Chemical bond and electronic states at the CaF₂-Si(111) and Ca-Si(111) interfaces

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The first stage of formation of the CaF₂-Si(111) and Ca-Si(111) interfaces is studied through the employment of the surface linear-muffin-tin-orbital approach in the atomic-sphere approximation. The interfaces are simulated by monolayers of F-Ca and Ca on Si(111), respectively. Both valence- and core-electron states have been calculated: their analysis gives important information about the nature of the Ca—Si and Ca—F bonds. These results are successfully compared with the available experimental data. The importance of considering the Madelung contribution in the interpretation of surface-core-level shifts is pointed out.

I. INTRODUCTION

In the past few years, the CaF₂-Si(111) interface has received extensive attention from theoretical and experimental points of view.[1] Calcium fluorite is an excellent insulator, with an ∼12.1-eV band gap; moreover crystalline CaF₂ and Si have similar fcc structure, with a room-temperature lattice mismatch of only 0.6%. This feature allows the growth of high-quality epitaxial CaF₂ films on Si(111) and makes it one of the best candidates for the development of three-dimensional electronic devices. The CaF₂-Si(111) system is particularly attractive even from the theoretical point of view, because its structure is simple enough to allow a first-principles investigation of the interaction between two very different systems: a polar insulator with ionic bonding (CaF₂) and a homopolar semiconductor with covalent bonding (Si).

The investigation of the Ca-Si(111) interface assumes a particular relevance with respect to the study of the CaF₂-Si(111) system: although the exact atomic structure of the CaF₂-Si(111) interface is still not known, recent experimental data[2] suggest that this interface is not abrupt, but mediated by a CaSi₂-type layer, with no F atom between Ca and Si. The features of the Si—Ca bond become therefore essential in order to better understand the electronic properties of the CaF₂-Si(111) interface. The Ca-Si(111) interface deserves much interest even for its own features, since this rather simple system can provide important information on the nature of the metal-silicon bond at the interface.[3,4] Although the greater part of the existing experimental work is devoted to the analysis of alkali-metal or transition-metal–silicon junctions, there is a growing interest[1] for alkaline-earth-metal–silicon systems because they could show particular properties as a consequence of the low *d*-electron occupancy and low electronegativity of the alkaline-earth metal.

In this paper we present an analysis of Ca-Si(111) and CaF₂-Si(111) interfaces in the first stage of deposition; in particular we study the system formed by a monolayer of Ca adsorbed on Si(111) and the interface formed by a monolayer of Ca deposited on Si(111) followed by a F layer, i.e., a F-Ca-Si(111) system, considered the first phase leading to the formation of the insulator-semiconductor CaF₂-Si(111) interface.[2,4,5]

Our investigation of these interfaces is based on the surface linear-muffin-tin-orbital method.[6,7] The results we present will yield an accurate analysis of both valence- and core-electron states and of the nature of the interface bond.

II. THE SURFACE LINEAR-MUFFIN-TIN METHOD

The analysis of the electronic properties of surfaces and interfaces may be considered one order of magnitude more difficult than the corresponding bulk problem, due to the loss of periodicity in the direction perpendicular to the interface. The investigation of these systems is based on the supercell technique: the solid-vacuum interface is simulated by an infinite sequence of solid and vacuum films, which recovers the third-dimension periodicity. This three-dimensional crystal can now be directly studied by using the standard procedures of bulk compounds, provided that they are suitable to treat with a very large number of atoms in the unit cell. For this reason first-principles investigations for surfaces and interfaces are often based on the highly efficient linear methods, devised by Andersen.[8]

Our investigation of the Ca-Si(111) and CaF₂-Si(111) systems at the early stages of the interface formation is realized by the self-consistent linear-muffin-tin-orbital (LMTO) method in the atomic-sphere approximation (ASA), in the same version normally used for bulk problems.

Close packing is a necessary requirement for the appli-

cation of the ASA, where the muffin-tin interstitial region is "annihilated" through the expansion of the muffin-tin spheres and the neglect of the slight overlap. This approximation greatly reduces the complexity of the band calculation, but prevents direct application of the method to loosely packed solids and to surfaces, where the presence of a vacuum region clearly contradicts the close-packing requirement. In the bulk problem, the way to avoid the drawback is to introduce empty spheres (ES),[9] i.e., fictitious atoms with zero atomic number to be placed on void sites in order to obtain a close packing. With a suitable number of empty spheres even the loosely packed solids may be investigated by LMTO-ASA: this method has been successfully applied to the calculation of energy bands, total energies, and structural stability of group-IV semiconductors.[10,11]

Very recently we have demonstrated[6,7] that the LMTO-ASA method can also be used in the calculation of the electronic properties of clean surfaces and of interfaces at low coverage. The basic idea of this surface LMTO-ASA (SLMTO-ASA) approach is to describe the vacuum region by a solid formed by empty spheres. With the abstraction of atom type the Si-ES lattice, describing bulk Si, is bcc with equally spaced (111) planes forming an ABCABC... sequence. This bcc lattice is continued into the adsorption and vacuum regions, where now all sites are occupied by adatoms and empty spheres. The filling up of the vacuum region with empty spheres produces a negative charge on the empty spheres which drops on moving far from the surface, with the formation of a potential barrier at the solid-vacuum interface.

