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Energetics and valence-band offset of the CaF_2/Si insulator-on-semiconductor interface

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From local-density calculations of total energy and valence-band offset, we examine several models of the interface atomic structure of the CaF_2/Si interface. We find that the interface with one interfacial fluorine layer is unstable with respect to dissociation or disproportionation. The interface with two fluorine layers (having only Si—F bonds at the interface) is stable when there is excess fluorine. Interfaces with no fluorine layer (having only Si—Ca bonds at the interface) are stable when there is fluorine deficiency. Comparison of the calculated valence-band offset with the experimental value indicates the molecular-beam-epitaxy-grown structure to have only Ca—Si bonds at the interface. We illustrate the potential usefulness of the valence-band offset in the determination of interface atomic structure.

I. INTRODUCTION

The CaF_2/Si (111) heteroepitaxial interface, aided by the small lattice mismatch between the two bulk materials, grows as an atomically abrupt planar interface.[1] It is a prototype of the insulator-on-semiconductor interfaces with potential use in the future in achieving three-dimensional integrated circuits. In spite of extensive recent studies including Rutherford backscattering (RBS),[2] electron microscopy,[3] core-level photoemission,[4,5] Auger-electron spectroscopy, x-ray absorption,[6–8] etc., the atomic structure of the interface is still a matter of debate. The difficulty is enhanced by the fact that direct experiments such as high-resolution electron microscopy unfortunately are insensitive to the small fluorine atoms and experimental information about the fluorine atoms must come from other, more indirect means.

In this paper we theoretically study several models of the interface by examining total energies and magnitudes of the valence-band offset. Comparison of the calculated valence-band offset for the various models with the experimental value shows that the molecular-beam-epitaxy (MBE) grown interface consists primarily of a structure with no interfacial fluorine atoms. An additional principal point of this paper is the illustration of how the valence-band offset may be used to obtain important structural information at the interface.

II. METHOD

We consider structural models, shown in Fig. 1, with either zero, one, or two fluorine layers between the Ca and the Si layers at the interface, corresponding to the three inequivalent ways in which the CaF_2 crystal can be terminated to produce a (111) plane. The (111) plane is a natural cleavage plane in CaF_2; the cleaved surface contains the full CaF_2 triple layer, corresponding to the termination by a single fluorine layer. This being the case, model *A*, containing one interfacial fluorine layer, might seem to be the natural structure at the interface; in fact such a model has been proposed earlier by Himpsel *et al.*[8] On the other hand, Olmstead *et al.*[4] found the core-level photoemission experiment to indicate predominant Si—Ca bonds at the interface leading to the interface model with no fluorine layer at the interface (the *B* models). In models *B* or *B*′ the Ca atoms sit on top of the first-layer Si atoms while in models *B*″ or *B*‴ the Ca atoms sit atop the second-layer Si atoms. Models *B* and *B*″ are so-called "type *a*" while *B*′ and *B*‴ are "type *b*." These two types differ in the relative orientation of the CaF_2 part relative to the Si part. The orientation corresponding to type *b* is observed in RBS (Ref. 2) as well as in the high-resolution electron microscopy[3] experiments. Model *B*′ has been proposed by Olmstead *et al.*,[5] and recently Batstone *et al.*[9] have argued that this model is most compatible with their experimental data. Model *B*‴, recently proposed by Tromp and Reuter,[10] is similar to model *B*″ except that it has type-*b* orientation relative to model *B*″.

The interface model *A* contains complete triple layers of F—Ca—F, so that within the CaF_2 part ionic charge transfer from Ca to F is complete and there are no "extra" electrons to be contributed to the bonding at the interface. This means that the dangling bonds at the interface Si atoms continue to possess only *one* unpaired electron per atom thereby resulting in a metallic interface. Experimentally, however, after a rapid thermal anneal an insulating interface has been observed to result.[11] This insulating behavior is consistent with an interface model containing either no fluorine or two fluorine layers at the interface. Keeping this in mind, we also consider models with two interfacial fluorine layers (models *C* and *C*′). In model *C* the Ca atoms at the interface are not bonded to Si, while in model *C*′ (not shown in Fig. 1) the Ca atoms occur atop the first-layer Si.

