

AB-INITIO STUDY OF SILICON BASED MATERIALS FOR PHOTOVOLTAIC APPLICATIONS

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ABSTRACT. In order to optimize the optoelectronic properties of novel solar cell architectures, such as the crystalline-amorphous interface in Silicon heterojunction (c-Si/a-Si:H) devices, an analysis of the local microscopic structure at the interface is essential. To this aim, reliable physical models for c-Si and a-Si:H were developed.

1 Introduction

In view of a study of an amorphous-crystalline interface in Silicon heterojunction, reliable physical models for crystalline Silicon (c-Si) and hydrogenated amorphous Silicon (a-Si:H) were developed. The *ab-initio* PWscf (Plane-Wave Self-Consistent Field) code of the Quantum ESPRESSO suite was used [1, 2] to perform total energy calculations and Born-Oppenheimer Molecular Dynamics (BOMD) simulations of c-Si and a-Si:H models in order to check their ability in reproducing experimental and structural properties. PWscf performs many different kinds of self-consistent calculations of electronic structure properties within Density-Functional Theory (DFT) [3, 4], using a Plane-Wave (PW) basis set and Pseudo-Potentials (PP). All the calculations were performed in the supercell approximation with periodic boundary conditions (PBC) meant to mimic infinitely extended systems. We used the Si and H ultrasoft pseudopotentials with Perdew-Burke-Ernzerhof (PBE) [5] approximant GGA exchange-correlation potential, available in the Quantum ESPRESSO library [2].

2 Crystalline Silicon: c-Si

A cubic supercell composed of a $2 \times 2 \times 2$ array of fcc conventional cells and 64 Si atoms was considered to simulate the silicon crystalline structure. The electronic wave functions were expanded in a plane-wave basis set with a kinetic energy cut-off equal to 40 Ry, the charge density cut-off is set to 240 Ry and a $4 \times 4 \times 4$ Monkhorst-Pack mesh of k points is employed [6]. The kinetic energy cut-offs and the mesh of k points were optimized by preliminary calculations on Silicon and Hydrogen pseudopotentials. By using *ab-initio* zero-temperature total energy calculations we computed lattice constant a and bulk modulus B . The third-order Birch-Murnaghan equation of state was used to calculate the equilibrium

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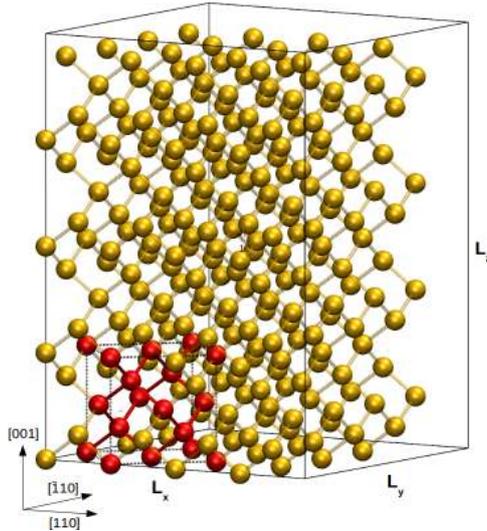


Figure 1: Tetragonal supercell used to build the Si(001) surface and its reconstruction. The silicon fcc conventional cell is highlighted in red.

lattice constant $a_0 = 5.47 \text{ \AA}$ and bulk modulus $B = 89 \text{ GPa}$. These results are in good agreement with the corresponding experimental values and with others *ab-initio* computations (see Table 1). Moreover, to check the mechanical stability of the system, the elastic constants C_{11} ; C_{12} and C_{44} were calculated. It is known that if the elastic constants obey the conditions $C_{11} - C_{12} > 0$; $C_{11} + 2C_{12} > 0$; $C_{11} > 0$ and $C_{44} > 0$ then the material is mechanically stable. The elastic isotropy is also examined by the evaluation of the ratio $A = 2C_{44}/(C_{11} - C_{12})$. In an isotropic solid $A = 1$. The following values were obtained: $C_{11} = 153 \text{ GPa}$, $C_{12} = 57 \text{ GPa}$ and $C_{44} = 75 \text{ GPa}$, from which we infer that the four conditions of mechanical stability are fulfilled. The full set of our results for crystalline Silicon are reported in Table 1 with experimental and other theoretical values. The comparison with experimental results faces the difficulty of the temperature dependence of the experiments.

