

Electronic structure of the $\text{CaF}_2/\text{Si}(111)$ interface

M. R. Salehpour and S. Satpathy

Department of Physics and Astronomy, University of Missouri-Columbia, Columbia, Missouri 65211

G. P. Das

Solid State Physics Division, Bhabha Atomic Research Center, Bombay 400 085, India

(Received 28 January 1991; revised manuscript received 29 April 1991)

The electronic structure of the $\text{CaF}_2/\text{Si}(111)$ interface calculated within the local-density-functional theory with the linear muffin-tin orbitals method is presented. We examine the interface states for three different structural models of the Ca-terminated interface. For each model a pair of two-dimensional interface bands is found. The unoccupied interface band around the zone center is a truly localized band while the occupied interface band is buried below the valence-band maximum in agreement with recent experimental results. The nature of the two-dimensional interface states and the extent of localization of the wave functions at the interface are also discussed.

I. INTRODUCTION

Understanding interfaces formed between two solids is an area of fundamental importance in solid-state physics. The $\text{CaF}_2/\text{Si}(111)$ interface is an excellent prototype of the semiconductor-on-insulator interfaces to study since both bulk Si and CaF_2 are well-understood systems and experimentally good, clean interfaces between these materials are easy to grow. This is facilitated by the small lattice mismatch ($\sim 0.6\%$) between the two bulk crystals which makes it possible to grow atomically abrupt interfaces. From a technological point of view semiconductor interfaces are key components in electronic devices. Of particular interest to the industry are semiconductor-insulator interfaces that can be formed on silicon using epitaxy. In view of the potential applications the $\text{CaF}_2/\text{Si}(111)$ interface has been studied extensively in the recent past.¹

The $\text{CaF}_2/\text{Si}(111)$ interface is grown² either by molecular-beam epitaxy or by chemical vapor deposition. Other chemically similar interfaces such as SrF_2/Si and LaF_3/Si have just begun to be grown and studied.³ Initial stages of formation and electronic structure of the $\text{CaF}_2/\text{Si}(111)$ interfaces have been examined with *in situ* photoemission,^{4,5} transmission electron microscopy (TEM),⁶ Auger electron spectroscopy, x-ray absorption,⁷ and very recently with x-ray standing-wave (XSW) experiments.⁸ The crystalline quality of the epilayers has been examined with a variety of experimental tools, such as high-resolution electron microscopy,⁹ medium energy ion scattering (MEIS),¹⁰ Rutherford backscattering (RBS),¹¹ and reflection high-energy electron diffraction (RHEED).^{12,13} These experiments have established the high quality of the CaF_2 epilayers.

The exact atomic structure of the interface is still under debate and the various experiments indicate that the structure may even depend on the experimental growth condition. Earlier it was believed that the (111) plane being a natural cleavage plane in CaF_2 with a fluorine sur-

face layer, the interface also contains a full triple layer of CaF_2 leading to a stoichiometric interface with fluorine termination. Such an interface was shown by us¹⁴ from total energy calculations to be unstable with respect to both dissociation and disproportionation. It is now established from experiments that in fact the epitaxial interface grows predominantly as Ca terminated even though under fluorine-rich growth conditions small parts of the interface may have fluorine termination. The preference for Ca termination is also supported from the fact that the morphology of Ge layers grown on $\text{CaF}_2/\text{Si}(111)$ markedly improves by initial electron irradiation which removes the outermost fluorine layer from the stoichiometric $\text{CaF}_2(111)$ surface.¹⁵ The orientation of the CaF_2 film with respect to the Si substrate has been determined from the RBS (Ref. 11) as well as from the high-resolution electron microscopy experiments.⁹ These experiments show the interface to be of "type-B" with a "twin boundary" at the interface plane with the CaF_2 part rotated by 180° with respect to the Si $\langle 111 \rangle$ axis. Based on empirical tight-binding cluster calculations, Nath and Anderson¹⁶ have argued that the type-B structure is favored over type-A from both energetic and dynamical considerations. In the structural models considered here we will therefore assume type-B orientation.

