, respectively), we present the results for two or three samples in order to examine the possible influence of fine structural details. The cell dimension c/a is slightly varying in the different samples, with positive and negative small deviations from the ideal value c/a=5.

Results for defect-free a-Si/c-Si samples. – We first focus on sample A, which, at variance with our typical procedure, has been obtained starting directly from a 320-atom supercell and not joining two separate a-Si and c-Si cells as described in step (i). The amorphization of the a-Si slab has been achieved by the WWW model [12]; then the sample has been treated with EDIP–MD for the volume optimization, and with a TB *athermic* annealing for a final optimization of the atomic positions. Sample A has only two three-fold coordinated defects, one at each interface. It has a clear semiconducting character, with a well defined energy gap, and a band alignment \(\phi_p=0.06\ \text{eV}\). In this case it is possible to calculate also the VBO, since the position of the topmost valence band edge in the amorphous slab with respect to \(E_F\) is clearly obtained from supercell calculations. We found VBO=0.04 eV, with c-Si higher, sizeably smaller than the predictions of Refs. [4] (0.25 eV and 0.19 eV respectively). The discrepancy may be ascribed to the fact that those calculations do not consider directly the interface; in Ref. [1], for instance, the electrostatic potential lineup is assumed to be zero.

Because of its constituents, sample A can be regarded as an isovalent lattice-matched semiconductor/metal crystalline heterojunction. Indeed it obeys the general trend of this class of junctions, where the VBO is a bulk-related effect, independent on the interface details [22]: remarkably, the two interfaces in the supercell, although slightly morphologically different, are really equivalent in terms of electronic structure, since *no electric fields* are present in the bulk slabs.

This behavior is consistent with experimental findings for the analogous system a-Si:H/c-Si [4], where a constant VBO=0.44 eV has been found for different samples characterized by the same amount of H but different thickness of the interface region. [22]

**Band alignment at Si/Si crystalline junctions.** – In order to examine the role played by the density and the crystalline symmetry on the band alignment, we consider two particular crystalline Si junctions: the unstrained diamond/strained diamond and the heterocrystalline cubic diamond/hexagonal diamond interfaces. For the former case we consider specifically a positive strain of 1% along
the (111) direction, for a direct comparison with the case of hexagonal diamond which naturally exhibits such strain: we found VBO=0.05±0.01 eV (with the strained slab higher) after optimization of the internal degrees of freedom in the strained Si slab. The contribution to the VBO due to the change in density is 0.02 eV, related to the hydrostatic deformation potential \[23\]. The remaining contribution comes from the strain-induced splitting of the valence band top edge (0.10 eV).

We simulate the heterocrystalline cubic diamond/hexagonal diamond Si junction with a supercell with 30 atoms, namely with 3 unit slabs for both phases along the (111) direction \[24\]. After a careful optimization of the macroscopic and microscopic degrees of freedom, which gives for the structure of the hexagonal diamond results close to those of Ref. \[25\], we found VBO=0.23±0.01 eV, with hexagonal diamond higher than cubic diamond, as in Ref. \[20\]. Remarkably, the VBO is much larger than in the previous junction, although the change in the density between the constituent slabs is the same. The largest contribution to the VBO comes from the fact that in the hexagonal diamond the valence band width is larger than in cubic diamond, and the valence top has a splitting of 0.30 eV.

The common feature of the semiconducting a-Si/c-Si interface and of crystalline Si/Si junctions is the reduced symmetry of one of the constituent slabs: this can be indeed considered as the origin of the VBO in these systems, through a splitting of the valence band top edge manifold, more pronounced for the structure having the largest anisotropy (hexagonal diamond).

Results for other a-Si/c-Si samples – We discuss now the results obtained for other a-Si/c-Si samples, which are characterized by a concentration of defects in the a-Si region at least of the order of ~10% and by a semimetallic behavior due to defect-induced gap states. Sample B is obtained following the same procedure for sample A, except that the starting configuration is obtained joining two separate cells (c-Si and a-Si, treated with the WWW model \[24\]); sample C is obtained without the use of the WWW model, and following exactly all the steps (i)−(iv) previously listed, with a slow quench rate in step (i) in order to keep the number of defects very low; sample D is obtained with a higher quenching rate in step (i) and a TB finite-temperature annealing in step (iv); sample E with a TB athermal annealing; finally, sample F with the use of EDIP–MD only (i.e., steps (iii)−(iv) were skipped).