3 Silicon (001) surface

To analyse the Si(001) surface and its reconstruction, we considered a tetragonal cell composed of 32 fcc cells and 256 Si atoms. The x , y and z axes correspond to the $[110]$, $[\bar{1}10]$ and $[001]$ directions of Silicon fcc conventional cell, respectively (see Fig 1). The cell has $L_x = L_y = 4 \times \frac{a_0}{\sqrt{2}}$, and $L_z = 4 \times a_0$. Using

Table 1: Calculated values of equilibrium lattice constant a_0 , bulk modulus B , elastic constants C_{11} , C_{12} , C_{44} and elastic isotropy A . Values computed in this work are compared with both numerical and experimental results from literature.

	a_0 (Å)	B (GPa)	C_{11} (GPa)	C_{12} (GPa)	C_{44} (GPa)	A
Cal.	5.47	89	153	57	75	1.56
Refs.	5.43	99[7]	168[7]	65[7]	80[7]	1.55[7]
	5.44[8]	98[8]				

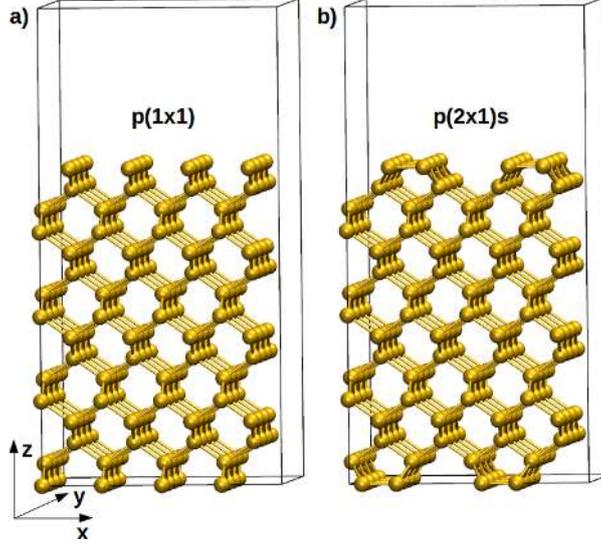


Figure 2: a) The unreconstructed (ideal) Si(001) surface. b) The symmetric $p(2 \times 1)$ reconstructed Si(001) surface.

the previous values for the kinetic energy cut-offs and a $2 \times 2 \times 2$ Monkhorst-Pack mesh of k points we found the same value for the equilibrium lattice constant $a_0 = 5.47 \text{ \AA}$. Surfaces were constructed using the previous tetragonal cell with 256 Si atoms adding a void region ($\sim 10 \text{ \AA}$) in z -direction to suppress the interaction due to the periodic boundary conditions. This was checked to be sufficient to eliminate interactions between mirror images in the z -direction. In Fig. 2a) is shown the unreconstructed (ideal) Si(001) surface. Moreover, the symmetric $p(2 \times 1)$ reconstructed Si(001) surface was analysed (see Fig. 2b). The reconstruction is formed by surface atoms moving together in pairs to form dimers and therefore the dangling bonds from the unreconstructed Si(001) surface are halved. Distance of the dimers is 2.30 \AA , and the energy gain for each dimer is 1.5 eV/dim . In Ref. [9] the following values were found : 2.23 \AA and 1.8 eV/dim .

We examined surfaces with increasing number N of layers, each of them composed of 16 Si atoms, then we calculated the total energy of the surface systems with respect to the number of slabs (up to $N = 16$) and using $2 \times 2 \times 1$ k point mesh. Two class of configurations were considered: surfaces in which all atoms were kept fixed, and relaxed surfaces in which only the bottom four layers of atoms were kept fixed. The latter choice were done to attain the semi infinite bulk crystal beneath the surface.