The interface atomic arrangement is thus completely determined if we know the position of the Ca atoms with respect to the silicon substrate. The three likely positions of the Ca atoms are shown in Fig. 1. In the first of these^{17,18} the Ca atom occurs on top of the first-layer Si atom with the Ca site having a threefold symmetry (the Ca atom has fivefold coordination). We refer to this as the "top-site" structure following earlier nomenclature. In the other two models, the Ca atom sits either on top of the second-layer Si atom (T_4 structure) or on the threefold hollow site on top of the fourth-layer silicon (H_3 structure). The top-site structure is favored by the transmission electron microscopy results of some workers^{18,19} but not of others.²⁰ The T_4 structure is suggested

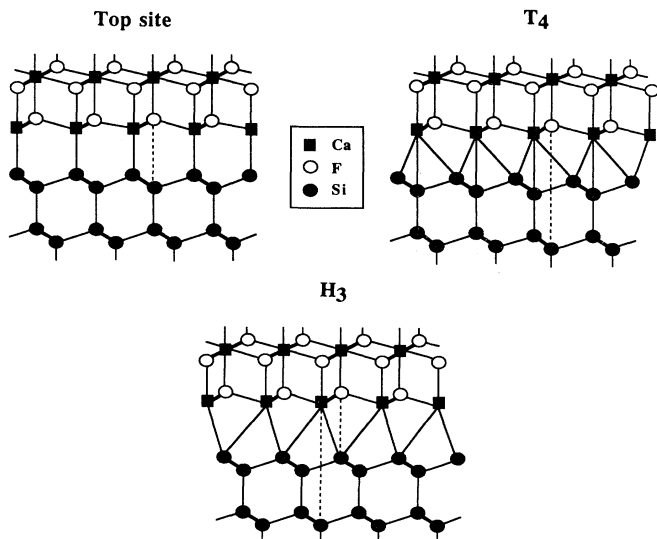


FIG. 1. Possible structures of the $\text{CaF}_2/\text{Si}(111)$ epitaxial interface. All three models represent a Ca-terminated interface with “type-B” orientation. The top-site structure has the interface Ca atom occurring on the top of the first-layer silicon. In the T_4 structure the Ca atom occurs on top of the second-layer Si, while in the H_3 structure it occupies the hollow site on top of the fourth-layer silicon. A dashed line between two atoms indicates one atom to be directly above the other.

from the MEIS experiments¹⁰ while the XSW experiment⁸ indicates the presence of both the T_4 and the H_3 structures at higher temperatures. Total energy calculations for the bulk CaSi_2 have recently been reported to show that the total energy difference between the T_4 -like and the H_3 -like sites for Ca are less than 0.01 eV per formula unit.²¹ One might extend the analogy to the case of CaF_2 on Si and expect both sites to be likely in the epitaxial interface. This indicates that the interface atomic structure may in fact depend on the experimental growth condition.

In this paper we focus on the two-dimensional electron bands of the $\text{CaF}_2/\text{Si}(111)$ interface. As is well known, the presence of an interface can introduce new electronic states in the band structure and thus influence its physical properties. The electronic structure of the $\text{CaF}_2/\text{Si}(111)$ interface has been studied experimentally using angle-resolved photoemission²² and optical second-harmonic generation.²³ The experiments indicate the presence of a pair of interface electron bands with the occupied band buried in the Si valence bands and separated from the unoccupied band by about 2.4 eV. The dispersion of the occupied band in the Brillouin zone is about 0.8 eV. On the theoretical side, there exists only one paper devoted to the interface bands by Fujitani and Asano,²⁴ who examined the top-site and the T_4 structures. In this paper, we examine the nature of the interface electronic states for all three structural models and compare the results of our calculations with existing theoretical and experimental results.