Our key-result is that for all the samples from B to F the band alignment has almost the same value \(\phi_p=0.22\) eV, independent on structural details such as concentration and distribution of defects and density of the amorphous slab. The average electrostatic potential in the crystalline slab \(V_C\) is very sensitive to the defect concentration, and infact the values for the samples with intermediate defect concentrations (B, C) are very different from those with high defect concentrations (D, E, F), even by 0.48 eV (see Tab. 1). Nonetheless, the Schottky barrier \(\phi_p\) varies within a very small range (of 0.04 eV) for all these samples.

This result for defect-rich samples is consistent with the general trend reported for the semiconductor/metal junctions \[21\], i.e. that the Schottky barrier is poorly sensitive to the metal type but depends on the semiconductor. In fact, what changes from sample B to F is only the highly defected a-Si slab, which acts as the “metallic” constituent. Moreover, since c-Si is homopolar, neither interface-specific details could change the band alignment, as instead it may occurs in case of heterovalent semiconductor heterostructures and metal/polar-semiconductor junction. The independence on interface details is also numerically verified from our calculations: in all our samples electric fields within the c-Si slabs are absent, whereas they would be present if the two interfaces within the supercell were non-equivalent.

Conclusions. - Present results for amorphous/crystalline Si interfaces can be rationalized along the findings of the linear-response theory of the band alignment at semiconductor interfaces \[21\] and summarized as follows: (i) the band alignment is almost vanishing for defect-free samples and sizeable in the case of defect-rich samples; (ii) in the latter case it is independent on the particular defect concentration and distribution: such result can be ascribed to the semi-metallic behavior of the amorphous region, and explained by analogy with the case of Schottky barriers which are almost independent on the metal type; (iii) in any case it is not an interface-specific effect, but rather it is a bulk-related effect; (iv) by inspection of the different a-Si/c-Si samples for comparison with other Si/Si crystalline junctions, the largest contribution to the band alignment is not due to changes in the density but rather to a broadening of the valence band and a splitting of its top manifold which typically occurs in the phases of reduced symmetry.

This work was supported by the INFM Parallel Computing Initiative.

\[1\] A. Fantoni \textit{et al.}, Thin Solid Films \textbf{383}, 314 (2001).
\[2\] Y.J. Song \textit{et al.}, Solar Energy Mat. and Solar Cells \textbf{64}, 225 (2000).
\[3\] S. Gall \textit{et al.}, Solar Energy Mat. and Solar Cells \textbf{49}, 157 (1997).
\[4\] M. Sebastiani \textit{et al.}, Phys. Rev. Lett. \textbf{75}, 3352 (1995).
\[5\] C. Van de Walle and L.H. Yang, J. Vac. Sci. Technol. B \textbf{13}, 1635 (1995).
\[6\] L. Ley \textit{et al.}, in Proc. of the 17th Int. Conf. on Phys. of Semic., edited by J.D. Chadi and W.A. Harrison (Springer, New York, 1985), p. 811.
TABLE I. Main structural and electronic properties of the six different a-Si/c-Si samples considered in this work. The percentages of atoms in the amorphous part which are under-coordinated ($T_{NN<4}$) and over-coordinated ($T_{NN>4}$), where NN means “nearest neighbors”, are indicated in the second and third columns.

| Sample | $T_{NN<4}$ | $T_{NN>4}$ | c/a | $E_F$ (eV) | $\langle V \rangle_c$ (eV) | $\phi_p$ (eV) |
|--------|-------------|-------------|-----|------------|----------------|-------------|
| A      | 1%          | 0%          | 5.039 | 6.26       | −0.11          | 0.06        |
| B      | 7%          | 6%          | 5.126 | 6.22       | −0.30          | 0.20        |
| C      | 0.5%        | 9%          | 5.100 | 6.33       | −0.24          | 0.24        |
| D      | 2%          | 36%         | 4.922 | 6.71       | 0.18           | 0.21        |
| E      | 3%          | 27%         | 4.922 | 6.70       | 0.15           | 0.23        |
| F      | 0.5%        | 36%         | 4.922 | 6.68       | 0.14           | 0.22        |