There is a linear growth of the total energy E_{slab}^N with respect of the number of the slabs N , this permit to calculate the surface energy σ for both Si(001) surfaces using the following equation [10]:

$$E_{slab}^N \approx 2\sigma + NE_{bulk}$$

where E_{bulk} is the bulk total energy. Calculations of the surface energy per unit area $\gamma = \sigma/A$ (where $A = L_x \times L_y$), gave $\gamma = 2.12 \text{ J/m}^2$ for unreconstructed Si(001) surface and gave $\gamma = 1.42 \text{ J/m}^2$ for symmetric $p(2 \times 1)$ reconstructed Si(001) surface. Other numerical calculations gave similar results. In Refs. [11, 12] it was calculated $\gamma = 2.36 \text{ J/m}^2$ and $\gamma = 2.39 \text{ J/m}^2$ for the former surface and $\gamma = 2.51 \text{ J/m}^2$ and $\gamma = 1.45 \text{ J/m}^2$ for the latter one.

The surface relaxations of the Si(001) surfaces were also analysed. Surface relaxation can be characterized as the percent change $\Delta_{ij} = (d_{ij} - d_0)/d_0$ of the spacing d_{ij} between layers i and j versus the equilibrium layer spacing d_0 . For the Silicon (001) surfaces d_0 is $a_0/4$. A positive value indicates expansion, whereas a negative one indicates a contraction of the spacing. The surface relaxation of the unreconstructed Si(001) surface system with 16 Silicon slabs with the four bottom atom layers kept

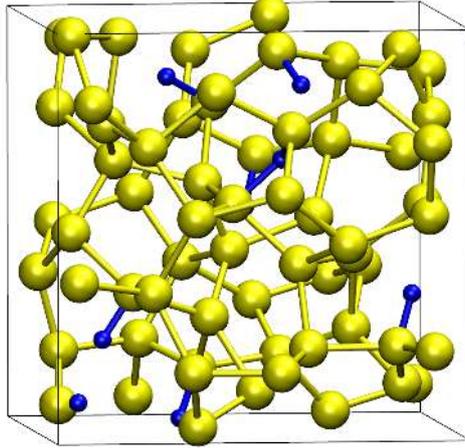


Figure 3: Schematic of the a-Si:H in the simulation box. Hydrogen atoms and bonds with Silicon atoms are in blue, Silicon atoms and their bonds are in yellow.

fixed, was found to be $\Delta_{12} = -1.7\%$, $\Delta_{23} = -0.38\%$, and $\Delta_{34} = -0.66\%$. While for the symmetric $p(2 \times 1)$ reconstructed Si(001) surface we measured $\Delta_{12} = -21.4\%$, $\Delta_{23} = 0.21\%$, and $\Delta_{34} = 0.13\%$.

4 Hydrogenated amorphous Silicon: a-Si:H

The model of the hydrogenated amorphous Silicon was generated using a simulate annealing quench from a melt simulation protocol, currently used to generate high-quality amorphous samples [13]. A system of 64 Si + 8 H atoms in a cubic supercell with size $L=11.06 \text{ \AA}$, with a density of 2.214 gr./cm^3 was considered. A BOMD simulation on the electronic ground state at constant volume and constant temperature ($T=300 \text{ K}$) was performed for 6.5 ps (timesteps $ts = 20 \text{ Ry}$), controlling the ionic temperature by using Andersen thermostat. In Fig. 3 it is shown the a-Si:H system at the end of the simulation. The initial 1.5 ps of simulation was sufficient to thermalize the system, then the remaining 5 ps of simulation was used to characterize the system. Fig. 4 shows the radial pair correlation functions $g(r)$ yielded in this 5 ps of simulation. The yellow line was computed taking in consideration only the Silicon atoms, whereas, the blue line was computed considering Si and Si + H atoms. There is a peak at 2.37 \AA for the Si/Si $g(r)$, and there is a peak at 1.52 \AA for the Si/Si+H $g(r)$. Moreover, the coordination analysis was performed in the last 5 ps of simulation (see Tab. 2). A geometrical criteria was adopted for identify the number of bonds in the coordination analysis. The following distance cutoffs were chosen: 2.9 \AA for Si-Si pairs and 1.8 \AA for Si-H pairs. It is observed that 4 Silicon atoms have three-fold coordination (6.3%), 58 Silicon atoms have four-fold coordination (90.6%) and the remaining 2 Si atoms

Table 2: Coordination analysis of the hydrogenated amorphous Silicon: a-Si:H.