II. METHOD

The band structures of the interfaces were calculated within the local-density approximation (LDA) to the density-functional theory²⁵ with the von Barth–Hedin exchange-correlation energy.²⁶ We used the supercell technique to overcome the absence of periodicity along the direction perpendicular to the interface. The supercells consisted of $[5(\text{Si}_2)][2(\text{CaF})\cdot 3(\text{CaF}_2)]$ layers. We found these supercells to be large enough for our purposes; test calculations using somewhat smaller supercells produced nearly the same results for the interface states. Similar supercell calculations for the NiSi_2/Si interfaces were recently performed by Das *et al.*²⁷

The linear muffin-tin orbitals method²⁸ in the atomic spheres approximation (LMTO-ASA) was used to solve the scalar-relativistic LDA equations. Since the atomic numbers of the constituent atoms are relatively small, the effect of spin-orbit coupling is small and was neglected in the calculations. We ignored the small lattice mismatch (0.6%) between Si and CaF_2 bulks and used the lattice constant of 5.43 Å corresponding to bulk Si. The distance between the interface Si layer and Ca layer can in principle be calculated from total energy optimization; however, there are too many lattice parameters involved here and in this paper this distance was taken to be 2.34 Å. This, for instance, means that the bond length of Ca with the second-layer Si in the T_4 structure is 3.12 Å which compares favorably with the experimental value of 3.06 ± 0.06 Å.¹⁰ We treated Si $3s^2, 3p^2$, Ca $4s^2$, and F $2p^5$ electrons as valence electrons and the rest as frozen core electrons.

As is standard in the LMTO calculations, empty spheres were used to better describe the electron charge density in the interstitial open positions of the unit cell. Sphere radii for all atoms and empty spheres in the bulk region of the supercell were chosen to be 1.34 Å. The positions and radii of the two empty spheres used in each interface region were chosen so as to achieve maximal space filling and minimal overlap between the spheres. Muffin-tin orbitals with spd angular momenta were retained on all atoms as well as on empty spheres. Self-consistency was achieved by using ~ 25 k points in the irreducible Brillouin zone (BZ).

III. RESULTS

In Fig. 2 we show the deviation of net charges in various atomic muffin-tin spheres from their corresponding bulk values. The charges on the two empty spheres at the interface, not shown here, are listed in Table I. The total

TABLE I. Integrated charge within the muffin-tin empty spheres at the interface together with the respective sphere radii.

	Top site		T_4		H_3	
	$E(1)$	$E(2)$	$E(1)$	$E(2)$	$E(1)$	$E(2)$
Radius (Å)	1.34	1.34	1.34	1.14	0.91	1.35
Charge ($ e $)	-0.49	-0.87	-0.73	-0.62	-0.24	-0.78

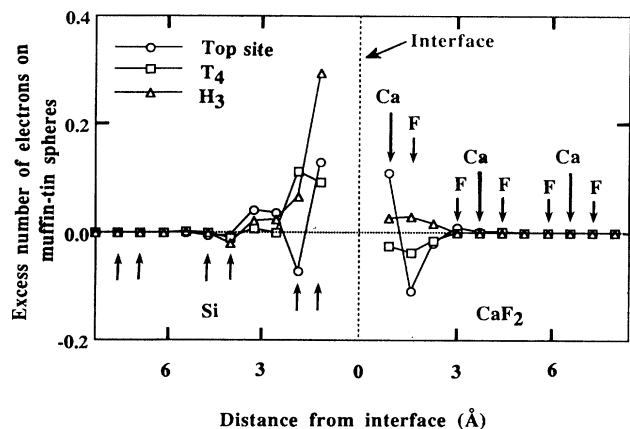


FIG. 2. Excess valence electrons on the muffin-tin spheres compared to their corresponding bulk values. The arrows indicate atom positions while the rest are empty spheres.

number of electrons on various spheres reaches the bulk values within a few atomic layers from the interface. The bulk values were calculated to be $+0.68|e|$ for the Si muffin-tin sphere and $-0.68|e|$ for the corresponding empty spheres. The corresponding values for CaF_2 bulk were as follows: $1.56|e|$ (Ca), $-0.64|e|$ (F), and $-0.28|e|$ (empty). Differences from the bulk are noticeable only close to the interface.