The advantage of the SLMTO approach[6,7] with respect to other first-principles methods relies on the possibility of treating complex systems, without particular effort. While other first-principles methods are presently limited at systems corresponding to slab sizes ≤ 10 layers, in our approach this limit can be exceeded without difficulties. It is therefore possible to investigate complex systems, like reconstructed surfaces. To ensure accurate results, the slab should be thick enough to obtain a central layer projected density of states (PDOS) which closely resembles the bulk spectrum.

In our calculation we simulate the Si-adatom-vacuum interface by a 12-layer Si(111) slab covered with one or two layers of adsorbed atoms on each side and a vacuum region of thickness ≥ 0.4 that of the Si slab.

We also modified the LMTO code in order to calculate core electron energies and wave functions.[12]

III. THE Ca-Si(111) AND CaF$_2$-Si(111) INTERFACES

In the case of the Ca-Si(111) interface no information exists, to our knowledge, about the nature of the adsorption site: the deposition of Ca on Si(111) produces indeed a reacted region with Ca-Si intermixing.[3] The only existing experimental work about a stable nonintermixed Ca-Si(111) interface is a study of Olmstead and co-workers[4,13] on a Si(111)-Ca 3×1 interface obtained as a stable reconstructed phase after the annealing of a well-ordered CaF$_2$-Si(111) one: by core-level and angle-resolved photoemission spectroscopy they investigate the

nature of the Ca—Si bond and the valence-band structure of this interface. However their results give no indications about the exact interface geometry. Due to the lack of experimental information, our calculations on the Ca-Si(111) interface have been performed by assuming the same adsorption geometry used for the F-Ca-Si(111) interface, with Ca atoms located at the threefold-filled site (TFS), directly above second-layer Si atoms: this triangular site is compatible with the 3×1 reconstruction. The three-dimensional unit cell we use in the study of the Ca-Si(111) interface is obtained from the F-Ca-Si(111) one (see below) with an empty sphere in place of a F atom, without any change either in the interlayer distances or in the spheres radius. The layer sequence is

$$\cdots \text{ES-Si-Si-ES-ES-Si-Si-ES-ES}_1\text{-Ca-ES-ES-ES-ES} \cdots .$$

The total number of atoms in the unit cell is 40: 12 Si + 12 ES for the Si side + 2 Ca atoms on both sides of the slab + 12 ES to simulate the vacuum, + 2 ES$_1$ to fill the space between Ca and Si.

Unlike the Ca-Si(111) interface, in the past few years a lot of experimental work has been done in order to understand the structural and electronic properties of the CaF$_2$-Si(111) interface.[1] Nevertheless its atomic structure is still an open question.[2,5,14] Several models have been proposed for this interface corresponding to the different terminations of the CaF$_2$(111) crystal. Basically these models differ by the presence of 0, 1, or 2 fluorine layers at the interface between the calcium and the silicon layer. Looking at the total energies, obtained by the LMTO-ASA method for a solid-solid interface, Satpathy and Martin[15] conclude that the interface with no interfacial fluorine layer is favored, although other models (with two interfacial F layers) cannot be ruled out.

Much progress has been made in the study of the initial stages of formation of the interface between CaF$_2$ and Si(111): deposition at low substrate temperature gives an interface with Si bonded to the F atoms, at higher temperature the first monolayer of CaF$_2$ loses half of its fluorine and Ca bonds to the surface.

Using high-resolution transmission electron microscopy, Batstone et al.[14] concluded that Ca is located on top of the surface Si; by careful medium-ion energy scattering analysis Tromp and Reuter[2] show that at one monolayer coverage Ca bonds to the Si substrate in a geometric arrangement virtually identical to CaSi$_2$ and that there is no F—Si bonding. Moreover they determined the detailed interface geometry: at the initial stages there is the formation of a F-Ca-Si(111) interface, with a monolayer of Ca deposited on Si(111) followed by a F layer. Ca adsorbs on the TFS and F on the threefold-hollow site (THS), the triangular site located directly above the fourth Si layer atoms. This conclusion was substantially confirmed by Zegenhagen et al.[5] investigating the interface with the x-ray standing-wave technique, even if they considered also the possibility of having some Ca atoms at the THS.

