Fermi-level pinning and interface states at CaF_2/Si(111)

Hideaki Fujitani
Fujitsu Laboratories, Ltd., 10-1 Morinosato-wakamiya, Atsugi-shi, Kanagawa-ken 243-01, Japan

Setsuro Asano
Institute of Physics, College of Arts and Sciences, University of Tokyo, 3-8-1 Komaba, Meguro-ku, Tokyo 153, Japan

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We examined the electronic structure at CaF_2/Si(111) interfaces using the linear muffin-tin orbitals method in the atomic-sphere approximation based on the local-density formalism. The Fermi level is pinned by interface states for the model with eightfold-coordinated Ca atoms at the interface, but Fermi-level pinning does not occur in models in which F atoms are dissociated from interface CaF_2. The interface states we obtained agreed well with experiments. We will discuss the interface atomic structure by comparing the electronic structures with experiment.

I. INTRODUCTION

CaF_2 grows on Si(111), and forms an epitaxial insulator-semiconductor interface. This system has many potential applications and offers a good opportunity to study bonding configurations and the epitaxial relationship at the ionic-covalent interface. CaF_2 has almost the same lattice constant as Si, and its epitaxial film has type-*B* orientation where the film is rotated 180° about the Si⟨111⟩ axis. $NiSi_2$ and $CoSi_2$ have the same crystal structure as CaF_2, and they also grow on Si(111) and form epitaxial metal-semiconductor interfaces. It may be possible to fabricate three-dimensional, fully epitaxial devices on Si with these materials. These interfaces give us an excellent opportunity to study the electronic properties of the interface between two dissimilar solids. Since the atomic structures of these interfaces are fairly well understood, it is now possible to determine the causes of many of the physical phenomena that occur at this interface.

Using high-resolution transmission electron microscopy (TEM) to examine the CaF_2/Si(111) interface, Batstone, Phillips, and Hunke related electrical properties to the interface atomic structure.[1] They grew a thick epitaxial CaF_2 film on Si(111) at 700 °C, and rapidly thermally annealed (RTA) it in a flash-lamp annealing system. From TEM images and the electrical properties of both as-grown and RTA films, they found that F atoms are removed from the interface during RTA leaving fivefold-coordinated Ca atoms, and this greatly improves the electrical properties of the interface. They concluded that the as-grown interface has an eightfold structure and the RTA film has a fivefold structure (Fig. 1).

Soon after Batstone's work, Tromp and Reuter (TR) reported medium-energy ion scattering from monolayer films of CaF_2 grown at 770 °C.[2] They discovered that the interface Ca atoms are located on the top of the second Si atoms. They proposed a new atomic model of the CaF_2/Si(111) interface (TR model).

More recently, McLean and Himpsel obtained band dispersion of an interface state using monolayer CaF_2 films grown at 700 °C and annealed at 800 °C for 4 min.[3] Himpsel had reported the surface sensitive core-level spectrum of 8 Å films grown at 750 °C, which corresponds to two or three CaF_2 layers.[4]

We studied whether these results can be explained by self-consistent calculations based on the Hohenberg-Kohn-Sham local-density approximation (LDA).

II. CALCULATIONS

We used the Andersen linear muffin-tin orbitals method in the atomic-sphere approximation (LMTO-ASA). We used the supercell technique to overcome the loss of periodicity perpendicular to the interface. The scalar relativistic calculations were performed with the LDA parametrization of Janak, Moruzzi, and Williams.[5] A nearly orthogonal representation was used for muffin-tin orbitals, and the combined correction was not included.[6]

We studied three interface models: the eightfold, fivefold, and TR models (Fig. 1). Supercells were formed by $9(Si_2)/10(CaF_2)$ for the eightfold model, $9(Si_2)/2(CaF)\cdot 8(CaF_2)$ for the fivefold model, and $9(Si_2)/2(CaF)\cdot 6(CaF_2)$ for the TR model. These supercells all have a space-group symmetry of D_{3d}^3 ($P\bar{3}m1$). We used the Si lattice constant (5.429 Å) and neglected lattice relaxation for the eightfold and fivefold models. For the TR model, we used the interface Si—Ca bond length (3 Å) determined by medium-energy ion scattering.[2]