The interface electronic structure was obtained by comparing the supercell bands with the bulk bands of Si and CaF_2 projected onto the two-dimensional interface Brillouin zone and, in addition, by examining the nature of the wave functions of the supercell electron states. In the supercell calculations the width of the bulklike valence bands of Si and CaF_2 are more or less the same as the widths in the corresponding bulk materials, i.e., 12.0 eV for Si and 3.0 eV for CaF_2 . The calculated bulk band gaps are 7.0 eV for CaF_2 and 0.5 eV for Si as compared to

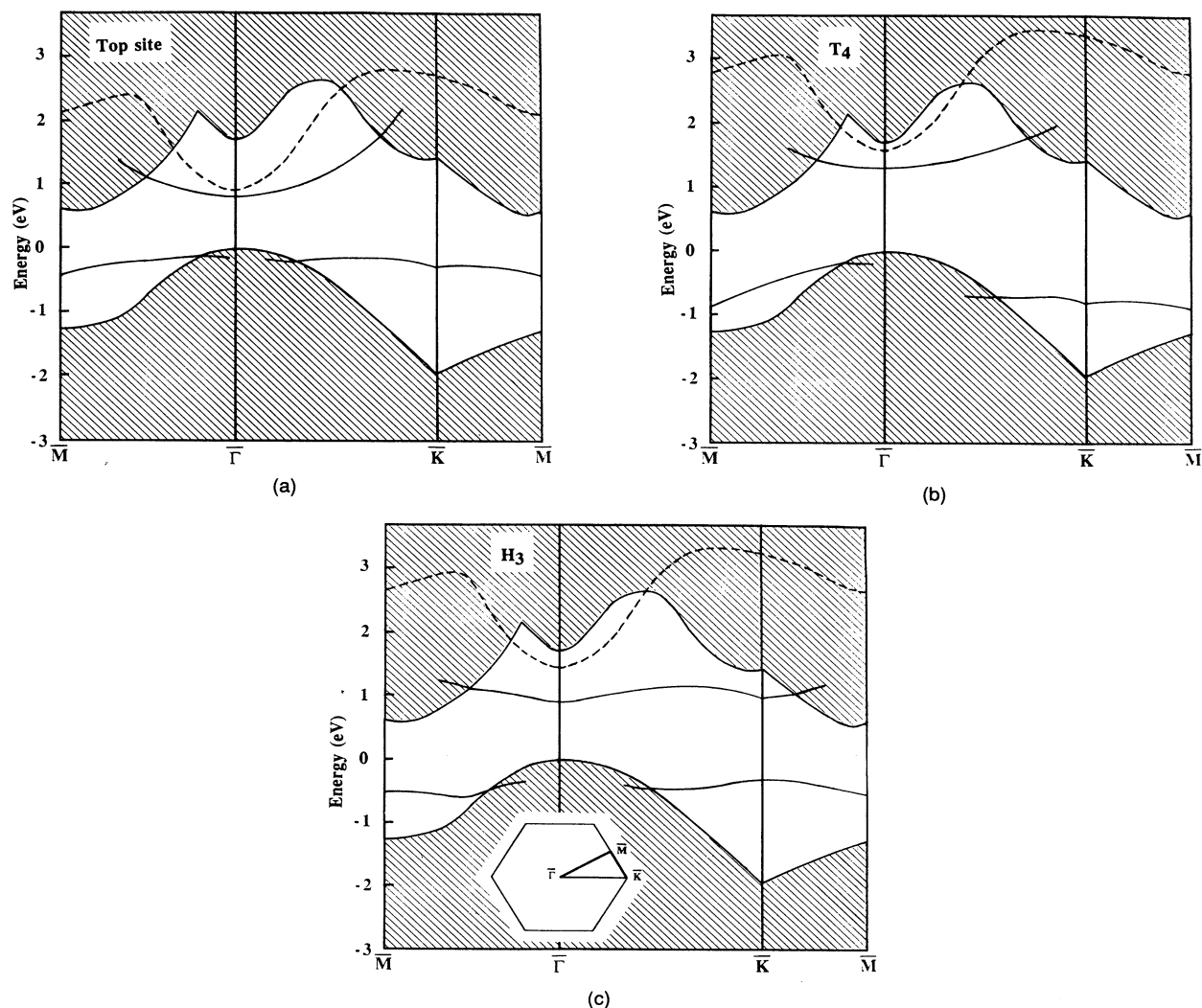


FIG. 3. Calculated interface electron bands of the three structural models in the fundamental gap region: (a) top-site structure, (b) T_4 structure, and (c) H_3 structure. The crosshatched lines indicate the bulk Si bands. The dashed line indicates the bottom of the CaF_2 conduction bands obtained from the calculation. In each structural model, there is a pair of occupied and unoccupied interface bands.

the experimental values of 12.1 and 1.1 eV, respectively. The calculated direct gap at the Γ point in CaF_2 is somewhat larger and is about 7.3 eV.

Since in the supercell we have *two* interfaces separated by a finite distance, an interface state localized at one interface interacts with a similar state localized at the other, producing in the supercell calculation a pair of bonding and antibonding states with a small energy difference. This energy difference depends on the k point in the Brillouin zone but was typically in the range of ~ 0.3 to 0.5 eV for our supercell. This energy separation diminishes gradually as the supercell size is increased. These two-dimensional states, localized at the interface, are readily identifiable as a pair of lines in the fundamental gap in the BZ in the supercell calculation. The electron states of the isolated interface are obtained by averaging the energies of the bonding and antibonding pair.