Other experimental information has been recently obtained by McLean and Himpsel.[16] They performed the angle-resolved photoemission study of the electronic

states of this interface, finding a two-dimensional inter-face band with its maximum at $\overline{\Gamma}$ (about 0.8 eV below the Si valence-band maximum). This state disperses down-ward toward the boundary of the surface Brillouin zone. Moreover with optical second-harmonic generation[17] the transition across the band gap between this filled bonding interface band and the corresponding antibonding empty band was measured to be 2.4 eV at $\overline{\Gamma}$.

In our calculation the electronic properties of the CaF_2-Si(111) interface at the early stages of interface for-mation are investigated through a 12-layer Si(111) slab covered with a monolayer of Ca and one of F atoms, forming a F-Ca-Si(111) structure. In our geometry the F and Ca atoms are adsorbed on the THS and TFS sites, re-spectively, like the Tromp-Reuter model.[2] In this model the Ca-F interlayer spacing is 0.78±0.03 Å, yielding a Ca—F bond length of 2.35±0.01 Å, which is the same Si—Si bond length in bulk Si. The bond length between Ca and first-layer Si is 3.09±0.03 Å and between Ca and second-layer Si is 3.06±0.06 Å, which is almost identical to the Si—Ca bond length in $CaSi_2$: 3.03–3.06 Å. In the calculation our layer sequence is

$$\cdots \text{ES-Si-Si-ES-ES-Si-Si-ES-ES}_1\text{-Ca-F-ES-ES-ES} \cdots .$$

In the bcc Si-ES lattice the distance between layers of spheres is 0.78 Å. For the Ca—F bond length we did not modify this distance. Therefore the Ca—F bond length is equal to that of Tromp-Reuter.[2] The Ca-surface Si inter-layer distance is 2.35 Å, the Ca-surface Si bond length is 3.23 Å, and the Ca-subsurface Si bond length is 3.13 Å in agreement with the data of Refs. 2 and 5. The total num-ber of atoms per unit cell is 40: 12 Si + 12 ES for the Si side + 2 Ca and 2 F atoms on both sides of the slab + 10 ES to simulate the vacuum +2 ES_1 to fill the space be-tween Ca and Si.

For the radii of the spheres we use the standard ASA procedure starting from nonoverlapping and touching spheres around each atom. In our geometry the sphere sizes are 1.357 Å for Si and for the ES in the Si and vacu-um region; 1.490 Å for the Ca atom; 1.225 Å for the F atom; 0.905 Å for ES_1.

IV. THE VALENCE STATES

We first present the results of our SLMTO-ASA calcu-lation of the electronic states of Ca-Si(111) interface. Fig-ure 1 shows our PDOS for a monolayer of Ca adsorbed on Si(111). The different panels show PDOS for the cen-tral, second, and interface Si layer, for the adsorbed Ca, and for the first empty-sphere layer on the vacuum site. The coupling between the Ca and Si atoms is strong and gives rise to different interface features which are also evident in the PDOS of the Ca layer. The orbitals in-volved are mainly the Si $3p$ dangling bond and the $4s\,3d$ states of Ca. The structure at the Fermi level has predominant Ca $4s\,3d$–Si $3p$ character, confirming the importance of having a scheme able to well describe the d states. We observe that the Ca-Si(111) system is a metal-lic one. This metallic character is easily understandable. We have a Ca adatom per Si surface atom, and the elec-tron counting at the interface gives one Si dangling-bond
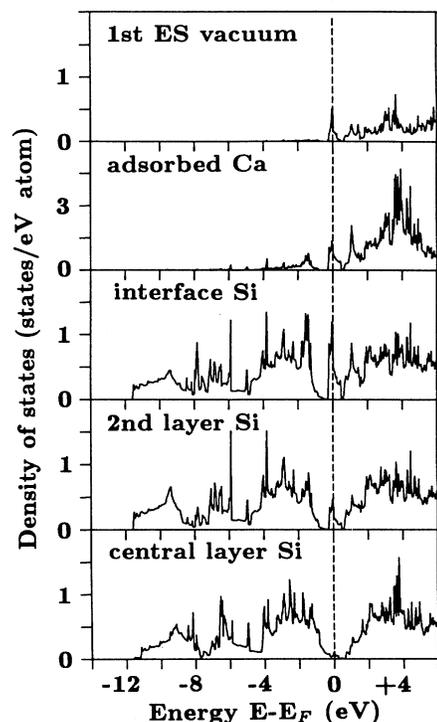
FIG. 1. Site-projected density of states for the Ca-Si(111) in-terface with Ca atoms adsorbed at the TFS geometry. Energies (in eV) are referred to the Fermi level.

electron plus two electrons from the Ca; these three elec-trons give rise to one filled and one half-filled interface bands and to a metallic interface.