Atomic-sphere radii were determined for bulk band dispersion, especially for the occupied states, to agree with those obtained by the Wimmer-Krakauer-Weinert-Freeman full-potential linear augmented-plane-wave method (FLAPW). The radii were 1.337 Å for Si, 1.466 Å for Ca, 1.249 Å for F, 1.336 Å for empty spheres in the Si region, and 1.358 Å for empty spheres in the CaF_2 region. At the interface, empty-sphere positions and radii

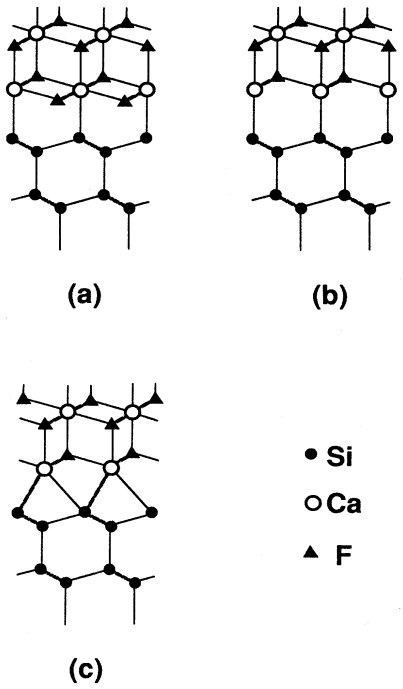

FIG. 1. The three different models of the CaF_2/Si(111) interface: (a) eightfold-coordinated Ca, (b) fivefold-coordinated Ca, (c) TR model proposed by Tromp and Reuter (Ref. 2).

are determined to fill interstitial spaces and decreased the overlap of the spheres.

To exclude the ghost bands, which sometimes appear in linearized band calculations, we expanded the muffin-tin orbitals from the resonance energy levels of atomic spheres. This was necessary to calculate the CaF_2 energy structure, because Ca and F atoms have shallow core levels (Ca 3*p*, F 2*s*).

The bulk band gaps calculated by the LMTO-ASA were 0.55 eV for Si and 6.96 eV for CaF_2, although measured values of the band gap are 1.12 eV for Si and 12.1 eV for CaF_2. Despite this discrepancy between the calculated and measured values, we obtained interface states which are in good agreement with experiments.[7]

III. RESULTS

Figure 2(a) is the local density of states (LDOS) of the eightfold model, which Batstone considered to be the interface structure of as-grown films. A large peak of the interface state occupies the Si band gap near the interface. Although this interface state remains at the Si layer farthest from the interface, it hardly penetrates the CaF_2 layer. The LDOS of the second CaF_2 layer from the interface was very similar to the bulk density of states (DOS). At the first Si layer, the LDOS decreases near the lower part of the conduction band, and at about -4 eV of the valence band compared with the bulk DOS of Si. This resembles the LDOS of free Si(111) surface (with the lattice not relaxed). The Fermi level of the eightfold model is pinned by the interface state in the Si band gap.

Figure 2(b) shows the LDOS of the fivefold model, which Batstone considered to be the interface structure of RTA films. When the interface F atoms were removed, the large peak of the interface states disappeared from the Si band gap, and the highest occupied states are