From the present calculations we estimate the magnitude of the valence-band offset to be 6.2 ± 0.5 eV for the top-site structure, 5.5 ± 0.5 eV for the T_4 structure, and 5.7 ± 0.5 eV for the H_3 structure. The uncertainty in the values reflects our finding that the calculated valence-band offset depends somewhat on the size of the supercell

and position of the interface empty spheres. Fujitani and Asano obtained the values of 5.3 eV for the top-site and 5.9 eV for the T_4 structure using somewhat larger supercells. The experimental value is between 7.3 and 8.5 eV. The calculated band offset differs from the measured value because of possible errors due to the local-density approximation. Furthermore, relaxation of the interface atoms could also change the calculated value of the band offset.

The interface bands obtained for the three different structural models are shown in Fig. 3. The projected bulk bands of Si into the two-dimensional BZ are shown by the crosshatched lines. The valence top of the bulk-like CaF_2 bands occurs outside the frame of the figures because of the large valence-band offset. The bottom of the CaF_2 conduction bands is indicated by the dashed line. Since in the LDA calculation band gap is underes-

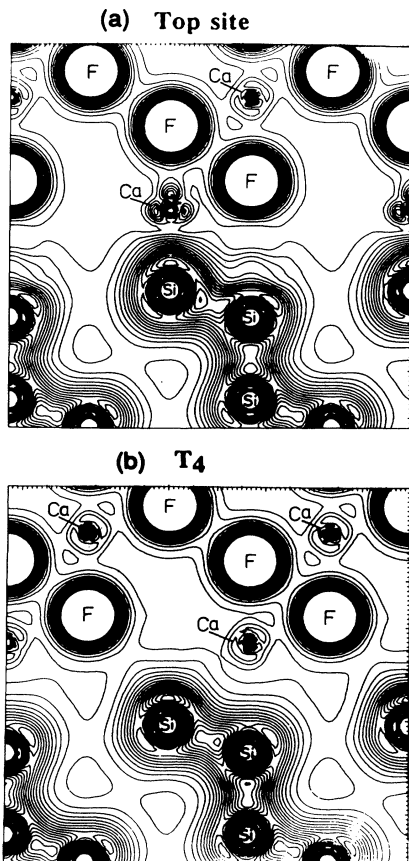


FIG. 4. Valence electron charge-density contours in the $(1\bar{1}0)$ plane for (a) top-site and (b) T_4 structure of the $\text{CaF}_2/\text{Si}(111)$ interface. The value of the lowest contour as well as the contour step are both 0.005 atomic units.

