Band discontinuities at heterojunctions between crystalline and amorphous silicon

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We present a theoretical investigation of the band lineups between crystalline and amorphous silicon, based on the first-principles pseudopotential method and the model-solid theory. We find that the offsets are very sensitive to the hydrogen content of the material; the valence-band offset for a junction with unhydrogenated *a*-Si is -0.25 eV, while for hydrogenated *a*-Si with a hydrogen content of 11% the offset becomes 0.20 eV. Consequences for the interpretation of experimental data are discussed. © *1995 American Vacuum Society.*

I. INTRODUCTION

Heterojunctions between amorphous silicon (*a*-Si) and crystalline silicon (*c*-Si) can be used to improve the performance of solar cells[1] and of heterojunction bipolar transistors.[2] In addition, they enable the study of the amorphous/crystalline interface, and may provide more information about density of states and other electronic or structural properties of *a*-Si. One of the key properties of the heterojunction, namely the band lineup at the *a*-Si/*c*-Si interface, has been a subject of controversy. For interfaces between *c*-Si and hydrogenated *a*-Si (*a*-Si:H) experimental results range from zero offset in the valence band[3] to zero offset in the conduction band,[4] with many values in between those extremes.[5–9]

We have performed a theoretical investigation of the band discontinuities at interfaces between crystalline and amorphous silicon, based on first-principles calculations for the electronic structure of *a*-Si and *c*-Si, and the model-solid theory.[10] The theoretical approach is discussed in Sec. II. We have applied the approach to unhydrogenated *a*-Si as well as to hydrogenated material (*a*-Si:H); the difference between the two cases is sizeable. The results are reported in Sec. III. In Sec. IV we discuss the dependence on hydrogen content, and address the effect of the density of the amorphous material on the resulting band lineups. Consequences for the interpretation of experimental results are discussed.

II. THEORETICAL APPROACH

The band discontinuities between two semiconductors are determined by the lineup of electrostatic potentials across the interface. The energetic positions of the valence-band maximum and conduction-band minimum in each individual semiconductor can be obtained from band-structure calculations for the bulk material. Obtaining band discontinuities in principle requires a calculation in which the two materials are explicitly included, joined by an interface; such a calculation (e.g., for a superlattice) then allows tracking the potential variation across the interface, which determines the band lineups. Calculations of this type are described, e.g., in Ref. 11.

In this article we address the band lineups between crystalline Si on one side, and amorphous Si on the other side. Because of the lack of long-range order, the electronic properties of *a*-Si are much harder to address with first-principles calculations than those of crystalline semiconductors. Nonetheless, it is possible to model the amorphous structure in a large supercell, which is then periodically repeated. While this approach allows one to obtain information on the electronic structure (valence- and conduction-band energies) of the bulk material, the large size of the supercell required to model an interface between *a*-Si and *c*-Si makes it prohibitive to carry out the type of superlattice calculation conventionally used to determine the potential lineup.

Fortunately, model theories have been developed which obviate the need for a superlattice calculation to determine the potential lineup, and instead rely only on properties of the individual bulk materials. The underlying assumption is that no interface-specific dipoles occur—an assumption which has been shown to be justified in the case of non-polar interfaces between isovalent materials.[10] The *model solid theory*, which we will apply here, uses an approximate electrostatic potential obtained by modeling the solid as a superposition of neutral atoms.[10] This approach has been quite successful for predicting band offsets at a wide variety of semiconductor interfaces.[10]

The model-solid approach was previously applied only to crystalline semiconductors with perfect tetrahedral coordination. In this work, we extend the application in two ways. First, to an amorphous network, in which the tetrahedral coordination is maintained (but the long-range order is lost); by nature of the model-solid approach (superposition of neutral atomic charge densities) one would expect the method to continue to work well. Second, to the case of hydrogenated *a*-Si, in which the network is no longer fully tetrahedral in nature, and an additional chemical component is introduced. The application of the model is more *ad hoc* here, and should be checked in the future by comparing with full-fledged interface calculations. Such calculations, as indicated above, are currently computationally too demanding.

The *a*-Si models were generated from *l*-Si phases based on the Stillinger–Weber potential.[12] The models were initially thermalized at 300 K for 10 picoseconds and then quenched by *ab initio* pseudopotential methods. Fifteen configurations were generated to average the valence-band maximum; the spread in the values obtained from the various configurations was less than 0.1 eV. For the a-Si:H models, we took the initial configurations of Guttman and Fong[13] and then quenched them by using *ab initio* pseudopotential methods. The *ab initio* pseudopotential approach is based on density-functional theory in the local-density approximation,[14] and Troullier-Martins pseudopotentials.[15] The plane-wave basis set for the potentials and wave functions had a kinetic-energy cutoff of 15 Ry. More details about the calculations for the amorphous material can be found in Ref. 16.