We use the linear muffin-tin orbitals (LMTO) method[12] applied to the supercell geometry in our theoretical calculations of total energy and valence-band offset. Exchange-correlation effects are taken into account within the local-density approximation to the density functional theory. In the calculation, the supercells consist of three double layers of Si and three layers of Ca with the appropriate number of F layers. The size of the supercell is large enough that the central Si and CaF_2 lay-

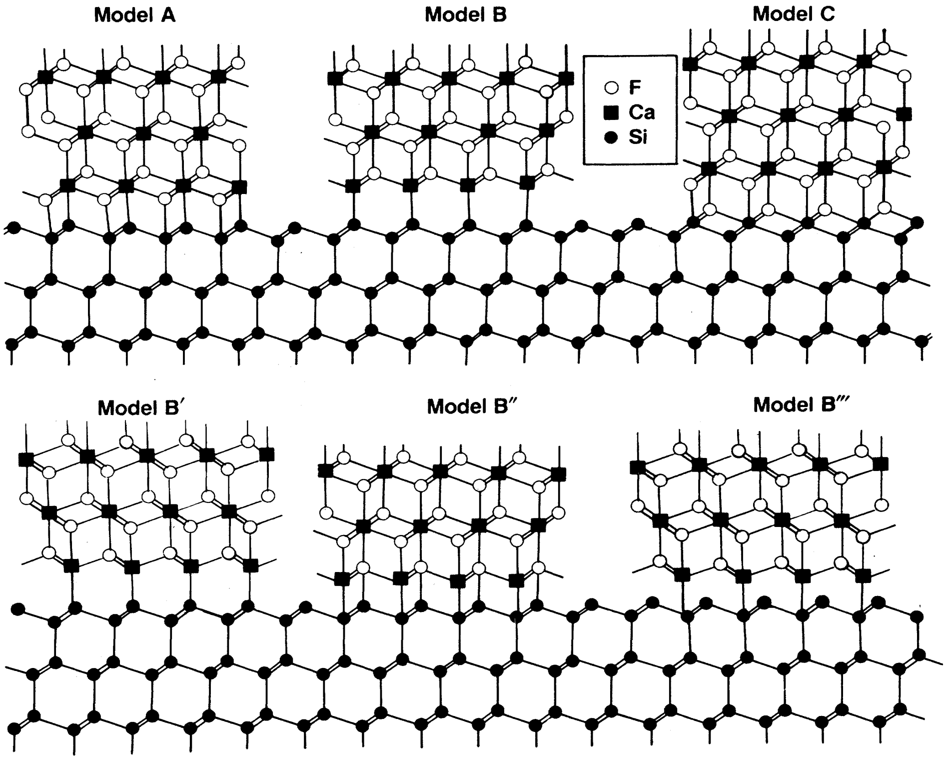

FIG. 1. Structural models of the CaF_2/Si (111) interface. Some of these models have been proposed earlier in the literature, viz., model *A* by Himpsel *et al.* (Ref. 8), model *B′* by Olmstead *et al.* (Ref. 5) and later by Batstone *et al.* (Ref. 9), and model *B‴* by Tromp and Reuter (Ref. 10). Models *B* and *B″* are the type-*a* versions of the *B′* and *B‴* structures, respectively, differing from the latter two structures in the relative orientation of the CaF_2 part with respect to the Si part. In the high-resolution electron microscopy experiments of Ponce *et al.* (Ref. 3), about 90% of the interface is observed to be of type *b* and the remaining 10% of type *a*. Our calculations of total energy and valence-band offset as discussed in the text indicate a structure with only Si—Ca bonds at the interface.

ers already exhibit bulklike properties, e.g., as judged by comparing the charge transfer between various atoms in the supercell to their calculated values in the bulk crystal. The small lattice mismatch (0.6%) between the Si and CaF_2 bulk materials was ignored and the value of the bond length used in our calculation is 2.35 Å. This is the bond length in bulk silicon. As is standard in the LMTO calculations, empty spheres were used to better describe the electron charge density in the hollow sites in both Si and CaF_2 parts. Self-consistency was obtained with about 40 *k* points in the full Brillouin zone. Our results for the total energies should be accurate to about 0.1 eV for the total energies of the interface. The accuracy should be much better, however, where we make a direct comparison, for instance, between the total energies of various *B* models.