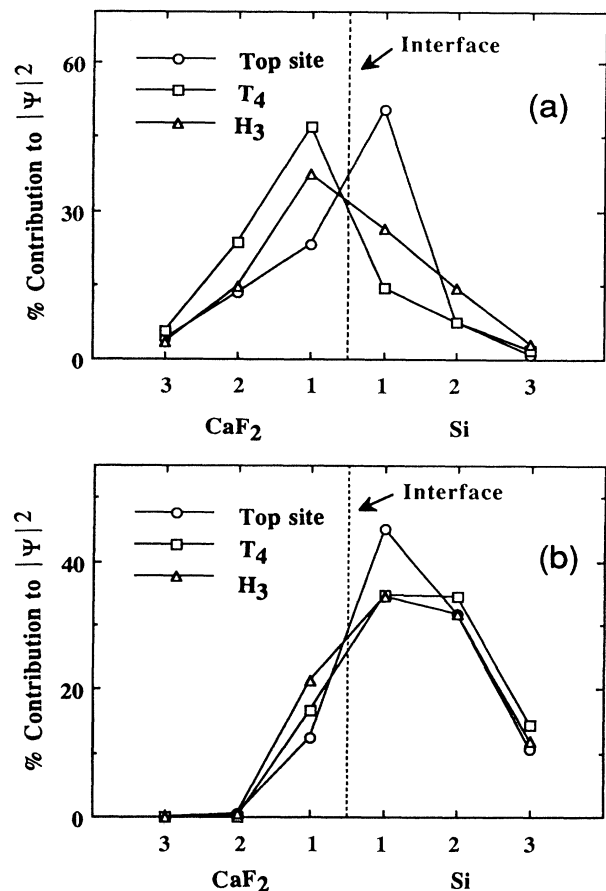


FIG. 5. (a) Contribution to the charge density $|\Psi|^2$ of the interface states from various double or triple atomic layers showing the localization of charge density in the interfacial region for the *unoccupied* interface state at $\bar{\Gamma}$. Each data point on the silicon side includes contributions from a Si_2 double layer and two empty spheres. On the CaF_2 side, each data point includes contributions from a CaF_2 triple layer and one empty sphere except the point closest to the interface which represents one Ca and F atoms each and two empty spheres. (b) Same for the *occupied* interface state at \bar{K} .

timated, the lowest conduction band of CaF_2 occurs in the fundamental gap while experiments indicate it to lie above the Si bands as follows.

The relative position of the CaF_2 conduction bands may be inferred from the measured valence-band offset. The band-offset value of 7.3–8.5 eV together with the CaF_2 gap value of 12.1 eV and the Si gap value of 1.1 eV imply that for the CaF_2/Si interface, the CaF_2 conduction-band bottom should lie between 2.5 and 3.7 eV above the Si conduction minimum. Since the bulk Γ - L line is projected onto the $\bar{\Gamma}$ point of the interface BZ, and the bulk Si L minimum is about an eV above the bulk Si conduction minimum, this implies that the CaF_2 bands occur about 1.5–2.7 eV above Si bands at $\bar{\Gamma}$.

For all three interface models the position and dispersion of the interface bands in the gap regions are qualitatively similar. We find a pair of occupied and unoccupied two-dimensional bands for each case. While the unoccupied state at the center of the interface BZ occurs inside the gap region forming a truly localized state at the interface, the occupied state occurs 0.1–0.2 eV, depending on the interface model, below the valence-band maximum. Such occupied resonance states were found in the angle-resolved photoemission experiment about 0.8 eV below the valence-band maximum. The dispersion of the top-most occupied band along the $\bar{\Gamma}$ - \bar{K} line is calculated to be between 0.3 and 0.7 eV depending on the model in qualitative agreement with the experimental value of 0.6 eV. However, since the McLean-Himpsel experiment²² was carried out with a monolayer thickness of CaF_2 it is likely that the energy and dispersion of the occupied interface bands could be somewhat different for an interface formed with a thick film. The interface band gap at $\bar{\Gamma}$ is calculated to be 1.0 eV for the top-site and the H_3 models and 1.5 eV for the T_4 model as compared to the experimental value of 2.4 eV which was in fact measured with a thick CaF_2 film ($\sim 500 \text{ \AA}$).²³ The discrepancy of ~ 1 eV between calculation and experiment could again be attributed to the fact that gaps are underestimated in the LDA calculations.