A well-defined interface feature is located in the occu-pied part of the spectrum at ~ 1.5 eV below the Fermi level: this structure is predominantly due to the Ca $4s$–Si $3p$ bonding interaction (see below). Experimentally a similar feature was observed at the same energy with photoemission spectroscopy for the Ca-Si(111) interface at monolayer coverage.[3] The antibonding Ca $4s$–Si $3p$ interface structure is located at ~ 1.2 eV above the Fermi level. The projected bulk band structure of Si (hatched areas) and the dispersion of the localized filled and empty interface states for the Ca-Si(111) system are shown in Fig. 2.

As expected, three distinct interface bands are present: the Ca—Si bonding and antibonding states and between them the interface state located around the Fermi level. This last band shows an upward dispersion of about 0.5 eV on moving towards $\overline{K}$, which is confirmed by experi-mental data: angle-resolved photoemission spectroscopy on the Si(111)-Ca 3×1 interface[4,13] shows a surface state with an upward dispersion of 0.4 eV towards the $\overline{K}$ point of the 1×1 surface Brillouin zone, in good agreement with our results. The energy location differs by ~ 1.7 eV from our result, probably due to the different amount of Ca atoms in the two cases: $\frac{1}{3}$ of monolayer in the experi-ment, 1 monolayer in the calculation.

We can evaluate the Fermi level E_F and the top of the
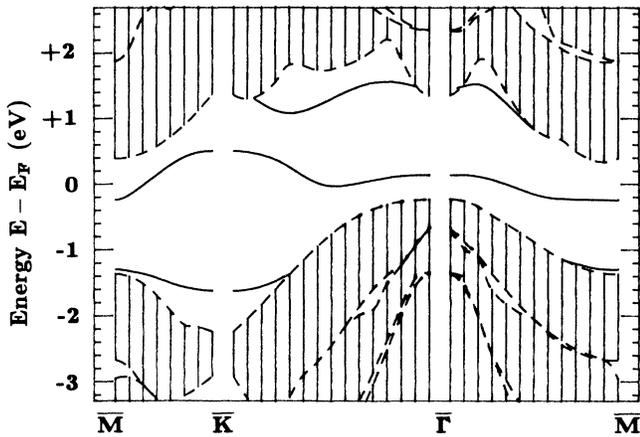
FIG. 2. The projected bulk band structure of Si (hatched areas) and the dispersion of the localized states for the Ca monolayer in the TFS geometry (solid lines). Energies (in eV) are referred to the Fermi level.

FIG. 3. Site-projected density of states for the F-Ca-Si(111) interface with Ca atoms adsorbed at the TFS geometry and F atoms adsorbed at the THS geometry. Energies (in eV) are referred to the highest occupied state.

silicon valence band E_v and therefore the (p-type) Schottky-barrier height given by $\Phi_p = E_F - E_v$; we obtain $\Phi_p = 0.23$ eV. Franciosi et al.[3] measured an experimental Schottky barrier of $\Phi_p = 0.42 \pm 0.1$ eV, while Olmstead et al.[4] give $\Phi_p = 0.35$ eV.

A first insight into the nature of Ca-Si interaction may be obtained by looking at the center of the LMTO-ASA bands. The center of the Ca 4s band is found ~ 2 eV above the Si gap, where the 3p dangling-bond orbital is located. Therefore the interface Ca—Si bond is mainly covalent in character, because in a predominant ionic bond we would expect these centers to be separated by several eV. This result agrees with the picture obtained by the surface-core-level shifts presented in Sec. V.

We will now discuss our self-consistent results for the F-Ca-Si(111) system. Figure 3 shows the calculated PDOS for the F-Ca-Si(111) interface. We observe in the PDOS relative to the F layer a very narrow F 2p peak corresponding to a quasiatomic level. This is due to the absence of a F—Si bonding. It corresponds to a F atom in a F$^-$ ionic state and to an ionic Ca—F bond. The energy separation between the onset of filled F 2p states and the empty Ca orbitals is ~ 7.0 eV; a LMTO-ASA analysis of bulk CaF$_2$ gives an energy gap of ~ 8.6 eV. The energy location of the F 2p peak is centered at about 7 eV below the highest occupied state of the Si side (E_v). It compares favorably with the quasiatomic peak observed at ~ 9 eV below E_v in the photoemission spectra from a submonolayer of Ca and F on Si(111).[13] The width of the F 2p band is ~ 1 eV in both theoretical and experimental results.