We obtained the valence-band offset by performing two fresh LMTO band calculations for the two bulk crystals in which the self-consistent potentials of the central layer atoms in the supercell geometry were used. The difference between the resulting valence-band tops of the two materials provided the magnitude of the band offset. For heterostructures between two chemically similar materials, calculations[13,14] within the local-density approximation seem to provide a reasonable estimate of the band offset (ΔE_v) as compared to experiments. Zhang *et al.*[15] have recently argued that ΔE_v for the AlAs/GaAs (100) heterojunction is increased by about 0.1 eV if many-body effects within their quasiparticle calculation are included. However, for an interface between two very different materials such as ours, many-body corrections may be quite large. From the results of Carlsson[16] for the band-gap underestimates in the local-density theory, we estimate that in the present system the magnitude of the valence-band offset obtained from the local-density calculation is too small by about 1.4 eV. We should keep this in mind in the analysis of our results.

III. RESULTS

A. TOTAL ENERGIES

We first calculated the total energies of the neutral Ca and F atoms which we will need in studying the energetics of some of the reactions. From the calculation of the atomic energies and the total energy of bulk CaF_2, we find a cohesive energy of 15.8 eV for the CaF_2 crystal per formula unit, which compares very well with the experimental value of 16.0 eV. We have used the calculated atomic energies and bulk total energies in studying the energetics of various reactions described below. The surface energies of the $CaF_2(111)$ and Si(111) surfaces where needed were taken from experiments.

The measured[17] energies of the $CaF_2(111)$ and Si(111) cleavage surfaces are 450 and 1240 ergs/cm^2, respectively (1.3 eV in total per unit interface area, i.e., an area of $\sqrt{3}/4a^2$, with a being the cube lattice constant). We have used this value throughout in our analysis of energetics in reactions where surface energies are involved. For instance, while in the disproportionation reaction [Eq. (2)] no crystal surfaces are formed, in the dissociation reaction interface A dissociates to produce bulk Si and CaF_2. In the process free surfaces of the two bulk materials are also produced. In a correct analysis of the energetics, the surface energies must be included and we have used the experimental values for the surface energies mentioned above in our analysis.

We now examine the stability of the interface model A with respect to dissociation, in which the structure separates into bulk CaF_2 and bulk Si with the resulting formation of two surfaces, or with respect to disproportionation into two different interface parts, one part with two interface fluorine layers (model C) and a second part with no interface fluorine layer (model B). We find that model A is unstable to dissociation:

$$A \rightarrow CaF_2(s)+Si(s)+\text{surfaces}+2.4\text{ eV} \quad \text{(dissociation)} \qquad (1)$$

as well as to disproportionation:

$$A \rightarrow B+C+0.6\text{ eV} \quad \text{(disproportionation)}\ . \qquad (2)$$

In Eq. (1) and elsewhere in the paper, $CaF_2(s)$ and $Si(s)$ denote the respective bulk solids, while the energies in the equations refer to unit interface area. These results, therefore, do not support the interface represented by model A to be a stable interface.

Of the two models that contain two interfacial fluorine layers, models C and C', a direct comparison of the total energies shows that model C has a total energy of 3.7 eV lower than that of C'. Of all B models with no interfacial fluorine atoms, model B''' has the lowest total energy: $E(B''')<E(B')<E(B)<E(B'')$. The energies differ from $E(B''')$ by 0.5 eV (B'), 0.6 eV (B), or 3.0 eV (B''). Even though the energy differences are large, keeping in mind the fact that we have made no attempt to optimize the distances between atoms in the CaF_2 and Si layers at the interface (we estimate that some interfaces can gain as much as 0.5–1 eV of energy as a result of this), we can discard only the B'' model on the basis of the total energy results. Therefore, models C as well as B, B', and B''' still remain viable models for the interface. We note here that the calculated total energy difference between the type-a B and the type-a B' is a mere 0.09 eV per interface atom, which is consistent with the observation in the high-resolution electron microscopy experiments[3] that the interface is predominantly type b with some of the interface being type a. On the other hand, model B'', the type-a version of model B''', is unfavorable on account of its high total energy.