In Fig. 4 we show the valence electron charge-density contours for the top-site and the T_4 structures which show a clear difference in the chemical bonding at the two interfaces. Just a layer away from the interface on either side, the Si—Si covalent bond as well as the Ca—F ionic bond are similar to those in the bulk materials. The T_4 structure has less number of electrons on the interfacial Ca atom compared to the top-site structure which is consistent with the corresponding muffin-tin charges shown in Fig. 2. In fact, in the T_4 structure there is no sign of any covalent bonding between the interfacial Ca atom and Si atoms from the contour plot. The contours resemble those of the bulk CaSi_2 obtained by Fahy and Hamann²¹ indicating that the bonding of the interfacial Ca atom to Si is similar to that in the calcium silicide.

To examine the extent of localization of the interface states we calculated the contribution of various atoms to the charge density $|\Psi|^2$ of the interface states. This was calculated from the charge density of the pairs of interface states which are present because, as mentioned ear-

lier, the supercell contained two interfaces. The charge density of such pairs of states were very similar as expected and we took their average value. Figure 5(a) shows the charge density of the unoccupied interface states at $\bar{\Gamma}$. For the top-site model, the maximum in $|\Psi|^2$ occurs in the Si_2 double layer closest to the interface, while for the other two models the maximum occurs in the Ca-F layers at the interface. The charge density decays exponentially away from the interface region as might be expected.

The interface states consist mostly of Si p , Ca s and Ca d characters. However, there is a significant amount of contribution from the second-layer Ca and third- and fourth-layer Si orbitals to the charge density. Thus unlike in the case of a Na monolayer adsorbed on Si(111) surface,²⁹ the formation of the interface band here should not be viewed as produced by simply an interaction between the Ca s orbital and the dangling Si bond orbital at the interface atoms. Another difference from the Si(111)-Na case is the proximity of the Ca- d bands to the Ca- s -like conduction minimum in bulk CaF_2 resulting in the participation of the d bands in the charge density of the interface states.

Since the occupied interface states at $\bar{\Gamma}$ are buried in the valence bands forming resonance states, it is difficult from our calculation to examine the characteristics of the charge density at the center of the BZ. However, we obtained the charge-density characters at the \bar{K} point for the occupied interface states which are shown in Fig. 5(b). Again as indicated from the figure the wave function is localized at the interface; however, the interface states are now mainly of Si p character with some contributions from the Ca-F layer adjacent to the interface.

IV. SUMMARY

The LDA calculations presented here show qualitatively similar features for all three models of the $\text{CaF}_2/\text{Si}(111)$ interface as far as the interface electronic structure is concerned. All three models showed the presence of a pair of occupied and unoccupied interface bands in the fundamental gap. The occupied interface band is buried in the Si valence band as indicated from the photoemission experiments; however, the calculated position of this band at the center of the BZ is found to be much closer to the valence-band maximum as compared to the experiment. The two-dimensional interface states are localized within several atomic layers in the interface region.

ACKNOWLEDGMENTS

The present work was supported in part by a Grant from the Weldon-Spring Foundation of the University of Missouri. Numerical computations were performed at the Pittsburgh Supercomputing Center under Grant Nos. PHY880084P and DMR910005P. One of us (G.P.D.) is grateful to P. Blöchl for helpful discussions and acknowledges the hospitality of the Max-Planck Institute during the course of this work.

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