The magnitudes of the valence- and conduction-band offsets should add up to the difference in band gaps between the two materials. Two definitions can be given for the band gap in a-Si: one is from mobility edge to mobility edge (optical gap), the other one is between the ends of the band tails, which should give a smaller gap. The type of experiments used to determine the band offsets (see Sec. IV) deals with carriers placed at the mobility edge, and hence the optical gap is the appropriate one to use. Our calculated band structure should also be associated with the optical gap, because the tail states arise from dangling bonds which are excluded from the particular (continuous random network) a-Si models used here. Our calculated band gaps suffer, of course, from the well-known underestimate of the band gap in density-functional theory. The band gap in c-Si is underestimated by about 0.4 eV; applying this same correction to the (unhydrogenated) amorphous network, the calculated gap is close to 1.5 eV, in agreement with experiment.

III. RESULTS

The position of the valence band in c-Si (at the experimental lattice constant) on an "absolute" energy scale, derived with the model-solid procedure outlined above, is $E_v = -6.98$ eV; this value is within 0.05 eV of the value obtained previously (see Ref. 10) with a different pseudopotential. This consistency check is reassuring; the difference is within the error bar on the model-solid values. Furthermore, this small shift will not affect band-offset values derived consistently with one pseudopotential.

A. Unhydrogenated *a*-Si

We first address the band lineups between c-Si and unhydrogenated a-Si. The computer-generated amorphous Si models do not include any point defects or voids. Within the model-solid theory, the electrostatic potential lineup is determined solely by the difference in density between the crystalline and amorphous materials, since the chemical composition of the two materials is the same. The difference in bonding between c-Si and a-Si has an effect on the positions of the valence and conduction bands as well, of course – but that effect is included entirely in the bulk calculations. As we will discuss below, the density of amorphous Si is not accurately known (or may depend on the preparation conditions). If we assume equal density for both materials, we obtain a valence-band offset of $\Delta E_v = -0.25$ eV, with the valence band higher in a-Si. We use a sign convention here whereby ΔE_v is positive if the valence band of c-Si (the smaller band-gap material) lies above the valence band of a-Si, and ΔE_c is positive if the conduction band in a-Si lies above the conduction band in c-Si. With this convention, the band-offset values should add up to the difference in band gap, i.e., $\Delta E_v + \Delta E_c = \Delta E_g$.

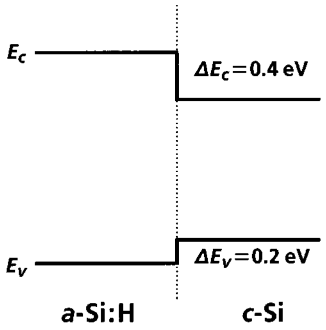

FIG. 1. Band offsets between c-Si and hydrogenated a-Si, based on pseudopotential-density-functional calculations and the model-solid theory. The results shown assume a hydrogen content of 11% in the a-Si:H, and a density for a-Si:H equal to that of c-Si. The sensitivity of the band offsets to these parameters is discussed in the text.

B. Hydrogenated *a*-Si

Once again, we first assume equal density for both materials. By nature of the model-solid approach, the average electrostatic potential in the a-Si:H material depends on the hydrogen concentration. The hydrogen concentration in the a-Si:H computer model is $\sim 11\%$. For this system, we obtain a valence-band offset of 0.20 eV (higher in c-Si). The band lineups for this case are illustrated in Fig. 1; experimental values for the band gaps are assumed. The effect of hydrogen seems to be to lower the position of the valence-band edge by about 0.04 eV for each % hydrogen in the system; however, it is not clear to what extent this conclusion, based upon one 54-Si and 6-H atom supercell, can be generalized.

C. Effect of the density

If the density of a-Si would differ from c-Si, the position of the valence band on the amorphous side would shift—an effect that can be accurately described by an absolute deformation potential.[17] The absolute deformation potential for the valence band, a_v, is defined as

$$a_v = \frac{dE_v}{d \ln \Omega} \tag{1}$$

where $d \ln \Omega = d\Omega/\Omega$ is the fractional volume change under hydrostatic strain.