We now turn to the examination of the stability of the remaining three B and the C models. The C model contains an extra layer of fluorine atoms; it is natural to consider whether this interface is stable with respect to dissociation into bulk materials and free fluorine atoms, as represented by the equation that follows. We find that for this case

$$C \rightarrow CaF_2(s)+Si(s)+F+\text{surfaces}-3.9\text{ eV} \qquad (3a)$$

so that this reaction would not go. The C interface is therefore stable with respect to dissociation. However, the free F atoms can form bonds with the Si surface; Seel and Bagus[18] estimated that the binding energy of F chemisorbed on the on-top site of the Si(111) surface is 3.2 eV. Even though this binding energy is large, using Eq. (3a) one finds that it is not enough to destabilize the C interface with respect to dissociation into a CaF_2 part and a F-terminated Si part:

$$C \rightarrow CaF_2(s)+Si(s)\text{—}F+\text{surfaces}-0.7\text{ eV}\ . \qquad (3b)$$

These results indicate that the C interface is stable.

The B interfaces can undergo reaction with extra fluorine atoms and could either dissociate or be converted into the C interface which contains excess fluorine. We find that

$$B'''+F \rightarrow CaF_2(s)+Si(s)+\text{surfaces}+6.9\text{ eV} \qquad (4)$$

and

$$B'''+2F \rightarrow C+10.7\text{ eV} \qquad (5)$$

so that our results show that the B''' (and indeed all B models) interface is unstable in the presence of excess fluorine. We note that the binding energy of a F_2 molecule being as small as 1.6 eV, this conclusion does not change if we use F_2 molecules instead of F atoms in Eqs. (4) and (5). The large energies involved in these two reactions are simply due to the fact that F forms strong bonds with both Ca and Si atoms. (The bond strengths[19] of the diatomic molecules are for F—F, 1.6 eV; for F—Si, 5.7 eV; and for F—Ca, 5.5 eV.) Rather than being in the atomic or molecular state, it is therefore energetically favorable for fluorine to form bonds with the interface Ca or Si atoms.

However, it is quite possible that in the MBE growth process, reactions (4) and (5) are not thermodynamically accessible. It is well known that fluorine etches silicon, and it is believed[18] that the etching is preceded by fluorine diffusing into the Si bulk. It might therefore be energetically favorable for F atoms to diffuse into the bulk Si rather than remain at the interface, thereby making the F atoms unavailable for the above two reactions. Also there is experimental indication that during the growth of the first CaF_2 triple layer, Ca is bonded to Si with the F atoms sticking outwards. Thus under the MBE growth condition, the interface naturally grows as fluorine deficient.

The B''' interface is stable with respect to dissociation into solids and free Ca atoms:

$$B''' \rightarrow CaF_2(s)+Si(s)+Ca+\text{surfaces}-1.1\text{ eV}\ . \qquad (6a)$$

The stability is retained even if we assume that in the above equation Ca atoms combine to form Ca bulk solid: The experimental cohesive energy of Ca going from neutral atoms to solid is about 1.84 eV/atom, and since only

TABLE I. Calculated values of the valence-band offset for the CaF_2/Si (111) interface models. n is the number of interfacial fluorine layers and ΔV denotes the calculated values of the offset.