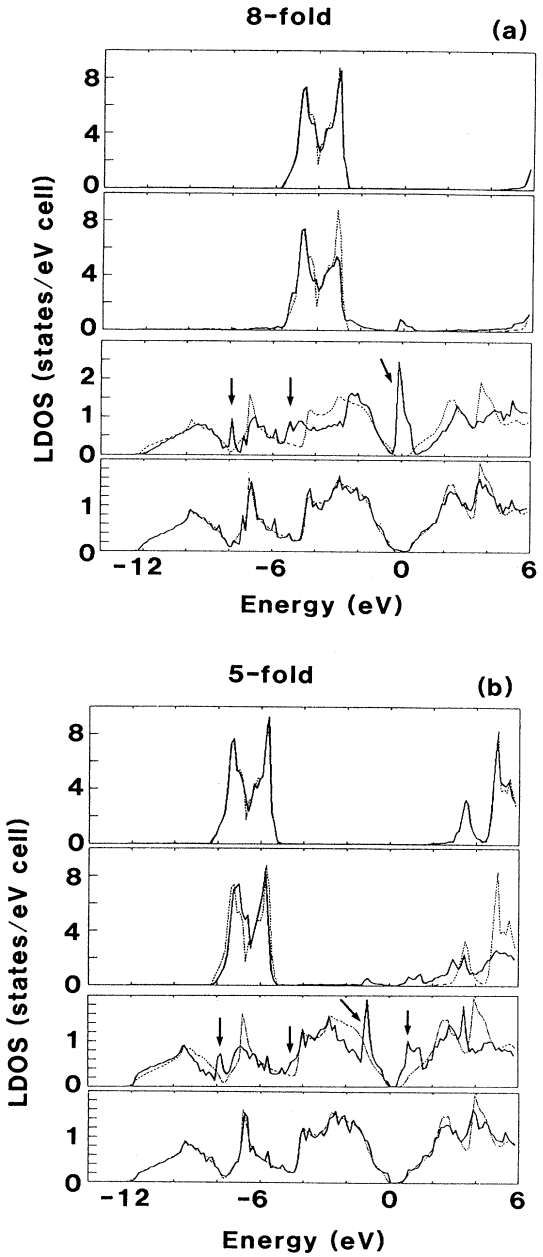

FIG. 2. Local density of states (LDOS) of the CaF_2/Si(111) interface: (a) LDOS of eightfold model, (b) LDOS of fivefold model. From top to bottom, they are fifth CaF_2 layer, first CaF_2 layer, first Si_2 layer, and fourth Si_2 layer from the interface. Dotted lines are bulk density of states of Si and CaF_2. The arrows show the interface states. The zero energy point is the Fermi energy of the supercell.

at the valence-band maximum of Si (E_{VBM}). The interface states are divided into occupied and unoccupied states. At the first Si layer, the bulk Si band does not decrease according to the eightfold model.

Band offsets between E_{VBM} and the top of the CaF_2 filled band are 2.41 eV for the eightfold model and 5.31 eV for the fivefold model.

Figure 3 shows the two-dimensional band structure of the eightfold and fivefold models. The band structures are obtained by examining the wave-function weights of the energy eigenvalues of the supercells in each atomic sphere of the Si and CaF_2 layers. To determine the interface states, we compared the band structure of both models with the calculations by the supercell containing $9(Si_2)$ layers and 41 empty-sphere layers. Since the interface states of the fivefold model are extended near the Γ point, it was difficult to distinguish the interface states from the bulk bands.

For the eightfold model, the interface states in the Si band gap have a very similar band dispersion to the surface state of Si (with the lattice not relaxed). They consist of two lines, which separate 0.13 eV at the Γ point and about 0.02 eV near the $M-K$ line. These are formed mainly by Si p orbitals, and occupied by electrons near the $M-K$ line. There are also interface states at -8 eV which appear at the Si surface.

For the fivefold model, there are unoccupied and occupied interface states in the Si band gap. They are both formed by two lines. The unoccupied interface states are strongly localized near the interface. They are formed by Si s orbitals and interface Ca d orbitals near the Γ point, and an amount of empty-sphere s orbitals at the interface increases near the $M-K$ line. The two lines of the unoccupied states are located 1.12 and 1.14 eV above E_{VBM} at the Γ point and are about 0.01–0.02 eV apart along the whole symmetry line.

The two lines of the occupied interface states separate near the Γ point. The upper line extends into the Si layer near the Γ point. It has the same energy as E_{VBM} at the Γ point, and is 1.00 eV lower than E_{VBM} at the M point and 1.20 eV at the K point. The lower line is hidden by the Si bulk band near the Γ point. It is localized near the interface so that it can be distinguished from the bulk Si band. This line reaches the Γ point which is 0.39 eV lower than E_{VBM} [not shown in Fig. 3(b)], and is located 1.12 eV at the M point and 1.19 eV at the K point. Both occupied interface states are formed mainly by Si p orbitals and by a small amount of the interface Ca orbitals.

From these energy structures, it is obvious that the interface Si atoms have dangling bonds in the eightfold model, and that the interface Si—Ca bonds are formed in the fivefold model.

We list the number of valence electrons in bulk Si and CaF_2 in Table I. Figure 4 shows the difference in valence electrons in each sphere at the CaF_2/Si(111) interfaces from the bulk values. The two empty spheres at the interface are not shown in Fig. 4. Their radii and number of electrons are listed in Table II.

