Structural, electronic and optical properties of the two isomers of Si(111)2x1

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Abstract. The Si(111)2x1 is one of the most studied surfaces. Its reconstruction is described by the Pandey model with a buckling of the topmost atoms. With relation to the sign of the buckling, there are two slightly different geometric structures (isomers), conventionally named positive buckling and negative buckling. STM measurements suggest that the positive buckling isomer is the stable configuration at room temperature, but a recent work, involving STS measurements, has shown the coexistence of both the isomers, at very low temperature, for highly n-doped Si(111)2x1 specimens. There is hence the necessity to deepen the study of the negative buckling isomer, almost completely neglected in literature especially for what concerns its optical properties. In this work we have studied the structural, electronic and optical properties of both the isomers of Si(111)2x1 within the Density Functional Theory in the Local Density Approximation. Our results show that the response to light of the two isomers is sizearly different; Reflectance Anisotropy Spectroscopy would be the right experimental tool to investigate the coexistence of the two isomers.

1. Introduction

The (111) surfaces are the natural cleavage planes of Si and the 2x1 is the reconstruction observed at low temperature after cleavage in Ultra High Vacuum. Si(111)2x1 is one of the most investigated surfaces and its atomic structure is well understood in terms of the Pandey model [1]. According to the latter, π-bonded atoms chains are present in the first atomic layer. Two adjacent atoms of the chain can tilt, with respect to each other, in two ways and so two different isomers of the surface, conventionally named positive buckling and negative buckling, can be distinguished (see Figure 1).

The geometry of the two isomers is very similar but only the positive buckling structure is observed by STM measurements [2] at room temperature. However, for highly n-doped Si(111)2x1 specimens, at very low temperature, the coexistence of the two structures has recently been shown by a comparison between experimental and theoretical STS [3]. A deeper understanding and the final proof of this coexistence can be obtained by the study of the optical properties of these two configurations. There is hence the need to investigate more deeply the negative buckling structure, in particular for what concerns the optical properties. In this work we have studied the geometry, electronic band structure and Reflectance Anisotropy Spectra of both the isomers by Density Functional Theory (DFT) ab-initio calculations.
2. Methods

We have performed DFT calculations in the Local Density Approximation (LDA), using the codes of \textit{Quantum Espresso} package \cite{4}. The surfaces have been modelled using the supercell method, employing slabs of 24 atoms separated by 7.42 Å of vacuum. We have used different values of cut-off energies: 30 Ry for geometry, 40 Ry for structural properties and 20 Ry for optical spectra. For what concerns the optical properties, we have focused on the RAS (Reflectance Anisotropy Spectroscopy) spectra. RAS \cite{5}\cite{6}\cite{7} is a powerful and efficient experimental technique widely used to study and characterize surfaces. The RAS signal measures the difference of reflectivity for light polarized along two perpendicular directions (x and y) on the plane of the surface:

$$ \frac{\Delta R}{R} = \frac{R_y - R_x}{R} $$

and it corresponds to the difference of the reflectivity corrections to the Fresnel (unperturbed) case for the two different light polarizations. For cubic crystals, the RAS signal comes from the surface anisotropy, since the bulk is optically isotropic. In the case of the supercell method, there is a simple theoretical expression for the RAS spectrum \cite{8}, involving the half-slab polarizability $\alpha_{ii}^{hs}$:

$$ \Delta R = \frac{4\omega d}{c} \frac{\pi \alpha_{ii}^{hs}}{\epsilon_b - 1} $$

$$ \alpha_{ii}^{hs}(\omega) = \frac{\pi e^2}{m^2 \omega^2 Ad} \sum_{k,v,c} |p_{vc}(\tilde{k})|^2 \delta(E_{c}(\tilde{k}) - E_{v}(\tilde{k}) - \hbar \omega) $$

where d is the half-slab thickness, A is the 2D cell area, $\epsilon_b$ is the bulk dielectric function, i is the direction of light polarization and the sum in the second equation runs over the k points in the Irreducible Brillouin Zone (IBZ) and over conduction (c) and valence (v) states. We have used 231 k points in IBZ and 800 total bands (48 filled states).

3. Results

3.1. Structural properties

Ground state configurations of both the isomers of Si(111)2x1 have been obtained minimizing DFT total energy. Here we show the most important geometric parameters, that are the buckling

\[ \text{Figure 1.} \] side view of Si(111)2x1 negative and positive buckling reconstructions.

\[ \text{Figure 2.} \] top view of Si(111)2x1 negative and positive buckling. The bigger atoms are the ones in the first atomic layer. The distance between atom A and atom B is the bond length along the Pandey chain while the difference in height between atom A and atom B is the buckling amplitude.
amplitude $\Delta$ and the bond length $d_\pi$ along the $\pi$-chains (defined in Figure 1 and 2):

$$\Delta_{pb}^n = +0.53 \text{ Å} \quad \text{and} \quad d_{\pi}^{pb} = 2.27 \text{ Å}, \text{ for the positive buckling}$$

$$\Delta_{nb}^n = -0.59 \text{ Å} \quad \text{and} \quad d_{\pi}^{nb} = 2.27 \text{ Å}, \text{ for the negative buckling}$$

Our results are in good agreement with literature [2][3][9][10][11][12].