Interface model	A	C	C'	B	B'	B''	B'''	Expt.
n	1	2	2	0	0	0	0	
ΔV (eV)	5.0	4.2	3.9	7.2	7.2	5.3	5.3	7.3–8.5

half of a Ca atom per unit interface area is involved, we have

$$B''' \rightarrow CaF_2(s) + Si(S) + Ca(s) + \text{surfaces} - 0.2\ \text{eV} . \quad (6b)$$

Interfaces B and B' are stable with respect to the dissociation of Eq. (6a), but not with respect to Eq. (6b). However, considering that B and B' are only about 0.5 and 0.6 eV higher in energy than B''', they are expected to be stable with respect to the dissociation, Eq. (6b), as well, if atom distances at the interface are optimized to minimize their total energies. Thus our results of the total energy calculations are that model C with two interfacial fluorine layers is stable and models B, B', and B''' with no interfacial fluorine atoms are stable when there is fluorine deficiency.

B. Valence-band offset

Formation of an interface out of two bulk materials leads the electron charge density to readjust in the interfacial region in such a way as to minimize the total energy of the system. The charge redistribution causes the electron bands of the two materials to align in a specific way. This leads to the well-known valence-band offset. The magnitude of this offset, which is crucial to the performance of a heterojunction in an electronic device, is a quantity accessible to both experiments and theoretical calculations.

It might be expected that the magnitude of the band offset would change if the atom positions at the interface are altered. This is especially so if one of the two constituent materials is polar, which is the case here. The measured value[4,7] for the valence-band offset of CaF_2/Si is between 7.3 and 8.5 eV, depending on the growth condition. In particular, presence of more fluorine during the MBE growth process seems to decrease the offset value.[20]

Using the LMTO local-density method, we have calculated the valence-band offset for models shown in Fig. 1. Qualitatively, one expects the model with no interfacial fluorine to have a larger offset than the "natural" interface, i.e., the model with one interfacial fluorine layer (model A). This is because one might expect the excess electron on the Ca atom to be transferred to the Si atom and occupy the dangling bond, causing an extra interfacial dipole. This raises the band energies on the Si side as compared to the natural interface. For the model with two interfacial fluorine atoms, however, the more electronegative fluorine atom close to the Si atom would tend to pick up the electron from Si, thereby decreasing the magnitude of the interfacial dipole as compared to that of the natural interface. This would lead to a smaller offset for the model with two interfacial fluorine layers.

The results of our calculations summarized in Table I indeed show this expected trend in the band-offset value. The calculated band offset for the natural interface, model A, is 5.0 eV. For the interfaces with two fluorine layers, models C and C', this quantity is 4.2 and 3.9, respectively. For the models with no fluorine at the interface, we find the offset value of 7.2 eV (models B and B') or 5.3 eV (models B'' and B'''). The lower offset values in the latter two B models are consistent with the fact that here the Si-Ca distances between the interfacial Ca and Si layers are significantly smaller than those in B or B', so that the charge transfer occurs over a smaller distance leading to a smaller interface dipole.

The two models C and C', with two interfacial fluorine layers each, have comparatively small band-offset values of, respectively, 4.2 and 3.9 eV. Such small values for the band offset are incompatible with the measured values of 7.3–8.5 eV for the MBE structure. Of the remaining models, models B and B' have a large theoretical offset of about 7.2 eV. The offset values for models A, B'', and B''' are 5.0, 5.3, and 5.3 eV, respectively. Considering our earlier estimate that the magnitude of the offset is underestimated in our calculation by as much as 1.4 eV, we should not discard any of the A or the B models. On the other hand, we have shown on the basis of the total energy calculations that model A with only one interfacial fluorine layer is unstable and the high total energy of model B'' makes it unfavorable.

Therefore our combined results for the band offsets and total energies favor models B, B', and B''' with no interfacial fluorine layers, so that there are only Si—Ca bonds at the interface. Experimentally, it has been shown[3] that it is possible to grow type-*a* interfaces. The above discussions indicate model B to be a good candidate to represent the atomic structure of the MBE-grown type-*a* interface. Of the two type-*b* models, B' and B''', our results presented here do not conclusively favor one over the other. It seems that by changing the MBE growth condition, it might be possible to grow either of the two type-*b* interfaces, viz., either the B' or the B''' structures. Further experiments on this aspect of the problem seem to be necessary.

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