The number of electrons near the interface differs from the bulk values depending on the interface structure. In the Si layers farther from the interface, electrons are fewer in Si spheres and more plentiful in interstitial spheres than bulk. Electric-dipole layers are formed by two Si atomic layers and two empty-sphere layers. This was also observed at $NiSi_2$/Si(111) interfaces.[8] In the farther CaF_2 layers, the number of electrons is about the same as the bulk values, so electric-dipole layers are not formed.

Although the interface F atom of the eightfold model has fewer electrons than bulk, it still takes electrons from the interface Ca atom. This prevents the formation of an interface Si—Ca bond. By removing the interface F

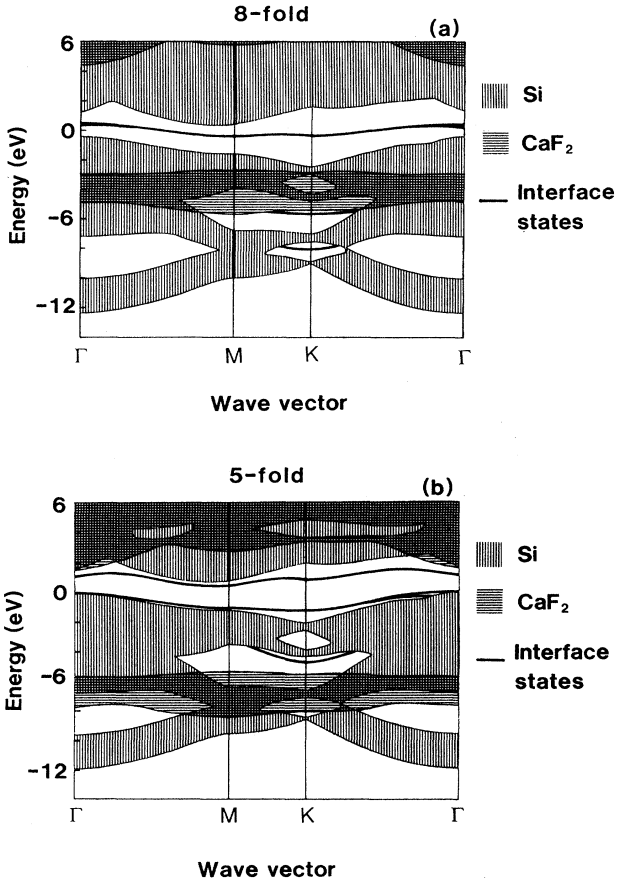

FIG. 3. Two-dimensional band structure of the CaF_2/Si(111) interface: (a) the eightfold model, (b) the fivefold model. The zero energy point is the Fermi energy of the supercell. Since this was calculated by use of the LDA, band alignments of both valence and conduction bands differ from the measured values.

TABLE I. The total valence electron number of each atomic sphere in bulk Si and CaF_2.

	Si	Emp.	Ca	F	Emp.
Number of electrons	3.214	0.786	0.707	5.465	0.363

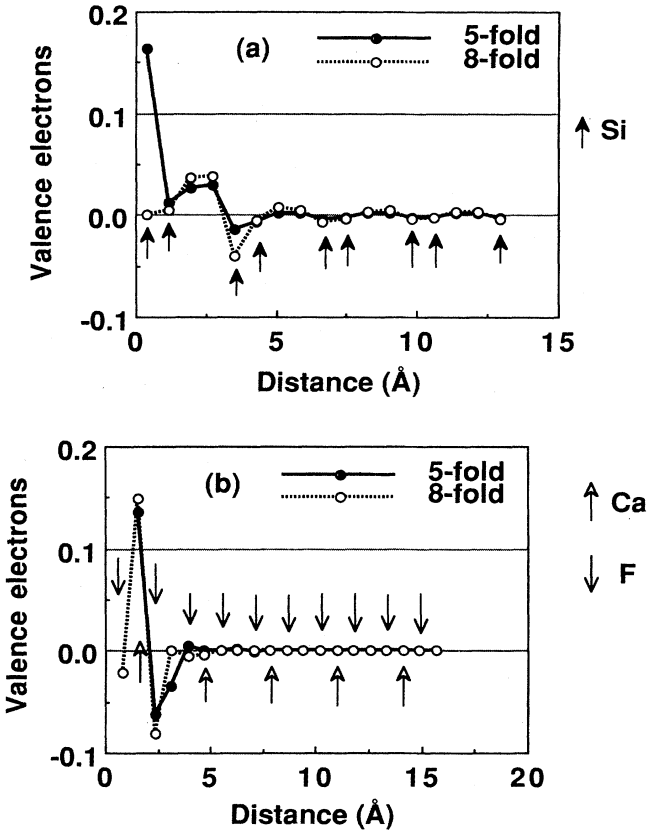

FIG. 4. Difference of the total valence electron number from the bulk values in Table I: (a) in the Si layer, (b) in the CaF_2 layer. The interface is on the left. Arrows indicate atomic sphere locations.