As we can see in Figure 3, the two isomers of Si(111)2x1 are both local stable energy minima. The energetic barrier, which separates the two stable configurations, can be roughly estimated by switching from one configuration to the other simply tilting the buckled atoms of the Pandey chain with respect to each other. We find that 0.06 eV/(2x1) is an upper limit for the energy barrier.

![Figure 3. Energy path from the negative buckling structure to the positive buckling configuration.](image)

In our calculations, the negative buckling is the most stable configuration, being favored by about 5.4 meV/(2x1) with respect to the positive buckling. Anyway the energy difference is so small that we can assume the structures nearly degenerate within DFT accuracy, as well known in literature [13][14].

3.2. Electronic properties

The calculated energy gaps between surface states at the surface high symmetry points of the Irreducible Brillouin Zone are reported in Table 1. We find a good agreement with previous DFT results [14][15].

|                         | Positive buckling | Negative buckling |
|-------------------------|-------------------|-------------------|
| $\bar{J}$              | 0.35              | 0.19              |
| $\bar{K}$              | 0.62              | 0.35              |
| $\bar{J}'$             | 1.67              | 1.54              |

The band structure along the $\bar{J}\bar{K}$ line for both the isomers is shown in Figure 4. The $\bar{J}\bar{K}$ direction in the reciprocal space corresponds, in real space, to the direction perpendicular to the
Pandey chains: the little dispersion that can be observed along that line is a direct consequence of the weak interaction between two adjacent $\pi$-chains (that are nearly 6.6 Å distant). The maximum value of the filled surface band is at $J$ for the positive buckling and between $\frac{JK}{2}$ and $K$ for the negative buckling; the minimum value of the empty surface band is between $J$ and $\frac{JK}{2}$ for both the isomers.

![Figure 4. Surface band structure for the positive buckling (solid black line) and the negative buckling (dashed blue line).](image1)

For all the $k$ points along $JK$ direction the highest occupied states are located on the upper atoms of the Pandey chain, while the lowest empty states are located on the lower atoms of the $\pi$-chain. As an example we show the squared modulus plot of the wavefunctions at $k$-point $J$ for the negative buckling isomer (see Figure 5 and Figure 6).

![Figure 5. Squared modulus plot of the DFT wavefunction of the highest occupied surface state at $J$ point for the Si(111)2x1 negative buckling.](image2)

![Figure 6. Squared modulus plot of the DFT wavefunction of the lowest unoccupied surface state at $J$ point for the Si(111)2x1 negative buckling.](image3)

3.3. Optical properties
RAS spectra have been calculated, within DFT-LDA (in the indipendent particle approximation), up to 6 eV and, as we can see in Figure 7, there are deep differences in the shape, the intensity and the peak position for the two isomers.

The Si(111)2x1 negative buckling presents a RAS peak (0.22 eV) at lower energies with respect to the peak of the positive buckling (0.48 eV), and this is related to the the fact that the electronic gaps of the positive buckling are larger than the electronic gaps of the negative buckling. The RAS peak of the negative buckling is the most intense (the intensity ratio between the two isomer is nearly 1.6): as we can see in Figure 4, the surface bands are more parallel for the negative buckling structure, thus enhancing the optical response.
The results obtained for the Si(111)2x1 positive buckling are in good agreement with previous DFT-LDA RAS spectra [15]. The difference of about 0.26 eV in the energy positions, found in the RAS peak, suggests that experiments would be able to distinguish the two isomers.

4. Conclusions
The isomers of Si(111)2x1 are both energetic stable local minima, almost degenerate in energy and separated by an energetic barrier. A slight difference in the geometry of the two configurations (they are inequivalent with respect to the third atomic layer) leads to deep differences in the electronic and, consequently, in the optical properties. In particular we have found that, within DFT-LDA approximation, the RAS peak of the negative buckling isomer is more intense and is redshifted by 0.2 ÷ 0.3 eV with respect to the positive buckling. In order to compare in a more quantitative way with experimental results, many body and excitonic effects must be included in the calculations, and this is the content of a forthcoming work.

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References
[1] K.C. Pandey, Phys. Rev. Lett. 47, 1913 (1981)
[2] S. Nie et al., J. Vac. Sci. Technol. A 22(4), 1671 (2004)
[3] G. Bussetti et al., Phys. Rev. Lett. 106, 067601 (2011)
[4] http://www.quantum-espresso.org/
[5] "Optical Characterization of Epitaxial Semiconductor Layers", G. Bauer, W. Richter, Springer-Verlag, 1996
[6] D.E. Aspnes et al., J. Vac. Sci. Technol. A 6, 1327 (1988)
[7] P. Weightman et al., Rep. Prog Phys. 68, 1251 (2005)
[8] F. Manghi et al., Phys. Rev. B 39, 13005 (1989)
[9] C.H. Patterson et al., Phys. Rev. B 84, 155314 (2011)
[10] F. Bechstedt et al., Phys. Rev. Lett. 87, 16103 (2001)
[11] M. Rohlfing and S. G. Louie, Phys. Rev. Lett. 83, 856 (1999)
[12] G. Xu et al, Phys. Rev. B 70, 045307 (2004)
[13] F. Ancillotto et al., Phys. Rev. Lett. 65, 3148 (1990)
[14] M. Zitzlsperger et al., Surf. Sci. 108, 377 (1997)
[15] O. Pulci et al., Phys. Rev. B 82, 205319 (2010)