From this PDOS we can evaluate the band offset of our semiconductor-insulator interface: the energy separation between the insulator filled band, i.e., the top of the quasiatomic F peak, and the Si valence-band maximum. The computed value is 6.5 eV. This result is consistent with the experimental evaluations of the CaF$_2$-Si thick films band offset, ranging from 7.3 to 8.5 eV.[13,18] Our re-

sult, obtained in the monolayer coverage limit, shows that the main contribution to this band offset is already established at monolayer coverage.
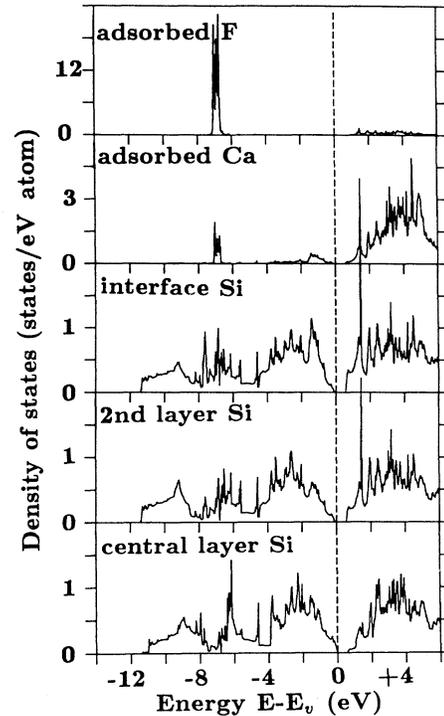
The PDOS of the central Si atom is very similar to that of the bulk Si.[6] Different features, due to the interface, are present in the PDOS of the interface Si atoms; the most interesting ones are the peaks located near the gap zone; one fully occupied near the top of the valence band, one empty located at the bottom of the conduction band. These structures are present even in the PDOS relative to the Ca adsorbed layer; they are originated from the bonding-antibonding interaction of Ca 4s and Si 3p dangling-bond orbitals. In agreement with the experimental data[13,19] the F-Ca-Si(111) interface is nonmetallic.

It is important to note that our results on the F-Ca-Si(111) system show relevant similarity with corresponding results we obtained for the Na-Si(111) interface:[7,20] the presence of the F$^-$ ion, as shown by our PDOS, leads the Ca interface atom in the 1+ oxidation state and determines the formation of a (F$^-$-Ca$^+$)-Si system with electronic properties similar to those of the isoelectronic Na-Si system. The Ca$^+$ configuration at the interface is confirmed by experimental data: the multiplet structure of the Ca 2p-3d transition in the near-edge x-ray-absorption fine-structure (NEXAFS) spectra obtained from a monolayer of CaF$_2$ on Si(111) (Ref. 19) shows indeed that Ca at the interface is in a 1+ oxidation state. Such a change in Ca oxidation state from the 2+ value,
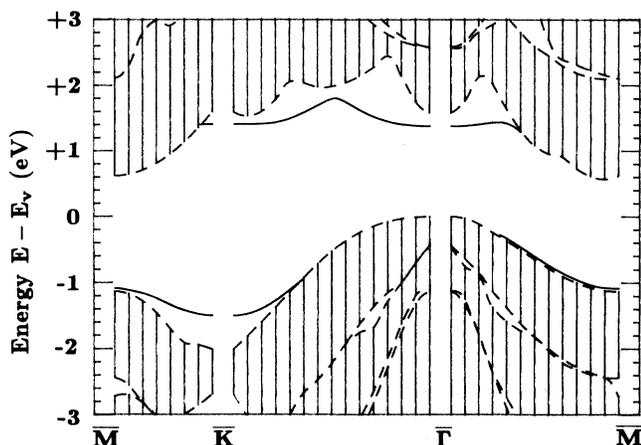
FIG. 4. The projected bulk band structure of Si (hatched areas) and the dispersion of the localized states for the F-Ca-Si(111) interface (solid lines). Energies (in eV) are referred to the highest occupied state.

characteristic of Ca in bulk CaF_2, to the $1+$ value found in the F-Ca-Si(111) system may be considered a first indication that the Ca atom is bonded differently with Si and F at this interface: while the Ca—F bond still shows a strong ionic character, the Si—Ca bond is mainly covalent. The covalency of the Si-Ca interaction is also confirmed by the position of the center of the Ca $4s$ band, which is located only ~ 1.8 eV above the Si $3p$ dangling-bond orbital.