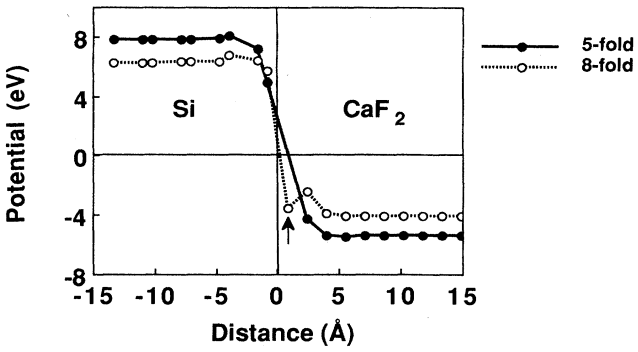

FIG. 5. Potential in each Si and F atom position. This was calculated by Madelung constants and charges in other atomic spheres. The center line is the interface. The arrow indicates the interface F atom.

atom, the Ca atom can give electrons to the interface Si atoms, so that the interface Si—Ca bond can be formed.

Figure 5 shows the potential at each Si and F site of the supercells. Its on-site value was calculated by summing up the products of Madelung constants and the charge in other spheres.[6,8] The difference between the eightfold and fivefold models reflects the band offset difference. In the eightfold model, there is a kink at the interface F atom site. If the kink was neglected, the eightfold model has a smooth potential curve like that of the fivefold model. The interface F atom seems to be an extra atom for the eightfold model.

IV. DISCUSSION

In our calculations, interface states are formed primarily by a pair of two lines. In the eightfold model, the interface states in the Si band gap extend farther into the Si layer at the Γ point than near the $M-K$, line, so that they separate more near the Γ point. With a $6(Si_2)/7(CaF_2)$ supercell, this separation was about 0.4 eV at the Γ point, which is larger than 0.13 eV of the $9(Si_2)/10(CaF_2)$ supercell. Since there is one Si atom at each interface in the supercell, the interface states of the eightfold model are formed by the dangling bond of the interface Si atom. Because the supercell has two interfaces in the unit cell, interface states have two lines in the two-dimensional Brillouin zone. They divide into bonding-antibonding states by the interaction between the tails in the Si layer.

In the fivefold model, extended interface states also show large energy separation. Since the occupied interface states near the Γ point interact with the bulk Si band, the upper line near the Γ point has almost the same electron distributions as the Si bulk energy states.

In reality, there should be one line of the interface state in the Si band gap in the eightfold model, and two lines (occupied and unoccupied) in the fivefold model. The interface F atoms of the eightfold model are threefold coordinated, whereas the F atoms are fourfold coordinated in bulk CaF_2. But in the LDOS of the eightfold model, there are no dangling orbitals in the CaF_2 layer. The interface F atom orbitals are filled by electrons, because CaF_2 is an ionic crystal. By removing the F atoms, interface Ca atoms have dangling bonds. With the Si and Ca orbitals, bonding and antibonding states are formed, so that the fivefold model has two lines of the interface states in the Si band gap. These Si—Ca bonds are weaker than the sp^3 bonds of the bulk Si, so the interface states appear in the Si band gap. Since this bond strength crucially depends on the distance between the Si and Ca atoms, the energy positions of the interface states may be changed slightly by lattice relaxation.

In Fig. 4, the electron distributions of the eightfold and fivefold models are almost the same except at the interface Si and F spheres. By the dissociation of the F atom, the interface Si sphere obtains electrons. But the inter-

TABLE II. The total valence electron number of the empty spheres at the interface.

	Eightfold		Fivefold	
Radius (Å)	0.768	1.258	1.459	1.087
Number of electrons	0.156	0.743	0.751	0.421

TABLE III. Core energy level shifts of atoms near the interface. The plus sign indicates a small binding energy and the minus sign indicates a large one in (eV).