Coordination	n	Si	Si+H
3	4	4 (3Si)	
4	58	51 (4Si)	7 (3Si+1H)
5	2	1 (5Si)	1 (4Si+1H)

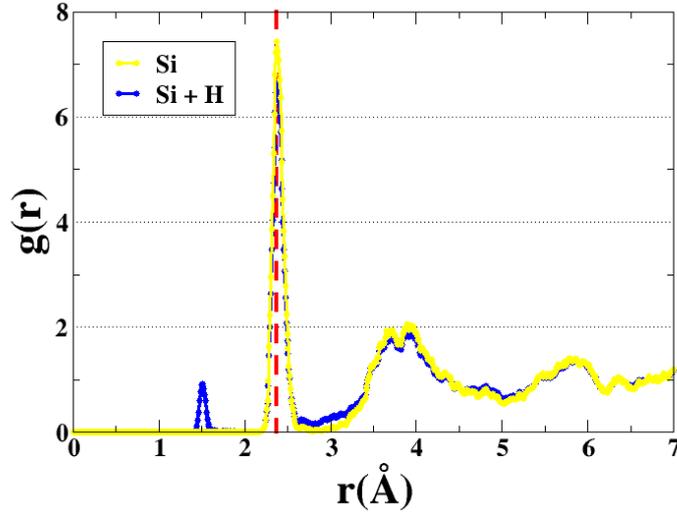


Figure 4: Radial pair correlation functions $g(r)$ computed considering Si and Si+H atoms (blue line) and Si and Si atoms (yellow line).

have five-fold coordination (3.1%). The first group of Si atoms (coordination 3) are surrounded only by Silicon atoms; 51 Si atoms of the second group are four-fold coordinated with others Si, whereas the residual 7 Si atoms are coordinated with 3 Si and 1 H. Finally, of the last two atoms, 1 Si is five-fold coordinated with others Si, and 1 is surrounded by 4 Si and 1 H.

References

- [1] P. Giannozzi *et al.* *J. Phys.: Condens. Matter.*, 21:395502, 2009.
- [2] www.quantum-espresso.org.
- [3] P. Hohenberg and W. Kohn. *Phys. Rev.*, 136:B864, 1964.
- [4] W. Kohn and L.J. Sham. *Phys. Rev.*, 140:A1133, 1965.
- [5] K. Burke J.P. Perdew and M. Ernzerhof. *Phys. Rev. Lett.*, 77:3865, 1996.
- [6] H.J. Monkhorst and J.D. Pack. *Phys. Rev. B*, 13:5188, 1976.
- [7] H.J. McSkimin and P. Andreatch Jr. *J. Appl. Phys.*, 35:3312, 1964.
- [8] J. Leszczynski M. Yengui, H. P. Pinto and D. Riedel. *J. Phys. Condens. Matter*, 27:045001, 2015.
- [9] G Brocks A. Ramstad and P. J. Kelly. *Phys. Rev. B*, 51:14504, 1995.
- [10] V. Fiorentini and M. Methfessel. *J. Phys. Condens. Matter*, 8:6525, 1996.
- [11] M. Cuma G-H. Lu, M. Huang and F. Liu. *Surface Science*, 588:61, 2005.
- [12] J. Furthmuller A.A. Stekolnikov and F. Bechstedt. *Phys. Rev. B*, 65:115318, 2002.
- [13] M. Legesse M. Nolan and G. Fagas. *Phys. Chem. Chem. Phys.*, 14:15173, 2012.