The projected bulk band structure of Si (hatched areas) and the dispersion of the localized filled and empty interface states for the F-Ca-Si(111) interface are shown in Fig. 4. The Ca—Si bonding-antibonding covalent interaction gives rise to two bands with different curvature and dispersion. The filled band has its minimum at $\overline{K}$ well inside the Si(111) projected bulk gap. While this state remains a well-localized interface state in the $\overline{K} - \overline{M}$ direction, it becomes a resonance near $\overline{\Gamma}$. Here two resonances are found: the strongest at -0.90 eV and the weakest at -0.22 eV. The energy location and dispersion of the filled band are in good agreement with the angle-resolved photoemission results of McLean and Himpsel,[16] as one can see from the calculated and experimental data shown in Table I. Moreover they compare well with the calculated interface band of a solid-solid

TABLE I. Calculated and measured energy values (eV) at the points of high symmetry of the occupied interface state of the F-Ca-Si(111) interface. Energies are referred to the valence-band maximum.

	$\overline{\Gamma}$	$\overline{M}$	$\overline{K}$
Theoretical	$-0.22, -0.90$	-1.09	-1.50
McLean et al. (Ref. 16)	-0.75	-1.35	-1.55
Fujitani et al. (Ref. 21)	$-0.08, -0.51$	-1.17	-1.48

CaF_2-Si(111) interface[21] (see Table I). The agreement between our F-Ca-Si(111) ultrathin interface and the CaF_2-Si thick interface of Ref. 21 is another confirmation that the interface electronic properties are already established at monolayer coverage. Concerning the antibonding empty band, it is a well-localized interface state in the $\overline{K}\overline{\Gamma}$ and $\overline{\Gamma}\overline{M}$ directions, becoming a resonance near $\overline{M}$. At the $\overline{\Gamma}$ point the interface state is located 1.40 eV above the valence-band maximum. We evaluate the energy differences between this empty band and the strongest resonance at $\overline{\Gamma}$ to be 2.30 eV, in good agreement with the 2.4-eV optical-second-harmonic result of Heinz et al.[17] We consider our results as a strong confirmation that at the first stage of growth the CaF_2-Si(111) system has the F-Ca-Si(111) structure, with Ca and F atoms located at the triangular adsorption sites.

V. THE SURFACE-CORE-LEVEL SHIFT

The surface-core-level shift is computed as the difference between the core-level eigenvalue of the surface layer and that of central (bulk) layer. All the core energy levels and wave functions were computed during every step of the self-consistent iterative procedure, i.e., the frozen-core approximation has been released. The convergency has been tested in both all-electron potentials and in core and valence eigenvalues. Different methods to compute the core eigenvalues in the LMTO scheme have been tested; the difference in the results is significant (~ 0.3 eV) only for the shallow levels.[12] This uncertainty is substantially reduced when the surface-core-level shifts are considered, since differences between bulk and surface core energies are practically insensitive to the details of the calculation.[12]

Our results refer to the local-density approximation (LDA) core eigenvalue shift ΔE_{LDA}. The observed shift of the core-level binding energy ΔE_B is equal to[22]

$$\Delta E_B = -\Delta E_{LDA} + \Delta E_R + \Delta(\Delta E_c) \, ,$$

where ΔE_R is the variation in the relaxation energy and $\Delta(\Delta E_c)$ is the second difference in the correlation energy, not incorporated in the core eigenvalue term. The crudest approximation of this equation is the neglect of final-state effects, i.e., $\Delta E_B = -\Delta E_{LDA}$. We will show that this approximation can be used to interpret the experimental surface-core-level shifts. Therefore the variations in E_R and ΔE_c on going from bulk to surface are not very important and the significant contributions originate from the variations in the initial-state LDA eigenvalue. This agrees with the results on the core-level shifts in Ni compounds[23] and on the surface-core-level shifts for the lanthanides,[24] performed with our same technique.