"Absolute" refers to the fact that the energetic position of the valence band is needed on an absolute energy scale, as opposed to other deformation potentials which describe the motion of bands *relative* to each other; e.g., band-gap deformation potentials describe the motion of the conduction band with respect to the valence band. Absolute deformation potentials for semiconductors can be derived within the model-solid theory.[10] The model-solid value for the absolute deformation potential in c-Si is $a_v = 2.46$ eV. Our investigation has indicated that this value remains virtually unchanged (within the error bar on the calculated value[10]) in the amorphous material (both unhydrogenated and hydrogenated).

IV. DISCUSSION AND COMPARISON WITH EXPERIMENT

The theoretical approach reveals the fact that, even without invoking interface-specific effects, the value of the offset is sensitive to the hydrogen concentration in a-Si:H. Some uncertainty also arises because of the lack of information about the density of a-Si(:H). We will discuss experimental determinations of the band discontinuities in light of these findings.

A. Comparison with experiment

To our knowledge, no experimental information is available about the band offsets between unhydrogenated a-Si and c-Si. Experimental data *are* available, however, for a-Si:H/c-Si heterojunctions.

Cuniot and Marfaing[6] used internal photoemission to obtain the valence-band offsets at junctions formed by sputtering deposition; they obtained $\Delta E_v < 0.15$ eV. Lequeux and Cuniot[3] investigated the spectral response of a-$\mathrm{Si}_{1-x}\mathrm{Ge}_x$:H/$c$-Si junctions deposited by glow discharge, and concluded that for $x = 0$, $\Delta E_v \approx 0$, and $\Delta E_c > 0.6$ eV. However, in 1991 the same group,[8] using current-voltage and photocurrent-voltage measurements, reported a smaller value for ΔE_c, namely 0.39 ± 0.04 eV.

Essick and Cohen[4] applied voltage filling pulse measurements to a-Si:H/c-Si heterostructure Schottky diodes, grown by plasma glow discharge, and obtained a nearly zero conduction-band offset ($\Delta E_c = 0.05 \pm 0.05$ eV). They also observed the threshold for optical release of holes at the valence-band discontinuity, leading to $\Delta E_v = 0.58 \pm 0.02$ eV. Their measurements revealed an anomalously large defect density in a region within 350Å of the interface.

Matsuura *et al.*[5] obtained $\Delta E_c = 0.20 \pm 0.07$ eV from capacitance-voltage measurements of glow-discharge a-Si:H/c-Si junctions. Mimura and Hatanaka[7] measured the band discontinuities by internal photoemission for glow-discharge a-Si:H/c-Si heterojunctions, and obtained $\Delta E_v = 0.71$ eV and $\Delta E_c = 0.09$ eV. They noted that the sum of their ΔE_v and ΔE_c values exceeded the band-gap difference between their a-Si:H and c-Si.

Lucovsky and Wang,[9] finally, have analyzed the dark conductivities and activation energies for μc-Si to develop a model for band alignment between Si crystallites and the intervening amorphous regions. They obtain $\Delta E_v = 0.30$ eV and $\Delta E_c = 0.25$ eV.

Table I summarizes the experimental results discussed here, listing them in order of increasing magnitude of the valence-band discontinuity. It is clear that the experimental results display wide variations, ranging from very small valence-band offsets (Ref. 3) to very small conduction-band offsets (Ref. 4), with plenty of values in between. Since band offsets are notoriously hard to measure, experimental inaccuracies probably play some role. However, it is likely that preparation conditions of the amorphous material have a substantial influence. The experimental papers cited here provide very little information about structural properties of the amorphous material. We will now discuss two factors that our theoretical analysis has highlighted as affecting the offsets: density and hydrogen content.

TABLE I. Experimental values for band offsets between crystalline silicon and hydrogenated amorphous silicon. ΔE_v is positive if the valence band of c-Si lies above the valence band of a-Si:H, and ΔE_c is positive if the conduction band in a-Si lies above the conduction band in c-Si. All values are in eV.

	ΔE_v	ΔE_c
Lequeux and Cuniot (Ref. 3)	~ 0	~ 0.6
Cuniot and Marfaing (Ref. 6)	< 0.15	> 0.45
Cuniot and Lequeux (Ref. 8)	0.20	0.39
Lucovsky and Wang (Ref. 9)	0.30	0.25
Matsuura *et al.* (Ref. 5)		0.20
Essick and Cohen (Ref. 4)	0.58	0.05
Mimura and Hatanaka (Ref. 7)	0.71	0.09