	Eightfold	Fivefold	TR	Expt.
First Si 2*p*	+0.16	+0.18	+0.01	+0.4[a]
Second Si 2*p*	+0.19	−0.44	−0.64	−0.8[a]
First Ca 3*p*	+0.30	+0.51	+0.01	+2.3[b]

[a]Reference 4.
[b]Reference 9.

face Ca sphere of the eightfold model has almost the same electron distribution as the fivefold model. This implies that the Si substrate changes the electronic states of the CaF_2 layer to dissociate the F atom from the interface CaF_2 layer.

A metallic CaF_2/Si(111) interface is formed when the CaF_2 layer is grown at a low temperature and not sufficiently annealed. Batstone *et al.* reported that for as-grown films on a *p*-type Si substrate it is difficult to form an inversion layer of minority carriers (electrons).[1] These properties are consistent with the Fermi-level pinning of the eightfold model. When the Si dangling bonds are terminated by the Ca atoms by removing the F atoms from the interface, the Fermi-level pinning disappears. This coincides with the dramatic improvement in the electrical properties measured by Batstone *et al.*

Olmstead *et al.* reported that the band offset changed by thermal annealing as the F atoms are dissociated from the interface.[9] According to our calculations, the band offsets are 2.41 eV for the eightfold model and 5.31 eV for the fivefold model. This is consistent with the observations of Olmstead *et al.*, but by their experiments, the band offset changed from 7.3 to 8.3 eV. Himpsel also obtained a band offset of 8.5 eV.[10] The calculated values are smaller than the measured values, because of LDA treatment for exchange and correlation.

The band dispersion of the interface state of the CaF_2/Si(111) was recently determined with angle-resolved photoelectron spectroscopy by McLean and Himpsel.[3] The unoccupied interface state is 1.65 eV above E_{VBM} at the Γ point, and the occupied one had a similar dispersion to the lower line of the fivefold model. Its energy values from E_{VBM} were 0.75 eV at the Γ point, 1.35 eV at the *M* point, and 1.55 eV at the *K* point. In the experiment, the occupied interface state was more hidden by the Si bulk band than those of the fivefold model.

According to our calculations with the TR model, the band offset was 5.88 eV and the highest occupied states were at E_{VBM}. Since the filled band of the CaF_2 layer was at a lower energy than that of the fivefold model, the empty band of the CaF_2 layer is lowered more than that of the fivefold model. The occupied states of the TR model were reasonably obtained, but unoccupied states were not so reliable. The occupied interface states had similar band dispersion to those of the fivefold model, and consisted of two lines. Their energy values from E_{VBM} were 0.08 (0.51) eV at the Γ point, 1.07 (1.26) eV at the *M* point, and 1.49 (1.47) eV at the *K* point (lower one). They were mostly hidden by the Si bulk band. Since the two bands are separated by bonding interactions between the tails, a real interface state may have the average energy values of the two bands. Compared with experimental values, the Γ point seems to be an exception because of the interaction with the Si bulk band. The TR model agrees better with the angle-resolved experiment than the fivefold model.

Table III shows the core-level shifts of the Si and Ca atoms near the interface. These were obtained by comparing them with the core levels farther from the interface. The measured Si 2*p* level shows both low- and high-energy shifts. This occurs only for the fivefold model in calculations, although the values are almost half the measured ones.

The TR model agrees with the angle-resolved experiment by McLean and Himpsel,[3] and the fivefold model is compatible with the core-level spectroscopy experiment by Himpsel *et al.*[4] The main difference between the samples in the two experiments is the thickness of the CaF_2 films. The McLean and Himpsel experiment used monolayer films and the Himpsel experiment used two or three monolayer films. It is probable that the interface atomic structure depends on the overlayer thickness.

V. SUMMARY

According to our calculations, the Fermi level is pinned by the interface state in the Si band gap in the eightfold model of the CaF/Si(111) interface, and the Fermi-level pinning disappears in the fivefold model. This supports Batstone's interface models. Our results suggest that the interface atomic structure of both the TR and fivefold models exists at the CaF_2/Si(111) interface after the dissociation of interface F atoms. The occupied interface states quantitatively agree with experiments, although the band offset is depressed by LDA.

ACKNOWLEDGMENTS

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[7]We performed calculations, matching the band gap of CaF_2 to the experimental value. Occupied interface states are about the same as those of LDA calculations. We present only LDA results in this paper.

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