In the following we limit our analysis to the Si $2p_{3/2}$ core level, presenting its variation for the two interfaces we studied. Since our core-level calculation is fully relativistic the $2p_{3/2} - 2p_{1/2}$ energy separation is an independent output which turns out to be 0.65 eV. Its experimental determination is 0.61 eV.[25]

The Ca-Si(111) interface. We observe two different variations of the Si $2p_{3/2}$ core level on going from the

bulk environment to the surface interaction with the Ca atom: we obtain a shift of $+0.30$ eV toward lower binding energy (BE) for the interface Si atom and of -0.16 eV toward higher BE for the subsurface Si. In spite of the fact that we do not include ΔE_R and $\Delta(\Delta E_c)$, our results are in excellent agreement with the two experimental structures found at $+0.45$ and -0.27 eV.[4,13]

The F-Ca-Si(111) interface. Our results of the F-Ca-Si(111) interface show two different shifts for the core level of the surface and subsurface Si atoms, like the Ca-Si(111) system. The surface Si core-level shift is of $+0.20$ eV, while the subsurface Si shift is of -0.36 eV. These shifts are similar to those found in the Ca-Si(111) interface confirming, as suggested by Olmstead et al.,[13] the similarity of the Ca—Si bond in the two interfaces. Even in this interface the agreement with the experimental core-level shifts is excellent. Two independent measurements have been performed: Olmstead et al.[13] ($+0.36$ and -0.57 eV) and Himpsel et al.[18,19]($+0.4$ and -0.8 eV).

We observe that the different shifts for the core level of the surface and subsurface Si atoms, obtained for both interfaces, do not imply that these atoms are oppositely charged with respect to the bulk silicon; our results show indeed that both interface and subsurface Si atoms are negatively charged with respect to the bulk reference of 0.1–0.2 electrons/atom. It is evident that a direct association of the observed shift with the charge transfer from Ca to Si is not correct: anything that changes the electrostatic potential in the core of an atom contributes to the variation of the core eigenvalue. We may single out two fundamental contributions to the observed shift: an intra-atomic contribution, due to the charge transfer on Si, that, in case of negatively charged Si atoms, shifts the Si core level toward the vacuum level, and an extra atomic contribution, due to the Madelung potential, that acts in the opposite direction, and may radically change the previous effect. Only the intra-atomic contribution to the core-level shift is directly related to the charge transfer; therefore it is necessary to subtract the Madelung potential (or its variation with respect to the Madelung bulk potential) from the core-level shift to obtain the intra-atomic contribution that turns out to be basically proportional to the charge transfer: Figs. 5 and 6 clearly show this effect for the Ca-Si(111) and F-Ca-Si(111) interfaces, respectively.