B. Density of amorphous silicon

Our analysis has indicated a clear dependence on the density of the amorphous material: the valence band in a-Si(:H) moves up with decreasing density of the material. The density of amorphous silicon does not seem to be accurately known. A major cause of the uncertainty is the presence of voids in the material. Among the experimental determinations for unhydrogenated material, we consider the recent results of Custer *et al.*[18] to be most reliable. They have derived the density of a-Si by measuring height differences between alternating stripes of a-Si and c-Si, where the amorphous regions are created by self-implantation. They found that a-Si is 1.8% less dense than c-Si. Theoretical and computer simulations of amorphous silicon have produced results for the density on either side of c-Si. The networks in the simulations do not include voids; this seems to be a factor in obtaining densities which exceed that of c-Si. The continuous random network in the simulations by Wooten and Weaire,[19] for instance, has a density 3%–4% higher than c-Si. For hydrogenated a-Si:H, the density of good-quality material is usually lower than c-Si (values up to 6% lower have been reported).[20,21]

The effect of the density on the band offset can be illustrated with the following examples. If the density of (unhydrogenated) a-Si is 1.8% lower than the density of c-Si, then Eq. (1) allows us to calculate the shift in the valence band as $a_v \Delta\Omega/\Omega = 2.46 \times 0.018 = 0.04$ eV; i.e., the a-Si valence band moves up by 0.04 eV, shifting the valence-band offset to $\Delta E_v = -0.29$ eV. If, on the other hand, the density of a-Si would be 4% *higher* than that of c-Si, as indicated in Ref. 19, the a-Si valence band would shift *down* by 0.10 eV, reducing the valence-band offset to $\Delta E_v = -0.15$ eV. As an example for hydrogenated material, if the density of a-Si:H is as much as 6% lower than for c-Si, the valence band would shift by $2.46 \times 0.06 = 0.15$ eV, reducing the valence-band offset to 0.05 eV.

It should be pointed out that, for the purposes of determining the band lineups, only the density of the amorphous material in a thin layer near the junction is relevant; the density in regions farther away will not influence the band offsets, although fluctuations in density will lead to variations in the local electrostatic potential. As pointed out above, the presence of voids tends to lower the density of the material—but this is a macroscopic effect. What we need to know for the band-offset problem is the local density of the material near the junction, in regions which are void-free. It would therefore be very interesting to have experimental information about the density of a-Si in void-free regions. Lacking specific numbers, we can still expect this density to be higher than any of the experimental values, since all of those probably include some contribution from voids. It may not even be unreasonable to speculate that the density of a-Si in void-free regions is *higher* than that of c-Si (cf. the theoretical results in Ref. 19). The latter would have the effect of *lowering* the valence band in a-Si compared to c-Si.

C. Hydrogen content of hydrogenated amorphous silicon

We have found a clear dependence of the band offsets on hydrogen content of a-Si:H: the higher the hydrogen content, the lower the valence band will lie in the amorphous material. Our result that the valence-band maximum in the hydrogenated material lies lower than in the unhydrogenated material (by more than 0.4 eV) is consistent with the results of Ley *et al.*,[22] who found that the valence-band maximum in a-Si:H moved down in energy with increasing H concentration. The experiments of Ley *et al.*[22] also revealed inhomogeneities in the H concentration; they found a pronounced enrichment in the first few atomic layers near the surface. It is conceivable that the H concentration near the interface with c-Si also differs from its bulk value, leading to perturbations in the band-offset values.

We note that, in addition to the effects described here, which are all bulk-related, there may also be interface-specific effects which influence the band offsets through the formation of interface dipoles. Lacking any information about the microscopic structure of the interface, we refrain from speculating about the existence or magnitude of such dipoles. We think it is important to note, however, that even in the absence of interface-specific effects the details of the amorphous silicon structure (density and hydrogen content) can give rise to shifts in the offsets which are of sufficient magnitude to qualitatively explain the wide variation in the experimental results.

V. SUMMARY

We have presented a theoretical study of band offsets between crystalline and amorphous silicon, based on the pseudopotential-density-functional method and the model-solid theory. Assuming a density for the amorphous material equal to that of c-Si, we find the valence-band offset for a heterojunction between c-Si and unhydrogenated a-Si to be -0.25 eV (the valence band in a-Si lying higher than in c-Si); for the valence-band offset between c-Si and hydrogenated a-Si with a H content of 11% we find a value of $+0.20$ eV. The hydrogen content thus has a significant effect on the valence-band position. In addition, changes in the density of the amorphous material affect the valence-band position through the deformation potential, for which we use the value $a_v = 2.46$ eV. We attribute the large scatter in experimental values to the dependence on density and hydrogen content which is highlighted by the theoretical approach.

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