It is true that the charge transfer and the Madelung potential are not well defined in a solid and therefore these results can be considered only from a qualitative point of view. Nevertheless we consider significant the results of Figs. 5 and 6 showing that the measured surface-core-level shift cannot be simply interpreted in terms of charge transfer, but that the interatomic Madelung contribution has to be considered. The importance of Madelung subtraction has been already established in bulk compounds,[26] where it generally results in a partial cancellation of the charge-transfer effect. Our relevant result in this contest is that, in the presence of an electropositive adsorbed atom, the Madelung potential variation at the interface may be so strong as to determine the sign of the surface-core-level shift. Therefore, if the Madelung correction is disregarded, the core-level-
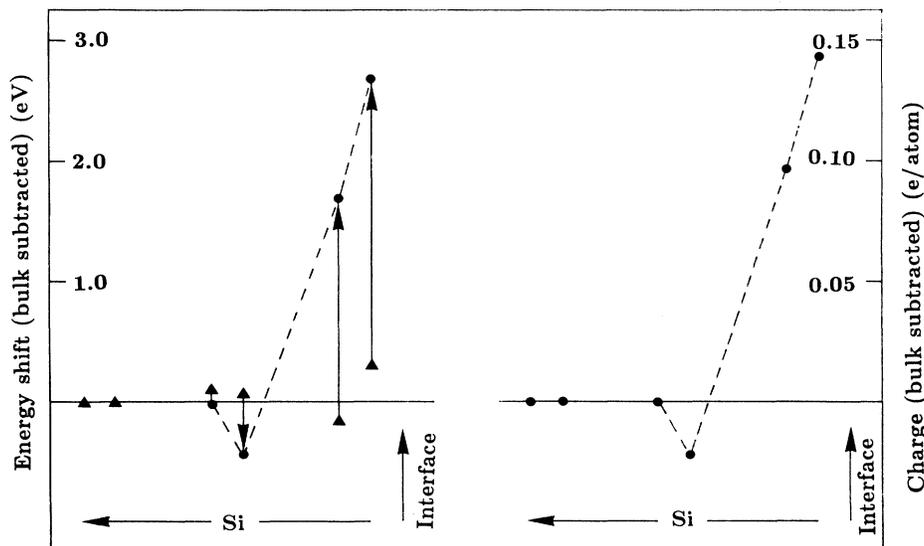
FIG. 5. Left panel: the surface-core-level shift (with respect to bulk Si) ΔE_{LDA} of the Si $2p_{3/2}$ state, for the different Si sites near the Ca-Si(111) interface. The total shift is shown by triangles, its intra-atomic contribution by solid circles. The intra-atomic contribution in a given site is obtained by subtracting from the total shift the Madelung shift, i.e., the difference between the Madelung energy in that site and the Madelung energy in bulk Si. Right panel: the difference in the number of electrons within the Si ASA sphere between a given site and the bulk Si. This charge variation is directly related to the intra-atomic contribution of the surface-core-level shift.
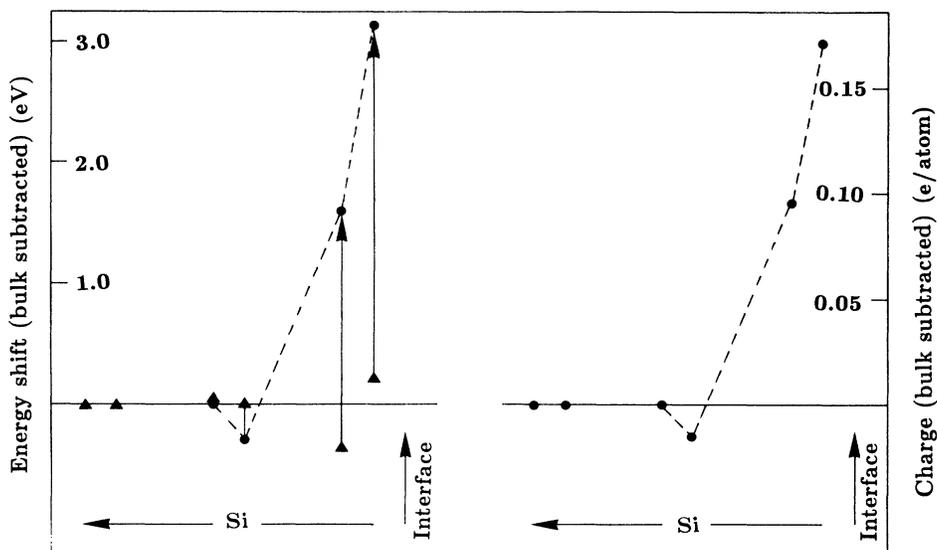
FIG. 6. Left panel: the surface-core-level shift (with respect to bulk Si) ΔE_{LDA} of the Si $2p_{3/2}$ state, for the different Si sites near the F-Ca-Si(111) interface. The total shift is shown by triangles, its intra-atomic contribution by solid circles. The intra-atomic contribution in a given site is obtained by subtracting from the total shift the Madelung shift, i.e., the difference between the Madelung energy in that site and the Madelung energy in bulk Si. Right panel: the difference in the number of electrons within the Si ASA sphere between a given site and the bulk Si. This charge variation is directly related to the intra-atomic contribution of the surface-core-level shift.

shift data may be easily misinterpreted: in the F-Ca-Si(111) system, for example, the presence of a negative shift (toward higher binding energy) would be related to a positive charging of the subsurface Si atoms, as in the case of a Si—F bond.[19,27] We showed that such a picture is not correct.

We finally observe that the charge transfer plotted in Figs. 5 and 6, which can interpret the experimental surface-core-level shift, has an order of magnitude which fully agrees with our analysis of the interaction between Ca and Si(111) surface in terms of a predominantly covalent chemical bond. As far as the F-Ca-Si(111) interface is concerned, it is important to stress that the basically covalent Si—Ca bond coexists with the strong ionic Ca-F interaction.

VI. CONCLUSIONS

In this paper the surface LMTO-ASA method is applied to the system formed by a monolayer of Ca adsorbed on Si(111) and to the F-Ca-Si(111) structure, the initial phase occurring during the formation of the epitaxial CaF$_2$-Si(111) interface. Both valence- and core-electron states have been calculated and their behavior discussed.

The valence interface states have been analyzed and successfully compared with the available experimental data. An excellent agreement with the experiments is found even for the surface-core-level shifts, theoretically computed through the initial-state core energy shifts. Moreover we have shown that Madelung subtraction is essential in order to successfully relate the core-level shift to charge transfer.

The overall picture which emerges from this analysis is that covalency plays a significant role in the surface bond between Si and Ca. This covalent character in the Si—Ca bond coexists with the strong ionic bond between Ca and F in the F-Ca-Si(111) interface. The experimental finding of F desorption and the formation of mediated CaSi$_2$ structure[2] may be considered as the replacement of an ionic Si—F bond with a covalent Si—Ca bond.

[1]See for example M. A. Olmstead and R. D. Bringans, J. Electron Spectrosc. Relat. Phenom. **51**, 599 (1990), and references therein.

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